Final Report

Groundwater Impact Evaluation Partnership For Using Tertiary Treated Recycled Water In A Large-Scale Streamflow Augmentation Project

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Prepared for:

Santa Clara Valley Water District

The Metropolitan Water District of Southern California
Agreement No. 41808

California Department of Water Resources
"Safe Drinking Water, Clean Water, Watershed Protection and
Flood Protection Act"

March 2009

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ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the contributions of the post-doctoral researchers, undergraduates, Master's students, visiting scholars and professors who contributed their expertise and enthusiasm to this project over the years, as well as authored and co-authored research included in this report. These people include Chris Gurr, Montserrat Lopez Mesas, Ph.D., Elisabeth Janssen, Eduard Hoehn, Ph.D., Andy Heidlberger, Eva Steinle-Darling, Ph.D., John Montgomery-Brown, Ph.D., Yongmei Li, Ph.D., and Bin Xu, Ph.D. Yongmei Li and Bin Xu (both from Tongji University, Schanghai, China) and Eduard Hoehn (ETH, Zuerich, Switzerland) were supported by their home institutions while working on this project. The authors also gratefully acknowledge the support of Alice Ringer and Elise Latedjou-Durand of the Santa Clara Valley Water District. Megan Plumlee was supported by a National Science Foundation Graduate Research Fellowship.

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EXECUTIVE SUMMARY

Water agencies in the U.S. and elsewhere are expanding wastewater reclamation (or water reuse) as part of their water supply portfolio to meet the needs of growing populations. Recycling water via stream flow augmentation is an example of an environmental application of reclaimed wastewater. The re-used water must be protective of both stream ecology and groundwater, and comply with local and regional regulations. Currently there are limited data available to assess such water augmentation schemes *a priori*, and detailed, site-specific evaluations are needed.

Water recycling for environmental applications requires consideration of a complex set of benefits and risks. Wastewater may contain trace levels of organic contaminants, some of which may be carcinogens, toxins, or endocrine disruptors. The presence of these microconstituents in the receiving water body may have ecotoxicological consequences, as well as pose potential human health risks. Although water reuse is generally regarded as a sustainable approach to water supply management, the presence of trace organic contaminants raises concerns about the use of this water in applications such as environmental enhancement.

The goals of the present study were to augment Coyote Creek in San Jose, CA with local recycled water as a research demonstration and to assess any potential impacts to water quality. It was hypothesized that potential impacts of wastewater-derived organic contaminants may be mitigated by significant natural attenuation of those compounds at the site. The overall project approach was divided into two components – the field site assessment and laboratory investigation of contaminant fate. Field site assessment included the selection of water quality constituents, their analytical method development, and sampling campaigns for the targeted analytes in the recycled water, surface water, and groundwater. Additional site characterization included assessment of stream and groundwater hydrology via well installation and planned stream gauging and tracer tests. The laboratory investigation of contaminant fate included biodegradation, sorption, and photolysis of particular organic contaminants. Additional objectives included the assessment of contaminant fate during percolation from Coyote Creek into groundwater under stream flow augmentation conditions and evaluation of appropriate pretreatment methods for the augmentation water if results indicated adverse effects on groundwater or stream ecology.

The assessment of the microconstituent risk associated with augmenting an urban stream with recycled wastewater is complicated by the fact that different constituents may be present in different concentrations in each water source. In this project, the water quality of the recycled water was better than the site water with respect to metals and microbes. However, the recycled water also contained some constituents which were not present in the creek, such as *N*-nitrosodimethylamine (NDMA) and alkylphenol polyethoxylate metabolites (APEMs). Some constituents were present in both, such as perfluorochemicals (PFCs), organophosphates, and *N*-butylbenzene sulfonamide (NBBS), even though there was no known wastewater discharge into Upper Silver and Coyote Creeks.

The detection of PFCs in the surface water and underlying groundwater highlighted the importance of baseline system characterization for decision making and risk evaluation in water reuse for environmental enhancement. As described above and expected from their occurrence in wastewater and persistence during wastewater treatment, PFCs were also detected in the recycled water from the San Jose/Santa Clara Water Pollution Control Plant intended for the stream augmentation. Concentrations of total PFCs ranged 350-587 ng/l. Concentrations of perfluorooctanoic acoid (PFOA) and perfluorooctane sulfonate (PFOS) ranged 83-180 and 190-374 ng/l, respectively. While many PFC monitoring studies focus on PFOA and PFOS, the results of the present study showed that inclusion of other PFCs in the monitoring program may identify several additional PFCs resulting in a much greater total PFC concentration.

With respect to ecotoxicological effects, PFC release via recycled water into sensitive ecosystems requires evaluation. PFCs bioaccumulate in aquatic and terrestrial organisms, and the resulting tissue concentrations constitute an internal exposure which may be more ecotoxicologically relevant than the aquatic PFC concentration. The recycled water and two of six urban creek sites exceeded a threshold concentration of 50 ng/L PFOS that is viewed by some researchers as protective of upper trophic level avian species that consume organisms in equilibrium with the water.

The laboratory investigation of NDMA fate showed that NDMA is poorly degradable biologically, a finding that was consistent with literature reports. Biotransformation of NDMA is not likely to be a significant process during river and groundwater transport in the Upper Silver Creek and Coyote Creek system. However, NDMA and six other *N*-nitrosamines were found to undergo direct photolysis when exposed to simulated sunlight. Irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12-15 min for the other nitrosamines. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43$ to 0.61 for the other nitrosamines. Products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98% and 79%, respectively. Because biodegradation is relatively slow and sorption to sediment is negligible, aquatic photolysis of NDMA is generally expected to be the most significant attenuation process even at relatively low levels of solar irradiation ($t_{1/2}$ = 8-38 h at 244-855 W/m^2, 51° N latitude, 1 m depth).

In contrast to the *N*-nitrosamines, PFCs (selected perfluorooctanesulfonamides) were found to undergo *in*direct photolysis when irradiated in a solar simulator in aqueous hydrogen peroxide solutions. Indirect photolysis mediated by hydroxyl radical was observed for *N*-EtFOSE, *N*-EtFOSAA, *N*-EtFOSA, and FOSAA. Final degradation products of the indirect photolysis of the perfluorooctanesulfonamides were PFOA and FOSA, which did not undergo additional degradation. A proposed reaction pathway for degradation of the parent perfluorochemical, *N*-EtFOSE, to the other perfluoroalkanesulfonamides, FOSA, and PFOA was developed and includes oxidation and *N*-dealkylation steps. Given the slow rates expected for biodegradation and limited sorption, indirect photolysis of PFCs may be important in the determination of their environmental fate. However, the rates of indirect photolysis observed were quite slow, and thus significant rates of transformation would not be expected over the creek study reach. Some transformation may be possible during additional travel time to San

Francisco Bay, depending upon the sunlight irradiation and reactive intermediates available to facilitate indirect photolysis of PFCs.

Biotransformation of the metabolites of alkylphenol ethoxylates (APEMs) was also assessed. Based on this study, some biotransformation of APEMs may be expected at the Coyote Creek site upon infiltration of water containing APEMs into the hyporheic and subsurface zones, particularly considering the slow travel times of groundwater. However, complete removal of APEMs is not expected, and instead, more stable forms of these compounds may be produced: Research available in the literature shows that under aerobic conditions, shorter, relatively stable APECs (with one to three ethoxy units, i.e. AP_nECs where n = 1-3) may be formed. Under anaerobic conditions, however, biodegradation may continue to form the smaller alkylphenols (APs). Further degradation of APs under anaerobic conditions is typically not observed, but some biotransformation under aerobic conditions may occur. Water quality monitoring of the surface and groundwater following stream flow augmentation with recycled water would be required to fully assess whether concentrations of APEMs were significantly reduced following the expected attenuation and dilution with site water.

Advanced treatment options are available for the removal of NDMA and PFCs in wastewater. In a laboratory study of the removal of PFCs by nanofiltration, rejections greater than 95% were measured for most PFCs tested and depended upon the solution pH (which controls the protonation state of the PFC) and the fouling layer. If nanofiltration or reverse osmosis were viable treatment options for wastewater prior to use in stream flow augmentation, these advanced treatment processes would result in adequate removal of PFCs.

As suggested by results obtained in a separate study for an advanced wastewater treatment facility at the time of this project, microfiltration (MF) of wastewater effluent is not expected to reduce NDMA concentrations and may in fact lead to NDMA formation when in combination with chlorination or chloramination used to prevent MF membrane fouling. However, reverse osmosis (RO) treatment of secondary effluent using thin-film composite membranes typically results in NDMA rejection of approximately 50 to 65%. For the overall treatment train, this rejection is an important contribution to NDMA removal. Lower rejection may be associated with changing feed conditions and fouling observed in real treatment systems. Thus, if RO was a viable treatment option for wastewater prior to use in stream flow augmentation, this advanced treatment process would likely result in a significant, though incomplete, removal of NDMA. UV irradiation in combination with RO treatment and in some cases, blending, may allow operators to reliably maintain the residual NDMA below the 10 ng/L CA drinking water notification level.

Abstract

Water recycling for environmental applications requires consideration of a complex set of benefits and risks. The goals of the present study were to augment Coyote Creek in San Jose, CA with local recycled water as a research demonstration and to assess any potential impacts to water quality. Field site assessment included the selection of water quality constituents and sampling campaigns of recycled water and site water. Laboratory investigations of contaminant fate included biodegradation, sorption, and photolysis of particular organic contaminants. Results showed that water quality of the recycled water was better than the site water with respect to metals and microbes. However, the recycled water also contained some constituents which were not present in the creek, such as *N*-nitrosodimethylamine (NDMA) and alkylphenol polyethoxylate metabolites (APEMs). Some constituents were present in both water sources, such as perfluorochemicals (PFCs), organophosphates, and *N*-butylbenzene sulfonamide (NBBS). The recycled water and two of six urban creek sites exceeded a threshold concentration of 50 ng/L PFOS that is viewed by some researchers as protective of upper trophic level avian species that consume organisms in equilibrium with the water. Laboratory investigations showed that NDMA is poorly degradable biologically but aquatic photolysis may be a significant attenuation mechanism. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43$ to 0.61 for other nitrosamines. In contrast to the *N*-nitrosamines, PFCs (selected perfluorooctanesulfonamides) were found to undergo *in*direct photolysis when irradiated in a solar simulator in aqueous hydrogen peroxide solutions. However, rates of indirect photolysis for PFCs were quite slow, and thus significant rates of transformation would not be expected over the creek study reach. Biotransformation of the metabolites of alkylphenol ethoxylates (APEMs) was also assessed and could be expected at the Coyote Creek site upon infiltration of water the hyporheic and subsurface zones. In a laboratory study of the removal of PFCs by nanofiltration, rejections greater than 95% were measured for most PFCs tested. NDMA rejection by reverse osmosis (RO) membranes was typically 50 to 65%. For the overall treatment train, this rejection is an important contribution to NDMA removal.

Keywords: water reuse, wastewater reclamation, emerging contaminants, NDMA, perfluorochemicals

1.0 INTRODUCTION

1.1 Overview

An increasing number of communities in California are turning towards water recycling as a means to meet the growing demand for water. The traditional solution to increase water supplies has been to import water from distant sources. However, this option has been vanishing with population growth spreading all across the Southwest. In cases where human uses have diminished the water source that an ecosystem depends on, one option is to treat impaired sources—including tertiary effluents—such that the treated water can replenish the water source. Water agencies in the U.S. and elsewhere are expanding wastewater reclamation (or water reuse) as part of their water supply portfolio to meet the needs of growing populations.

Recycling water via stream flow augmentation is an example of an environmental application of reclaimed wastewater. The re-used water must be protective of both stream ecology and groundwater, and comply with local and regional regulations. Currently there are limited data available to assess such water augmentation schemes *a priori*, and detailed, site-specific evaluations are needed.

Although the release of treated wastewater to surface water has historically been commonplace given the lack of alternatives, water recycling nevertheless requires consideration of a complex set of benefits and risks at sites where a natural source (rain, groundwater, rivers) is replaced or augmented with tertiary effluent. Wastewater may contain trace levels of organic contaminants, some of which may be carcinogens, toxins, or endocrine disruptors. The identification of these compounds in wastewater or the receiving water body depends on 1) the application of analytical methods to specifically target the desired compound or compounds and 2) the detection limits of the analytical method. The presence of these microconstituents in the receiving water body may have ecotoxicological consequences, as well as pose potential human health risks. Although water reuse is generally regarded as a sustainable approach to water supply management, the presence of trace organic contaminants raises concerns about the use of this water in applications such as environmental enhancement.

1.2 Background

The City of San José previously proposed to augment stream flow in Coyote Creek by up to 400% with recycled water. Several relevant supporting studies were conducted for the City. Chief amongst these studies was the "Revised Initial Study" (SCVWD, 2007), which evaluated the ecological and groundwater impacts of the augmentation. A primary objective of the San José scheme was to improve cold-water habitat in Coyote Creek, thus recycled water was to be dechlorinated and chilled significantly prior to release into the creek. For groundwater, the study noted that the Santa Clara groundwater basin, which contains the reach of Coyote Creek of interest, is divided into three zones: a shallow unconfined aquifer, a regional aquitard, and beneath the aquitard a potable deep confined aquifer. Considering the location of the City's proposed outfall at Singleton Landfill, recycled water in Coyote Creek would only flow over the regional aquitard and infiltration to the potable deep aquifer would be unlikely. The report noted that there is a low probability of infiltration to the shallow aquifer due to the clayey composition of the creek bottom; nevertheless, monitoring of shallow aquifer water quality was recommended to confirm that no recharge with recycled water was taking place.

Another concern that arose during the City of San José project was the degradation of water quality due to trace organics and endocrine disruptors. The appearance of these compounds in the aquatic environment is a recent environmental concern because some of them are biologically active and viewed as potentially harmful to wildlife and human health.

In late October 2000, the City of San José obtained a permit from the California Regional Water Quality Control Board (RWQCB) to implement a demonstration stream flow augmentation project in Coyote Creek. The City decided not to proceed with the project and the RWQCB permit expired in June 2003.

1.3 Project Rationale

The central rationale for this project is that it increases the potential for the expanded use of recycled water by the Santa Clara Valley Water District (SCVWD) in Santa Clara County, which is consistent with the desires and policies of the District Board of Directors (Board). It also has the potential to provide augmented creek flows for environment benefit as part of the "Environmental Stewardship" mission of the Board.

As described in the project work plan (SCVWD, 2008), it was also proposed that Stanford University (a project partner) would use the augmentation to test the central hypothesis that natural biological, physical, and chemical action during stream flow can improve the stream's water quality via natural attenuation of trace organics. Likewise, natural action during the infiltration of surface water into groundwater can further improve the water quality of the infiltrating water. The natural attenuation of any microconstituents present in the reclaimed wastewater would thus mitigate impact of these constituents on the environment and reduce any potential impact on drinking water supplies.

The hypothesis was based upon prior studies conducted by Stanford University researchers. With support from the Orange County Water District, Reinhard et al. conducted a similar study of water quality changes in the Santa Ana River in Southern California (Reinhard et al., 1999; Reinhard and Ding, 2001). The Santa Ana River carries nearly 100 percent tertiary treated water during the summer months (Gross et al., 2004). In that study it was found that trace organic contaminants such as pharmaceuticals and alkylphenol ethoxylate metabolites (biological degradation products of nonionic detergents) are significantly attenuated during river transport suggesting that the river itself acts as an efficient treatment system. The subsequent infiltration of river water into the ground led to significant additional water quality improvement in terms of total organic carbon (dissolved and particulate) and trace organics.

1.4 Project Objectives

The original objective of this research-scale study was to augment the stream flow of Coyote Creek in San José using recycled water produced at the San José/Santa Clara Water Pollution Control Plant (SJ/SC WPCP) and to examine any impacts upon the creek. As stated in the project work plan (SCVWD, 2008),

> The overall goal of the stream augmentation project is *to assess the potential impact of large-scale augmentation of the Coyote Creek flow with tertiary treated water on the water quality of the river and the underlying groundwater. If results indicate adverse effects, appropriate treatment methods will be evaluated. These treatment methods may include Reverse Osmosis treatment, soil treatment, or blending with higher quality water.*

The source of Coyote Creek is located in the upper reaches of the Santa Clara Valley, and flows over 20 miles through suburban and urban areas to its mouth in South San Francisco Bay. The tertiary treated recycled water was to be released into the stream approximately 15 miles upstream from the Bay. The study originally proposed to add from 2 to 6 cubic feet per second (cfs) of recycled water to Coyote Creek, corresponding to two to three times base summer flow (base flow readings are available at http://alert.valleywater.org/ gagestrm.html). This augmentation plan was later amended to involve temperature monitoring and flow adjustment due to concerns about temperature impacts on the stream, resulting in an estimate that the recycled water addition would be equal to or less than the base summer flow. In 2007, the SCVWD drafted an Initial Study/Mitigated Negative Declaration (SCVWD, 2007) prepared in compliance with the California Environmental Quality Act (CEQA) and the State CEQA Guidelines (not finalized; Appendix J).

In the spring of 2008, SCVWD cancelled the augmentation due to concerns over the presence of perfluorochemicals in the recycled water intended for the augmentation. As described in the project work plan, microconstituents originally assessed in the wastewater and stream included pharmaceuticals. The list of target analytes was reassessed and compounds including perfluorochemicals were added and surveyed in the recycled water and at the site. Following detection of perfluorochemicals in the recycled water at concentrations typical of wastewater, a brief assessment of perfluorochemical ecotoxicity was performed by Stanford University (Plumlee et al., 2008a). Based on a review of this information, SCVWD made the decision to cancel the augmentation.

Listed below are the project objectives as presented in the original project work plan. Although several of the objectives were met using both laboratory and field work, some objectives could not be met entirely due to the fact that the creek flow was not augmented using recycled water and subsequent monitoring of surface and ground water quality could not be performed.

The objectives of this study were:

1. To assess the potential of fate mechanisms – including photochemical degradation, adsorption, and biotransformation – to remove specific contaminants from tertiary treated recycled water used for large-scale augmentation of stream flow in Coyote Creek. The specific contaminants targeted for this study were selected based upon the results of a detailed characterization of the tertiary treated recycled water.
2. To assess the fate of contaminants during percolation from Coyote Creek into groundwater under stream flow augmentation conditions.
3. To evaluate the hydrological conditions of the study site—specifically the interactions between surface flow and shallow and deep aquifers
4. To evaluate appropriate treatment methods for the augmentation water, if results indicate adverse effects on groundwater or stream ecology.

2.0 PROJECT APPROACH

The overall project approach was divided into two components – the field site assessment and laboratory investigation of contaminant fate. To summarize, field site assessment involved the selection of water quality constituents, including emerging contaminants, their analytical method development if necessary, and the sampling campaigns for the targeted analytes in the recycled water, surface water, and groundwater. Additional site characterization included assessment of stream and groundwater hydrology via well installation and planned stream gauging and tracer test. The laboratory investigation of contaminant fate included biodegradation, sorption, and photolysis of particular organic contaminants.

2.1 Site Selection and Sampling

The original creek selection and surface water sampling sites were along Coyote Creek in San Jose, as shown in the Figure 1 map. Upper Silver Creek, a tributary to Coyote Creek, was selected in 2005 for discharge of the recycled water due to the creek's proximity to recycled water pipelines at the Yerba Buena pump station, as shown in the aerial photograph in Figure 2.

Thus the surface water sampling sites were modified to include both creeks. The objective was to choose sampling locations that permitted the monitoring of water quality changes in the creeks as the water flowed from the augmentation outfall point. Sampling points were selected such that, ideally, there were no additions/diversions that changed the quality or quantity of water in Coyote Creek. Additionally, a control site upstream of the augmentation outfall was selected.

The final selected sampling sites are shown in Figure 3 and described in Table 1. In addition to surface water sampling along Upper Silver and Coyote Creeks, groundwater wells were installed adjacent to the creek and sampled during the baseline phase to establish initial conditions, with the intention to monitor the wells every month for one year during augmentation to determine whether target compounds in the recycled water impacted groundwater quality. In addition to the installation of traditional groundwater wells, very shallow groundwater wells were installed in the creek bed at a depth of just 0.6-0.9 m to capture young groundwater in the hyporheic zone, a region in which surface and groundwater exchange and flow velocity, relative to the surface, is reduced by orders of magnitude (Hoehn and Cirpka, 2006). These "push wells" (PW1, 2, and 3) were installed in or adjacent to the creek.

In order to use temperature as a tracer for hydraulic residence time (Anderson, 2005), temperature monitors were installed at selected surface water sites and in push wells.

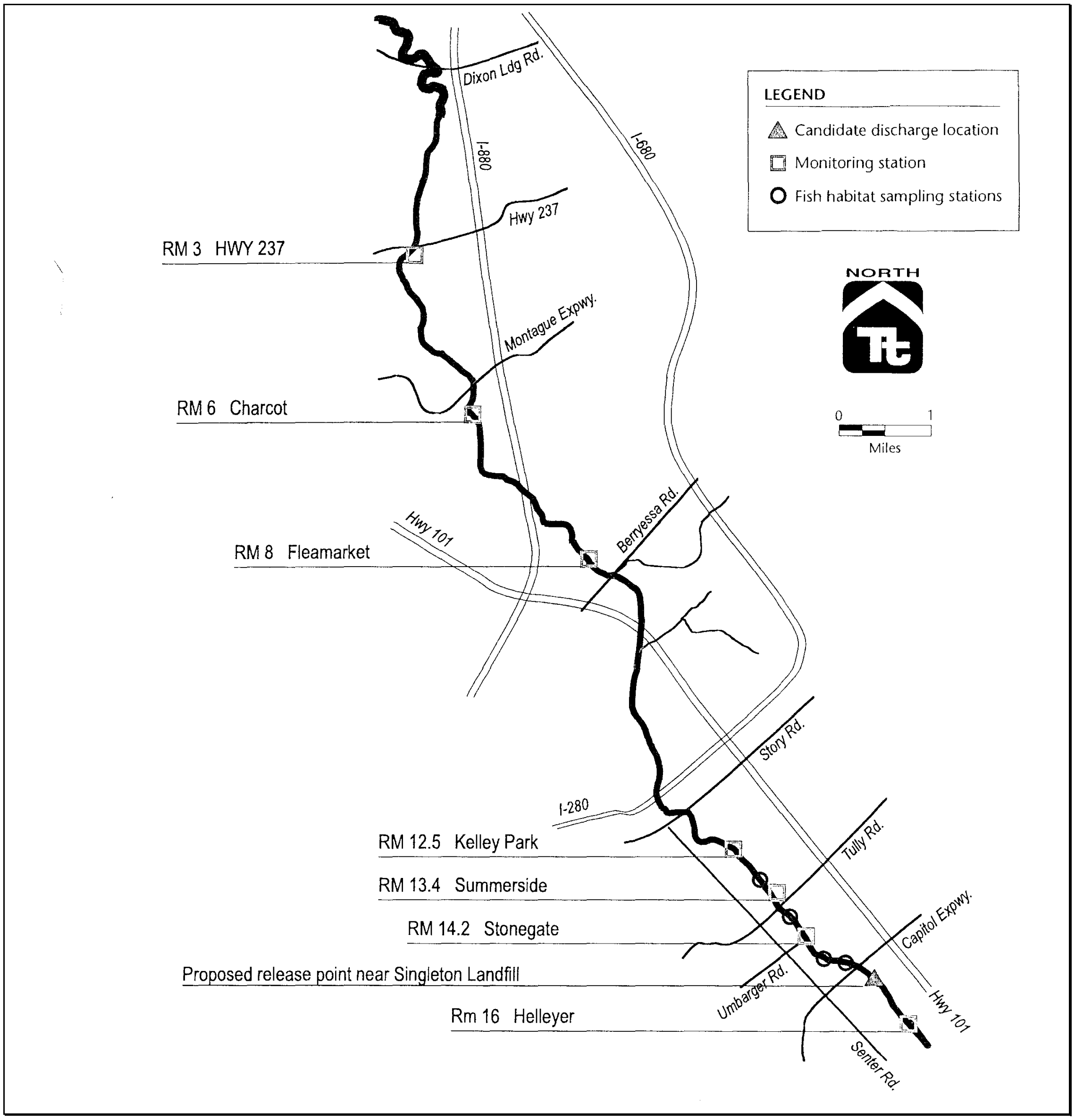


Figure 1. Sampling locations proposed in the Jones & Stokes *Initial Study (Jones & Stokes, 2000).*

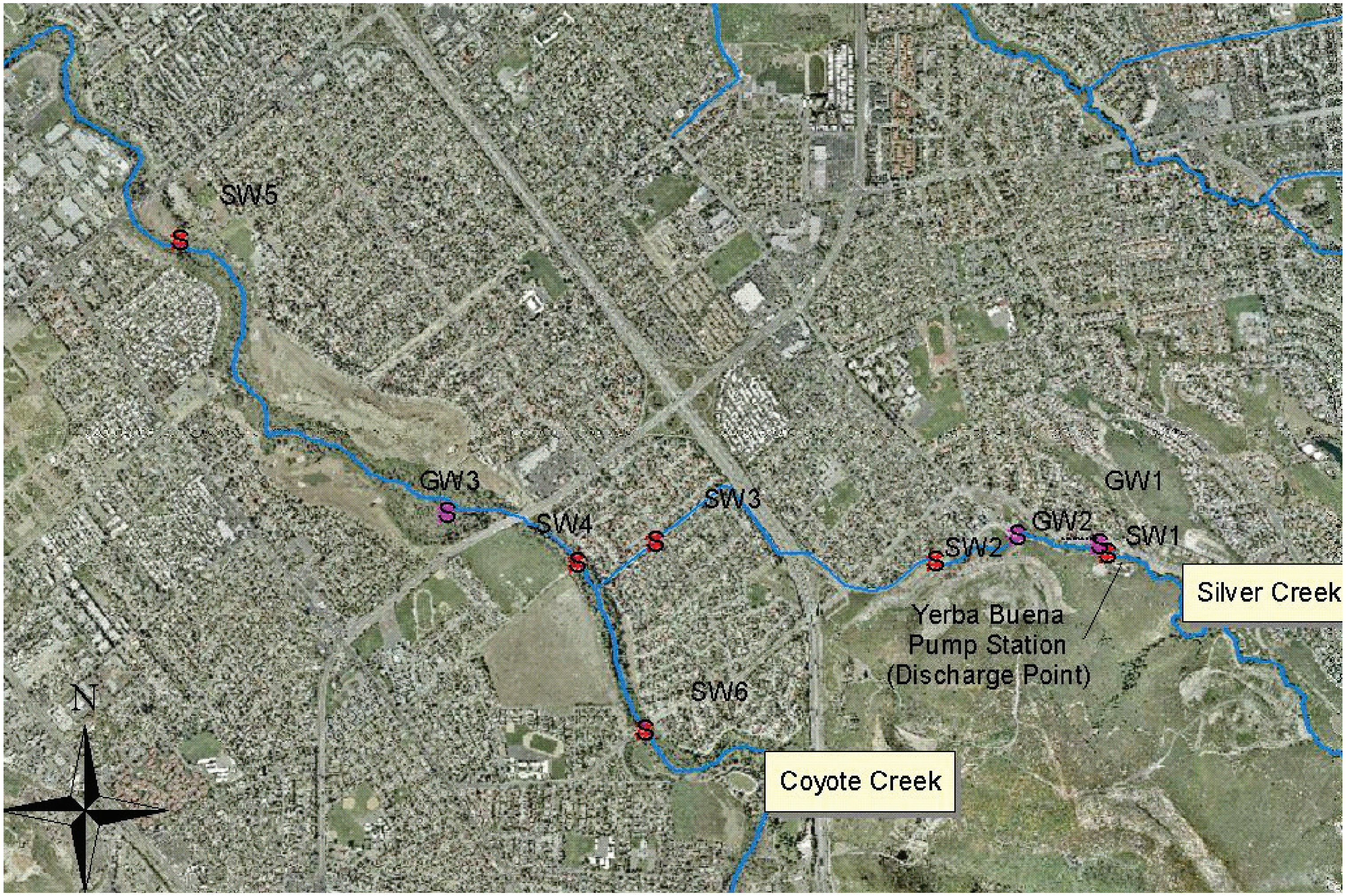


Figure 2. Aerial photograph of Upper Silver and Coyote Creeks with surface and groundwater sites shown. Creeks flow north.

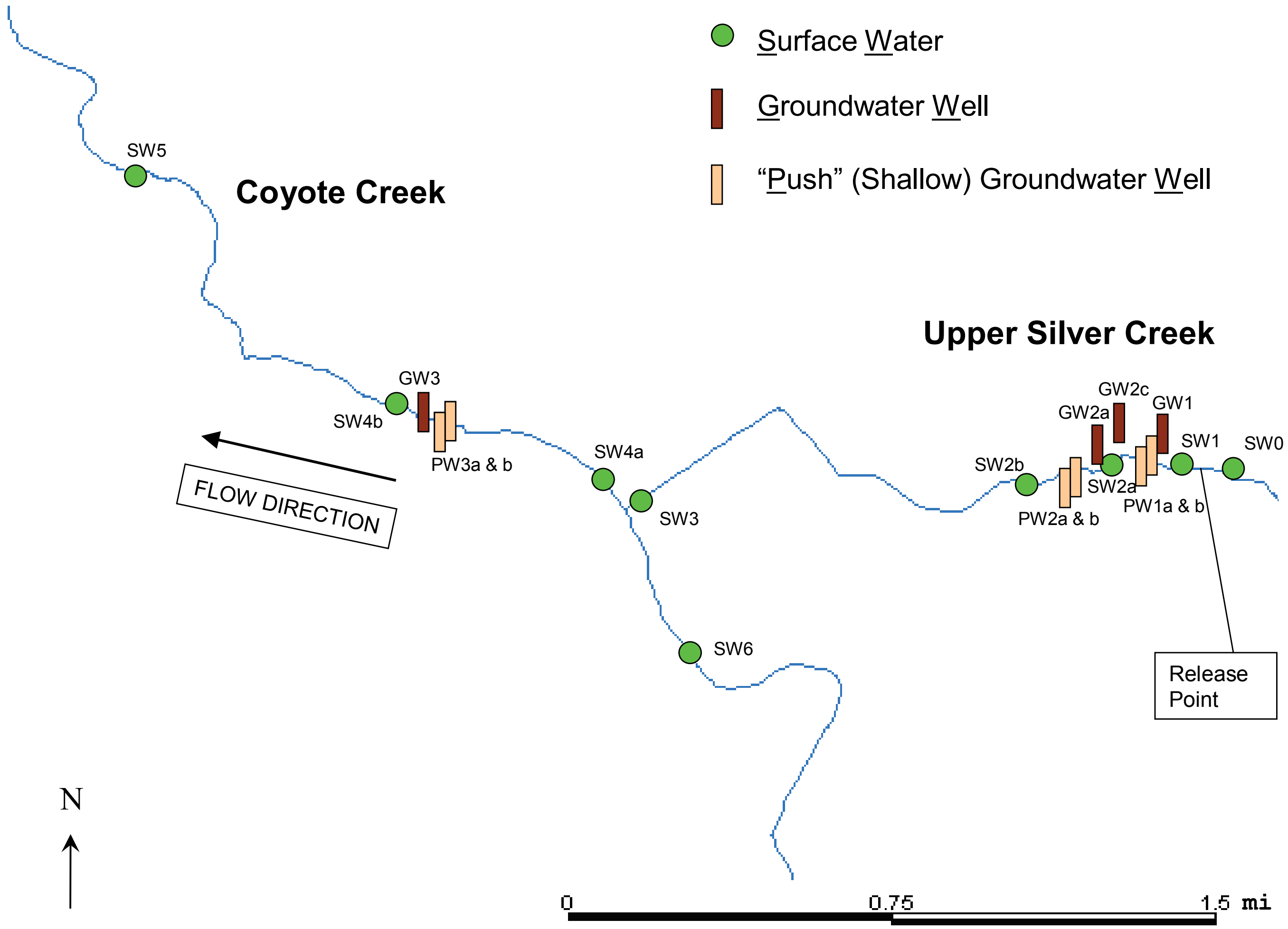


Figure 3. Final selection of surface, groundwater, and hyporheic groundwater monitoring sites along Upper Silver and Coyote Creeks.

Table 1. Description of sites from Figure 3, the final selection of monitoring sites along Upper Silver and Coyote Creeks.

SURFACE WATER SAMPLING POINTS :

Site Name	Description	Comment
SW0	0) Control site on Upper Silver Creek upstream of recycled water discharge	*site to be included following augmentation
SW1	1) Upper Silver Creek discharge point at Yerba Buena Pump Station	
SW2	2) Upper Silver Creek upstream of concrete channel	
SW3	3) Upper Silver Creek downstream of concrete Channel	
SW4	4) East bank of Coyote Creek near Singleton after Upper Silver Creek confluence	
SW5	5) Coyote Creek at Stonegate	
SW6	6) Coyote Creek control, at Yerba Buena Bridge upstream of confluence	
GROUNDWATER WELLS:		
Site Name	**Description**	
GW1	1) Near discharge point at Yerba Buena Pump Station	
GW2a	2a) near Upper Silver Creek at Silver Creek Line Park	
GW2c	2c) near Upper Silver Creek at Silver Creek Line Park	
GW3	3) After confluence near Coyote Creek	
"PUSH" WELLS (shallow, hyporheic zone wells):		
Site Name	**Description**	
PW1S PW1D	1) Slightly downstream of discharge point and GW1, in/near Upper Silver Creek bed	Shallow (2 ft) Deep (3 ft)
PW2S PW2D	2) At SW2, in Upper Silver Creek bed	
PW3S PW3D	3) Near GW3, in the Coyote Creek bed	
RECYCLED WATER:		
Site Name	**Description**	
RW1	1) Recycled water from SJ/SC WPCP at Yerba Buena Pump Station	

2.2 Analyte Selection

As a preliminary task, project personnel screened the recycled water and stream sites for a range of trace organics shown below (Table 2), and then made a final selection of those compounds detected regularly and/or in sufficient quantities to include in future monitoring. Analysis of the trace organics, including some emerging contaminants, was performed by Stanford University personnel.

In addition, SCVWD performed additional analysis for a number of compounds listed in Table 2, including metals, disinfection byproducts, and microorganisms.

On-site and general water quality parameters, such as pH, dissolved oxygen (DO), dissolved organic carbon (DOC), anions, etc. were also included and performed by both Stanford and SCVWD personnel depending on the campaign.

Water quality assessment of the stream, groundwater, and recycled water was performed to establish baseline conditions prior to augmentation. Monitoring campaigns of this type were executed, typically in the spring and summer months, during 2004, 2005, 2006, and 2007. These campaigns were carried out each year in preparation for augmentation planned to occur that summer, but each year the augmentation was postponed to the next year for various reasons (namely construction and/or permitting delays). The target analytes and particular field sites included each year varied slightly as the project focus and available analytical methods were refined.

Of particular concern to this study were organic contaminants that may occur at trace concentrations, commonly referred to as “trace organics” or “microconstituents”. These may include “emerging contaminants,” or microconstituents for which toxicological information is sparse and official water quality criteria (for drinking or wastewater) have not been established.

Trace organics surveyed in this project included pharmaceuticals (such as gemfibrozil, ibuprofen, naproxen, ketoprofen, carbamazepine), hormones (estrone, 17α-ethynyl estradiol, 17β-estradiol, estriol), the metabolites of alkylphenol polyethoxylates (APEMs), N-butyl benzenesulfonamide (NBBS), chlorinated tris-propylphosphates (TCPPs), N-nitrosodimethylamine (NDMA), and several perfluorochemicals (PFCs). The APEMs include alkylphenols (APs), short-chain alkylphenol polyethoxylates (APEOs), alkylphenol polyethoxycarboxylates (APECs) and carboxylated alkylphenol polyethoxycarboxylates (CAPECs).

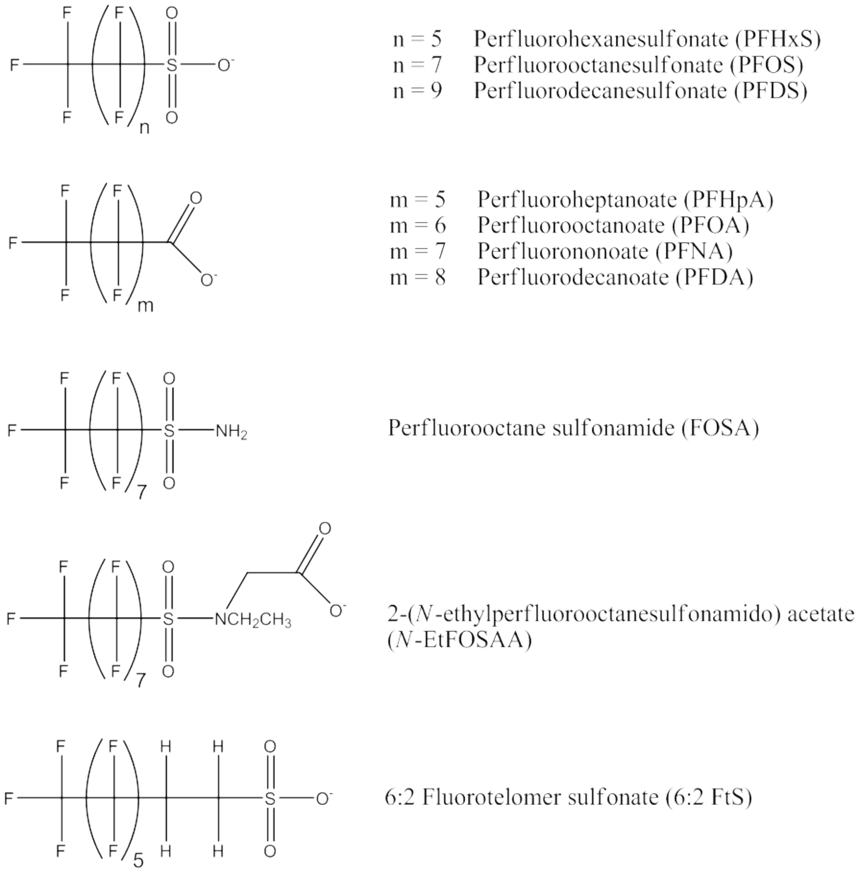
NDMA and PFCs were added to the list of target compounds when the pharmaceuticals and hormones were not detected or were detected only intermittently. Further, the presence of NDMA and PFCs in recycled wastewater is of particular concern: NDMA is a probable human carcinogen and disinfection byproduct, and PFCs may have a negative ecological impact that is the topic of current environmental research and debate. A list and structures of PFCs monitored in the present study is presented in Figure 4. More details on the environmental occurrence and toxicology of these compounds may be found in Appendices C and D (NDMA) and Appendix E and F (PFCs).

Table 2. Water quality parameters surveyed in stream, groundwater, and recycled water.

Fire Retardants	2
Tris (3-chloropropyl) phosphate	
Tris (2,3-dichloropropyl) phosphate	
Plasticizers	2
Bisphenol A	
N-butyl benzenesulfonamide	
APEMs	4 groups
Halogenated/Chlorinated APEMs	
APEOs	
Alkylphenols (nonyl-, octyl-)	
APECs, CAPECs	
NDMA (Disinfection Byproduct)	1
Perfluorochemicals	11

Organic Compounds	
Herbicides and Pesticides	9
Trihalomethanes	5
Haloacetic Acids	7
Metals	19
Microbes	3 groups
General Water Quality	10
On-site Parameters	4
Temperature, pH, Conductivity,	
Dissolved Oxygen	

Pharmaceuticals	11
Acetaminophen	
Caffeine	
Carbamazepine	
Carisoprodol	
Gemfibrozil	
Ibuprofen	
Iminostilbene	
Ketoprofen	
Naproxen	
Primidone	
Propanolol	
Hormones	4
Estradiol	
Estriol	
Estrone	
Ethynylestradiol	



n = 5 Perfluorohexanesulfonate (PFHxS)
n = 7 Perfluorooctanesulfonate (PFOS)
n = 9 Perfluorodecanesulfonate (PFDS)

m = 5 Perfluoroheptanoate (PFHpA)
m = 6 Perfluorooctanoate (PFOA)
m = 7 Perfluorononoate (PFNA)
m = 8 Perfluorodecanoate (PFDA)

Perfluorooctane sulfonamide (FOSA)

2-(*N*-ethylperfluorooctanesulfonamido) acetate
(*N*-EtFOSAA)

6:2 Fluorotelomer sulfonate (6:2 FtS)

Figure 4. Perfluorochemicals monitored in the present study.

2.3 Analytical Methods

The analytical method (sample preparation and instrumental analysis) depended upon the target analyte. The analytical methods utilized for microconstituent analysis by Stanford University personnel are described here and summarized in Table 3. Method detection limits, where known, are reported with the results.

Pharmaceuticals, hormones, organophosphates, plasticizers, oxadiazon, and APEMs (analyzed together)

For recycled, surface, and ground water, three to four liters were collected in 1 L amber glass bottles (rinsed three times with sample water) and packed on ice in coolers. To recycled water, 1 mL of a sodium thiosulfate solution was added to quench chlorination. Following return to the Stanford laboratory, samples were stored at 4°C.

For analysis (Gross et al., 2004; Lin et al., 2006), liters obtained from the same site were mixed to promote homogeneity and were filtered using 0.2 μm nylon filters and adjusted to pH 2.3. A blank of Milli-Q purified water was also prepared. C-18 cartridges with 1.0 g sorbent (Alltech, IL, USA, extract-clean columns, 8 mL) for the May analysis, C-18 with 2.0 g sorbent for the July analysis, and phenyl cartridges with 1.0 g sorbent (Phenomenex Strata End-Capped, 6 mL) for the August analysis were used to extract the target contaminants from 1 L samples by solid phase extraction (SPE). Each site was analyzed in replicate. SPE was performed using a 16-port vacuum extraction manifold. Cartridges were conditioned sequentially with 6 mL acetone, 6 mL acetonitrile, and 10 mL Milli-Q water (pH 2). The samples were then loaded through the cartridges by applying a vacuum at a flow rate of 10 mL/min or less. The cartridges were then washed with Milli-Q water and dried under vacuum. Analytes were eluted with 5 mL acetonitrile followed by 5 mL acetone.

The extract was concentrated by evaporation on a sand block at 30-40ºC to 30-50 μL and divided into two or three fractions. To one fraction, 10 μL of a 20 mg/L internal standard solution (chrysene-d_{12}) was added for neutral compounds analysis (some APEMs, some pharmaceuticals, oxadiazon, NBBS, BPA, and organophosphates). The second aliquot was used to analyze for acidic compounds (carboxylated APEMs, some pharmaceuticals). In this aliquot, carboxylic acids were converted into their respective propyl esters by adding 10 μL of 90/10 (v/v) *n*-propanol/acetylchloride to the evaporated samples and heating for 1 hour at 85ºC. After propylation, the samples were evaporated to near dryness and 10 μL of the chrysene-d_{12} internal standard solution was added. If the third fraction (for hormones, BPA, and some pharmaceuticals) was prepared, it was similarly derivatized but by silylation using 10 μl of MTBSTFA and heated for 3 hours at 95ºC, followed by internal standard addition.

Quantitation was performed by gas chromatography-mass spectrometry (GC-MS) by sample injection onto an Agilent 6890N GC with a 5973 MSD. A DB-5 capillary column (30 m x 0.32 mm I.D., film thickness 0.25 μm; Agilent, Wilmington, DE, USA) or an equivalent column was employed using helium as the carrier gas.

All analytes in the neutral and propylated fractions were monitored in the total ion current (TIC) mode (mass range m/z = 50 – 550; scan time 0.5 s) and quantified using their base ions. Compounds in the silylated fraction were monitored using single-ion monitoring (SIM) mode of their base ions. Since APs, APEOs, APECs, and CAPECs occur as complex mixtures, the different isomers are manually differentiated with respect to the number of ethoxy groups and the length of their alkyl-chain (i.e., octyl or nonyl). APECs and CAPECs, which produce many of the same mass spectral fragments, are generally reported as the sum of the APECs and CAPECs (denoted as A+CAPECs). Because no commercial standards were available for tris(3-chloropropyl)phosphate or some of the pharmaceuticals including iminostilbene, these compounds were tentatively identified in the samples by comparing the spectral characteristics of the sample peak with spectral characteristics in the NIST (National Institute of Standards and Technology) mass spectral library.

Concentrations of the individual compounds were determined *semi-quantitatively* by comparing the base ion with the m/z 240 ion of the internal standard, chrysene-d_{12}.

Thus, all reported concentrations are based on the assumption that the response factors for the internal standard and the analyte are the same.

N-Nitrosodimethylamine (NDMA)

An analytical method for NDMA in wastewater and surface water was developed for this project and is summarized here; it is also available in the publication included as Appendix C (Plumlee et al., 2008b). For recycled, surface, and ground water, three to four liters were collected in 1 L amber glass bottles (rinsed three times with sample water) and packed on ice in coolers. Following return to the Stanford laboratory later the same day of collection, samples were stored at 4°C. For analysis, liters obtained from the same site were mixed to promote homogeneity and were filtered using 0.2 or 0.45 μm nylon filters. A blank of Milli-Q purified water was also prepared.

NDMA was extracted from 500 mL or 1 L of sample water (each site analyzed in replicate) by solid phase extraction (SPE) with a 16-port vacuum extraction manifold using reservoirs packed with activated charcoal. Activated charcoal was washed with Milli-Q water at the same pH as the sample, dried overnight at 110ºC, and 1.0 g was packed into empty 8 mL SPE reservoirs fitted with a frit and filter at the base. The sorbent was wetted with Milli-Q water before loading the water sample under vacuum at a flow rate less than 5 mL/min. After loading the water sample, the bottles were rinsed three times with Milli-Q which served to wash the charcoal. The cartridges were drained except for a small amount of water left behind, which was eluted into 15 mL glass collection vials. NDMA was eluted from the charcoal using 2 mL acetonitrile (two times), 2 mL methanol (two times), and 2 mL acetone (two times). The extract was evaporated on a sand bath at 37ºC leaving 1-2 mL of solvent-free water. For instrumental analysis, the concentrated extracts following elution were returned to a pH of 5 – 9 by adding a small amount of concentrated NaOH. 0.3 mL of 110 ppb internal standard, NDMA-d6, was added to 1.0 mL of extract and stored at 4ºC until analysis.

NDMA was quantified using liquid chromatography-tandem mass spectrometry (LC-MS/MS) by injecting 50 μL at a flow rate of 0.15 ml/min onto a liquid chromatograph from Shimadzu LC-10AD *VP* with a Shimadzu SIL-10AD *VP* autosampler (Columbia, MD) equipped with a triple quadrupole mass spectrometer from Applied Biosystems API3000 (Foster City, CA). The instrument detection limit was typically 1 ppb and instrument reporting limit was 2 ppb NDMA, from which the method detection limit is 4 ng/L for 500 mL of loaded water sample.

Perfluorochemicals (PFCs)

An analytical method for PFCs in wastewater and surface water was adapted for this project from an available sediment method (Higgins et al., 2005) and is also available in the publication included as Appendix E (Plumlee et al., 2008a). To summarize, water samples of recycled, surface, and ground waters were collected (6 to 250 mL) in polypropylene bottles, after rinsing bottles three times with the sample water, and packed on ice in coolers until returned to the Stanford laboratory.

Each water sample was prepared for replicate analysis. Sample preparation involved the addition of a sample aliquot to a methanol-containing microcentrifuge tube, centrifugation, and transfer of the mixture to a vial containing a 70:30 (v/v) mixture of methanol and 0.01% aqueous ammonium hydroxide. An internal standard solution containing ^{13}C-labelled PFCs was added for quantitation.

PFCs were quantified using liquid chromatography-tandem mass spectrometry (LC-MS/MS) by large-volume injection of 490 μL onto a liquid chromatograph from Shimadzu LC-10AD *VP* with a Shimadzu SIL-10AD *VP* autosampler (Columbia, MD) equipped with a triple quadrupole mass spectrometer from Applied Biosystems API3000 (Foster City, CA). Calibration standards containing each of the 10-11 PFCs analyzed in the study were carefully matched in solution makeup to the sample preparation method, to minimize matrix effects and to achieve a linear calibration curve.

Table 3. Summary of Analytical Methods

Target Analyte	Method
On-Site Parameters Temperature Electrolytic Conductivity (E.C.) Dissolved Oxygen (D.O.) pH	Appropriate sensors
DOC	TOC Analyzer
Anions: nitrate, sulfate, etc	Ion Chromatography (IC)
Microconstituents	Gas Chromatography/ Mass Spectroscopy (GC/MS) or Liquid Chromatography/Tandem Mass Spectroscopy (LC/MS/MS)

2.4 Laboratory Investigations of Contaminant Fate

Throughout the course of the planning and (partial) implementation of the augmentation project, a variety of laboratory investigations were conducted to assess contaminant fate. Contaminants detected in the recycled water were selected for these studies. The results are summarized in the Project Outcomes below.

Of particular interest in this project was the detection of NDMA and PFCs in the recycled water to be used for the stream flow augmentation of Upper Silver and Coyote Creeks. It was noteworthy, too, that PFCs were detected in the surface and groundwater at the site (as characterized during the baseline studies executed). Following a review of the pertinent literature, laboratory investigations of particular attenuation mechanisms for these compounds were carried out.

Specifically, rates of biodegradation of NDMA and APEMs were assessed using sediment and water collected from the site. Extensive testing of the photosensitivity of

NDMA and PFCs to natural sunlight was also carried out. In adequately sunlit surface water systems, photochemical degradation may act in combination with biodegradation and sorption (and also volatilization and dilution) to naturally attenuate the concentrations of organic contaminants. Obviously, photolysis (via direct or indirect mechanisms) plays a particularly important role in the overall environmental fate of a trace organic compound when biodegradation and sorption are slow or negligible.

In some cases, photolysis may provide a reduction in the risk associated with the starting compound when the products of the reaction are harmless; in other cases, photolysis may result in transformation of the starting compound to a chemical or chemicals of concern. It is important to determine the identities of these products for a more complete evaluation of environmental fate and toxicity. Thus, product characterization was included in the photolysis studies of both NDMA and PFCs.

3.0 PROJECT OUTCOMES

3.1 Task Descriptions

The project outcomes listed below correspond to tasks specified in the Amended Work Plan.

Task 1: Work Plan Preparation

The work plan was completed and submitted to the Metropolitan Water District of Southern California in December 2004 and amended in July 2008, fulfilling the requirements of Task 1.

Task 2: Design and Installation of Monitoring Well(s) System

Sub Tasks:

Identify and Secure Needed Permits. Determine Augmentation Scheme, Groundwater Monitoring Requirements and Ecological Monitoring Requirements

SCVWD personnel was responsible for securing various permits required related to the discharge, including those for groundwater well installation. Permits for conducting a tracer test (release of rhodamine WT dye into the stream) were never finalized once the augmentation was cancelled (spring of 2008). SCVWD personnel also managed a consultant team to assess the issues associated with recycled water temperature and subsequent impacts on stream temperature. The overall augmentation scheme (such as sampling site selection, discussed below, and goals for volume and temperature of recycled water) underwent continuous revision over time based on discussions between SCVWD and Stanford University personnel, but was never fully implemented due to augmentation cancellation. Although some ecological monitoring was discussed (to be conducted in addition to the water quality monitoring), an ecological monitoring plan was never developed due to project scope and limited funding.

Select Recycled Water Outfall

A site at Upper Silver Creek (a tributary to Coyote Creek) near the Yerba Buena Pump Station was selected in 2005 for discharge of the recycled water due to the creek's proximity to recycled water pipelines at the Yerba Buena pump station, as shown in the aerial photograph in Figure 2.

Review of Historical Data and River Hydrology

A review of relevant historical data was conducted and submitted in a Technical Memorandum to the SCVWD in 2004 (Appendix I). To characterize stream hydrology, a tracer test using rhodamine WT and bromide as well as installation of stream gauges were planned but not executed following the 2008 cancellation of the augmentation with recycled water. The study originally proposed to add from 2 to 6 cfs of recycled water to Coyote Creek, corresponding to two to three times base summer flow of about 1 cfs. This augmentation plan was later amended to involve temperature monitoring and flow adjustment due to concerns about temperature impacts on the stream, resulting in an estimate that the recycled water addition would be equal to or less than the base summer flow.

Because possible infiltration of wastewater-derived microconstituents into the groundwater basin due to the augmentation was a concern, the hydrogeology of the system was considered. A more detailed discussion is provided in the separate report given in Appendix B. To summarize, it was concluded that if the creek feeds the hyporheic zone and underlying groundwater, sorption of contaminants to subsurface materials would enhance natural attenuation. A loss of creek water to riverbed and subsurface materials may, however, threaten the productive groundwater of the Santa Clara Valley basin. In the period between March and July 2006, the site was instrumented with i) three wells drilled at vertical distances of up to 50 *m* (160 *ft*) from the creek, ii) two wells pushed into the creek's bed (shallow "push wells"), and iii) temperature loggers in the creek and these wells. Additional push wells were installed later as depicted in Figure 3. The exploration of the site included i) an assessment of the hydraulic conductivity of subsurface materials, ii) a preliminary analysis of temperature time series, iii) an interpretation of an ongoing time series of water chemical analyses, and iv) radon water analyses.

A tracer experiment with rhodamine WT and bromide was also planned to complement the exploration work (though never executed once the augmentation was cancelled). Detailed modeling work was done to design the tracer experiment and to predict the tracer response in surface water and groundwater based on data from temperature response curves and estimated flow characteristics of stream flow (not shown). However, because the tracer experiments were not done, models could not be validated and the effort was abandoned.

The existence of a hyporheic zone below the creek's bed was inferred from the temperature data. Flow from the creek's bed into shallow alluvial ground water could not be detected, although the ground water of the drilled wells is young and originates from the same catchment as the creek's water. It was concluded that contamination of the deeper productive aquifer with augmented water from the experimental site at Upper Silver Creek would not be probable. From the composition of the ground water in a well near Coyote Creek, which is similar to that of the creek itself, some downwelling of creek water was hypothesized. A tracer test would be required to gain insight into the mixing rates of recycled water with the various natural waters.

Select Surface Water Sampling Locations

As described in the Project Approach section, grab samples of surface water were collected from the sites shown in Figure 3 along Upper Silver Creek and Coyote Creek over a reach of approximately 5 km. Samples were obtained from these sites and from the nearby Yerba Buena pump station (recycled water) in San Jose, CA at intervals of approximately once per month during spring and summer months during 2004-2007 to establish baseline water quality conditions.

Design and Installation of Well Systems

In addition to surface water sampling along Upper Silver and Coyote Creeks, groundwater wells were installed adjacent to the creek and sampled during the baseline phase to establish initial conditions, with the intention to monitor the wells every month for one year during augmentation to determine whether target compounds in the recycled water impacted groundwater quality. Groundwater samples were obtained from four monitoring wells (Figure 3; GW1, 2a, 2c, and 3) installed to depths of 5-10 m. Depth-to-water ranged 2-5 m for the four wells. Additional plans for augmentation which were not carried out due to the cancellation were to monitor water quality in the infiltration flow path so that contaminant attenuation could be assessed as a function of distance and residence time.

In order to use temperature as a tracer for hydraulic residence time (Anderson, 2005), temperature monitors were installed at selected surface water sites and in push wells.

Further descriptions of site hydrogeology determined from historical records or field investigations employed in this project, including the use of temperature and radon as groundwater tracers, may be found in a separate report given in Appendix B.

In addition to the installation of traditional groundwater wells, very shallow groundwater wells were installed in the creek bed at a depth of just 0.6-0.9 m to capture young groundwater in the hyporheic zone, a region in which surface and groundwater exchange and flow velocity, relative to the surface, is reduced by orders of magnitude (Hoehn and Cirpka, 2006). These "push wells" (PW1, 2, and 3) were installed in or adjacent to the creek. More details may be found in Appendix B.

Task 3 Baseline Data Collection and Analysis

Sub Tasks:

Characterization of SJ/SC WPCP Effluent

Previous studies (March, June and July 2002) showed the presence of halogenated alkylphenol polyethoxylate metabolites (APEMs) in San Jose/Santa Clara Water Pollution Control Plant (SJ/SC WPCP) effluent. Chlorinated APs and APEOs as well as chlorinated and brominated APECS were detected at concentrations up to 15 µg/L. These halogenated compounds are probably formed during chlorine disinfection in the presence of bromide. *All* other target compounds might also be present as halogenated derivatives, but since no commercial standards are available, no analytical methods are available.

As a preliminary screening for constituents that may occur in the final recycled water, SJ/SC WPCP effluent was sampled at the plant during two times (morning and afternoon) during one day in June 2005. Two pharmaceutical compounds, carisoprodol and iminostilbene, were detected at concentrations ranging 0.01-0.02 and 0.05-0.15 µg/L, respectively (with no obvious pattern in timing). APEMs were also detected at total concentrations ranging 0.5 to 7.4 µg/L. No halogenated APEMs were detected except for 0.07 µg/L for one of the morning duplicate samples.

Baseline Analysis of Water Quality at Coyote Creek Sampling Locations

Presented below are the detections observed for each analyte or analyte group in all sample waters (recycled water from Yerba Buena pump station and surface and ground waters from Upper Silver and Coyote Creeks) and sites for the baseline characterization of 2005. The 2005 monitoring campaign included pharmaceuticals, hormones, organophosphates, plasticizers, APEMs, NDMA, and perfluorochemicals. Highlights are given in sections 3.1.1-3.1.4 and a more detailed data summary (detects and non-detects) is given in section 3.1.5.

A limited baseline water quality analysis was performed in May of 2006 for the same 2005 sites plus additional push wells and groundwater wells.

Prior to the final cancellation of the augmentation using recycled water, samples of the surface water, groundwater, and recycled water were collected in June of 2007. NDMA and perfluorochemical data analysis was completed and the results are presented here. Data analysis was not completed for the other trace organics upon cancellation of the augmentation.

Additional water quality analyses were performed in 2005-2007 by SCVWD. These data are presented in Appendix A and included the following water quality constituents: herbicides and pesticides; trihalomethanes; volatile organic compounds (VOCs); metals; haloacetic acids; microbes; and general water quality.

Pharmaceuticals, hormones, organophosphates, plasticizers and oxadiazon

No hormones and few pharmaceuticals were detected in much of the baseline 2005 study. Tables 4 and 5 show the detections of two pharmaceuticals, carisoprodol and iminostilbene, in the recycled water and caffeine in the creek water. In a previous investigation these same two pharmaceuticals were identified in the SJ/SC WPCP secondary effluent in June 2005. No other pharmaceuticals were detected in the recycled water. Note that all measurements only reflect the particular day and time sampled; pharmaceutical concentrations emitted in wastewater effluents may be quite variable even over a single day. One reason for the absence of many targeted compounds may be that the final effluent is chlorinated, which can oxidize many organics.

Caffeine was detected at three creek sites in 2005, spanning both Silver and Coyote Creeks. Caffeine has been demonstrated for use as a marker for wastewater contamination of surface waters (Buerge et al., 2003). The detection limits noted in the tables were determined from a statistical analysis of a calibration curve.

Table 4. Detection of two pharmaceuticals in recycled water. The detection limit of iminostilbene is not known as a standard was not available.

Recycled Water 2005	July	August	DL*
Carisoprodol (ng/L)	217	195	60
Iminostilbene (ng/L)	98	96	--
Carisoprodol: muscle relaxant, blocks pain			
Iminostilbene: intermediate in synthesis of analgesics and antipsychotic agents			

*DL: detection limit

Table 5. Detection of caffeine in three sites along Silver and Coyote Creek in July of 2005.

Surface Water July 2005	SW 3 (Silver)	SW 4 (Coyote)	SW 5 (Coyote)	DL*
Caffeine (ng/L)	72	19	23	10
Caffeine: stimulant added to analgesics to enhance effect				

*DL: detection limit

NBBS, a plasticizer used in nylon production that is commonly found in US water bodies and is reportedly neurotoxic (Duffield et al., 1994), was found in recycled, creek and ground waters throughout the baseline 2005 study (Figure 5). Creek concentrations were generally similar to recycled water concentrations, with the exception of May when the creek levels at sites 3, 4, 5, and 6 were higher than the recycled water. A detection limit of 7 ng/L was determined based upon the statistical analysis of a calibration curve.

NBBS was tentatively identified in July SW5 and August GW3 but concentrations fell below the limit of quantification.

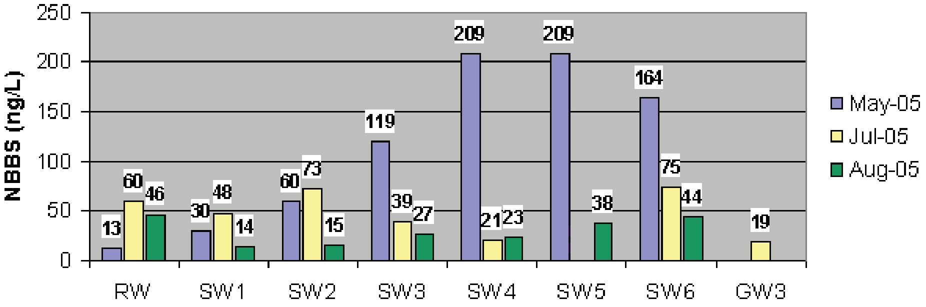


Figure 5. Concentrations of NBBS at all sites for three 2005 sampling events. Note that the groundwater well 3 was not sampled in May. Detection limit is 7 ng/L.

A single detection of BPA, 18 ng/L, was found in the July 2005 groundwater well 3 (GW3). BPA is a plasticizer used in polycarbonate plastic and epoxy resins and is considered estrogenic. The detection limit for this analyte has not been determined.

Results from the 2005 baseline monitoring for tris(3-chloropropyl)phosphate and tris(2,3-dichloropropyl)phosphate, organophosphates used as fire retardants, are shown in Figure 6 and Figure 7, respectively. Both are on the EU priority list for carcinogenic suspicion. Tris(3-chloropropyl)phosphate (Figure 6) appears fairly consistently through most of the sampling sites except in the groundwater in August (not measured in May). Note the log scale; concentrations are much higher in the recycled water than in the natural waters, and are also higher in the creek than in the groundwater. Tris(2,3-dichloropropyl)phosphate (Figure 7) appears more sporadically, with a concentration on the order of µg/L noted in May surface water site 1. Because a standard was available for tris(2,3-dichloropropyl)phosphate, a detection limit of 10 ng/L was determined based upon the statistical analysis of a calibration curve.

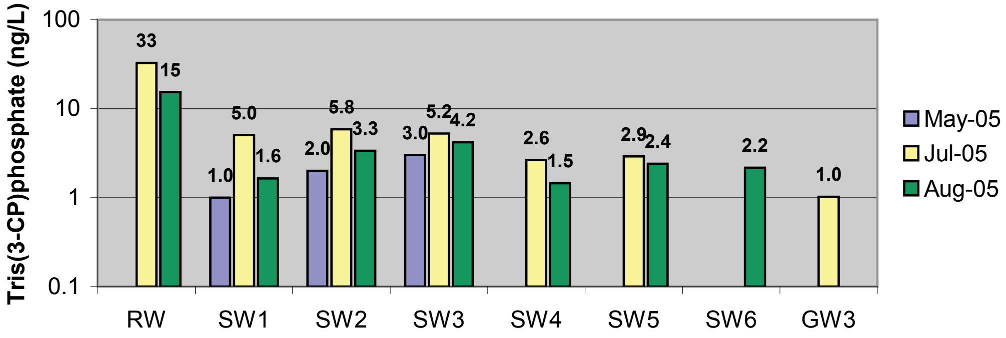


Figure 6. Tris(3-chloropropyl)phosphate concentrations for the baseline 2005 study. Detection limit unknown (no standard available).

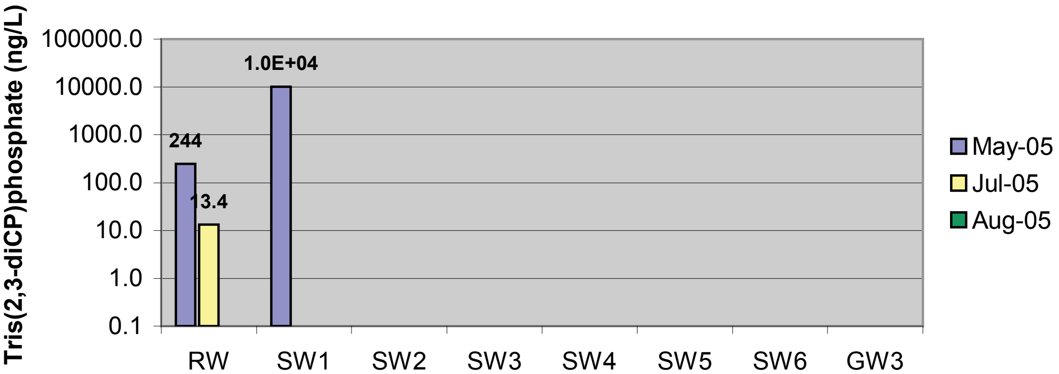


Figure 7. Tris(2,3-dichloropropyl)phosphate concentrations for the baseline 2005 study. Detection limit is 10 ng/L.

The herbicide oxadiazon was added to the project analyte list after its discovery in preliminary analyses of the Coyote Creek surface water. It was not found in the recycled or ground water, and was only found in the surface water during the 2005 baseline study in one month (July) at the three sites on Silver Creek, as shown in Table 6.

Table 6. Concentration of oxadiazon found at Silver Creek sites in July 2005 surface water. Detection limits have not been determined.

Surface Water July 2005	SW 1 (Silver)	SW 2 (Silver)	SW 3 (Silver)
Oxadiazon (ng/L)	12	12	3
Oxadiazon: herbicide applied in CA (600 pounds in Santa Clara County, 2003 (www.pesticideinfo.org)); developmental/reproductive toxin, suspected carcinogen			

A limited baseline water quality analysis was performed in May of 2006 for the same 2005 sites plus additional push wells and groundwater wells. Some pharmaceuticals and the hormones were omitted from the analysis (those belonging to a step in the analysis in which compounds are derivatized by silylation), because previous data showed few or no pharmaceutical and hormone detections. To save time and expense, the *surface* water samples were not analyzed for pharmaceuticals and other trace organics once it was determined that the augmentation would not occur in 2006, and instead only the push and groundwater well samples were analyzed (as the 2005 data set for those sites is limited). The 2006 data is reported in Table 7.

Most notably, the pharmaceutical compounds carisoprodol and iminostilbene, as wells as *N*-butylbenzene sulfonamide (NBBS), the organophosphates, NDMA and PFCs were detected in the recycled water, which is consistent with 2005 data.

Table 7. Summary of trace organics compounds analyzed in May 2006, with the exception of PFCs which are shown in Table 10. Surface water samples were only analyzed for NDMA and PFCs.

Analytes	RW	PW1	PW2	GW1	GW2A	GW2C	GW3	SW1	SW2	SW3	SW4	SW5	SW6	BLANK
Pharmaceuticals (ng/L)														
Caffeine	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Carisoprodol	**9**	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Gemfibrozil	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Ibuprofen	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Iminostilbene	**160**	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Ketoprofen	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Naproxen	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
APEOs & APEMs (ng/L)														
Octylphenol	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Others (ng/L)														
NBBS	**103**	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
NDMA	**26**	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Tris(2,3-dichloropropyl)phosphate	**36**	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Tris(3-chloropropyl)phosphate	**61**	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d
Oxadiazon	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.d

Alkylphenol ethoxylate metabolites (APEMs)

Figure 9 shows the results for summed metabolites of alkylphenol ethoxylates (APEMs), which are metabolites of nonionic surfactants, for the 2005 baseline water quality analysis. APEMs were excluded from the analysis, with the exception of octylphenol (Table 7). Example structures from this complex family of compounds are shown in Figure 8. Carboxylated APEMs (A+CAPECs: alkyl- and carboxyalkyl ethoxycarboxylates) and halogenated APEMs were detected in the recycled water each time it was sampled during the 2005 baseline study. Halogenated APEMs are chlorinated and brominated forms of the APEMs produced during wastewater disinfection. Halogenated APEMs made up 10, 19, and 5% of the total APEMs for May, July, and August 2005, respectively. Detection limits are largely unknown because pure standards are not available for most of these compounds; however the detection limit for individual APECs (and assumed to be the same for CAPECs) applied in this study is approximately 0.5 ng/L. No APEMs were detected in creek surface or ground waters.

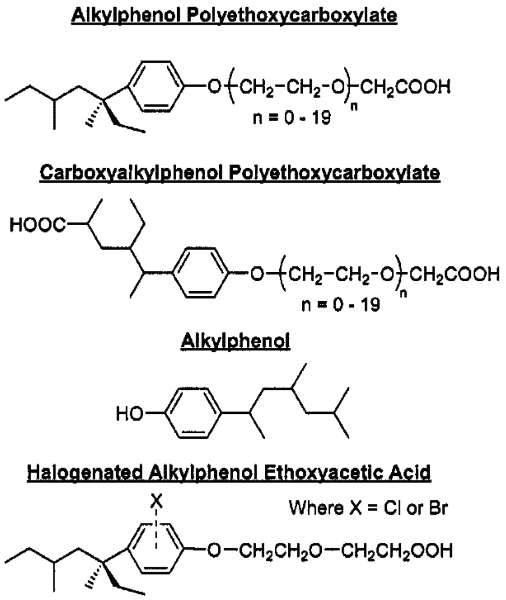


Figure 8. Structures of several APEO metabolites (NPEC, CA_8PEC, NP, and a halogenated NP_2EC, respectively). Reproduced from Montgomery-Brown and Reinhard (2003).

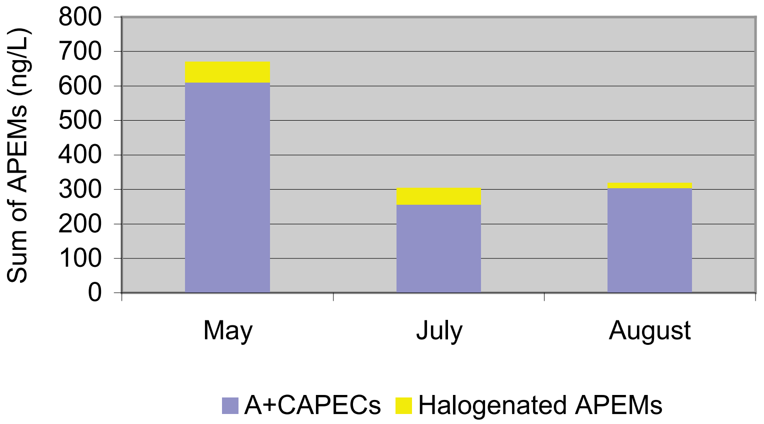


Figure 9. Concentration of APEMs in recycled water sampled during the baseline 2005 study. APEMs detected consisted entirely of A+CAPECs and halogenated APEMs.

N-Nitrosodimethylamine (NDMA)

NDMA is a disinfection byproduct formed during chloramination of waters containing dimethylamines and is considered a probable carcinogen. As shown in Table 8, NDMA was only found in the recycled water (all sampling events) and not found in the surface or ground waters during the 2005 baseline monitoring campaign. NDMA was also monitored during the May 2006 sampling campaign and was again detected in the recycled water (Table 7).

Table 8. Concentrations of NDMA for baseline 2005 study. Detection limit is 4 ng/L.

NDMA (ng/L)	RW	SW 1 (Silver)	SW 2 (Silver)	SW 3 (Silver)	SW 4 (Coyote)	SW 5 (Coyote)	SW 6 (Coyote)
June	51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
August	46	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
October	61	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
November	111	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*DL: detection limit

In contrast to the 2005 and 2006 data, NDMA was not detected in the recycled wastewater collected in 2007. It is possible that the concentration of NDMA found in wastewater varies throughout the day, and that at the time of the June 2007 sampling event, the concentration was simply below the method detection limit (2 ng/L). In agreement with previous data, NDMA was not detected at any of the surface and groundwater sampling locations. This is expected since NDMA is a wastewater disinfection byproduct, and the stream sites did not receive any known wastewater discharge.

Perfluorochemicals (PFCs)

Perfluorochemicals have structures or substructures (carbon skeletons) that are fully fluorinated. PFCs are used for many purposes such as textile and paper coatings, fire fighting foams, and fluoropolymer manufacturing. They can be found in products from the commonly used brands/products Teflon, Scotchguard, Gore-Tex, and Stainmaster (Plumlee et al., 2008a). There are many persistent degradation products of which ten were chosen for this project because of their frequent occurrence in wastewaters and/or relevance to other research.

Table 9 gives a summary of the results from the 2005 baseline study (note, PFBS was eliminated from future analyses when it became undetectable after method modifications were made). The compounds were found in the recycled and surface waters, with higher concentrations (three to four times for the higher level PFCs) in the recycled water. The detection limits are shown with the data and vary slightly by compound and sample batch. Baseline concentrations of PFCs were reassessed in the spring of 2006 and again in 2007 when augmentation was postponed to these years. The 2006 and 2007 data for the field site (surface and groundwater) are presented in Table 10, showing results from additional groundwater and push wells installed after 2005. A summary of PFCs detected in the recycled water between 2005-2007 is given in Table 11.

Additionally, Table 9 shows a test of Teflon tubing compared to the groundwater well 3 October result. The groundwater was sampled with Teflon tubing, which is not recommended for perfluorochemical analysis but was carried out since perfluorochemicals were not considered during initial project planning. One to two months after sampling, the same Teflon tubing was obtained and rinsed with MQ water; one 60 mL sample in polypropylene was taken and analyzed for Perfluorochemicals in replicate. The results show that indeed some perfluorochemicals may originate from the tubing, including perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and perfluorononanoic acid (PFNA), but it is also likely that these ubiquitous chemicals were simply present in the MQ water. Of these, PFOS was detected in the groundwater (at approximately three times greater concentration). Additionally, PFHxS was detected in the groundwater and not in the tubing. PFOS should be considered a tentative groundwater identification since it was detected in the test of the Teflon tubing. These issues highlight some of the difficulties of perfluorochemical analysis.

Table 9. Perfluorochemical concentrations (ng/L) for the baseline 2005 study, also showing the detection limits applicable to each sample set. Additionally, results for the groundwater sample and test of the Teflon tubing used to sample the groundwater are shown. Sample names include site (RW = recycled water, SW = surface water) and date.

Sample	Date Sampled	PFBS (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	PFDS (ng/L)	6:2 FtS (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	FOSA (ng/L)	EtFOSAA (ng/L)	**Total PFCs (ng/L)**
Detection Limit	n/a	42	1.0	2.1	2.1	4.2	1.0	1.0	1.0	1.0	1.0	2.1	
RW_0705	Aug-05	50	20	341	7.7	n.d.	13	103	15	4.6	2.1	30	587
RW_0805	Aug-05	44	8	258	6.1	5.3	12	113	14	4.5	1.7	21	488
Blank_1005	Oct-05	n.d.	n.d.	n.d.	n.d.	n.d.	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	2.0
RW_1005	Oct-05	n.d.	7.9	160	n.d.	n.d.	n.d.	67	12	3.8	2.2	14	266
SW1_1005	Oct-05	n.d.	9.5	77	n.d.	n.d.	n.d.	27	3.7	7.3	4.3	n.d.	129
SW2_1005	Oct-05	n.d.	9.2	57	4.2	n.d.	8.2	26	3.2	4.3	5.2	7.2	124
SW3_1005	Oct-05	n.d.	9.2	62	n.d.	n.d.	n.d.	28	3.8	4.6	4.5	n.d.	112
SW4_1005	Oct-05	n.d.	1.7	12	n.d.	n.d.	n.d.	4.4	10	n.d.	n.d.	n.d.	28
SW5_1005	Oct-05	n.d.	2.1	15	n.d.	n.d.	n.d.	5.6	n.d.	n.d.	n.d.	4.9	28
SW6_1005	Oct-05	n.d.	n.d.	4.2	n.d.	n.d.	8.0	n.d.	n.d.	n.d.	n.d.	n.d.	12
Detection Limit	n/a	n/a	1.0	1.0	1.0	4.2	1.0	0.4	0.4	0.4	0.2	1.0	
Blank_1105	Nov-05	n.m.	n.d.	n.d.	1.9	n.d.	n.d.	0.6	n.d.	n.d.	n.d.	1.7	4.2
RW_1105	Nov-05	n.m.	6.7	201	4.5	7.3	6.8	83	14	4.9	2.8	19	350
SW1_1105	Nov-05	n.m.	4.8	52	3.0	n.d.	4.3	19	2.4	5.1	2.4	2.5	95
SW2_1105	Nov-05	n.m.	4.5	50	3.9	n.d.	4.7	19	2.3	5.1	3.2	2.1	94
SW3_1105	Nov-05	n.m.	n.d.	67	5.1	n.d.	5.1	20	3.5	5.7	3.7	4.1	114
SW4_1105	Nov-05	n.m.	n.d.	7.3	n.d.	n.d.	n.d.	3.1	0.6	0.7	0.3	1.3	13
SW5_1105	Nov-05	n.m.	n.d.	7.2	2.7	n.d.	n.d.	3.1	1.1	0.8	0.6	3.2	19
SW6_1105	Nov-05	n.m.	n.d.	2.3	1.2	n.d.	n.d.	1.1	n.d.	n.d.	n.d.	1.4	5.9

Sample	Date Sampled	PFBS (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	PFDS (ng/L)	6:2 FtS (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	FOSA (ng/L)	EtFOSAA (ng/L)	**Total PFCs (ng/L)**
Detection Limit	n/a	42	1.0	2.1	2.1	4.2	1.0	1.0	1.0	1.0	1.0	2.1	
GW3_1005	Nov-05	n.d.	8.4	26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	34
Teflon Test	Dec-05	n.m.	n.d.	8.4	n.d.	n.d.	n.d.	2.7	3.0	n.d.	n.d.	n.d.	14

Table 10. Perfluorochemicals[a] (ngl^{-1}) in Upper Silver and Coyote Creeks monitored during the dry months of 2006 and 2007. PFNA and 6:2 FtS were also monitored but were not detected above detection limits of 4 and 10 ng/l in May 2006 and 10 and 4 ng/l in June 2007, respectively. Sites are depicted in Figure 3.

	PFHxS		PFOS		PFDS		PFHpA		PFOA		PFDA		FOSA		EtFOSAA	
	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07
Detection Limit	4	2	10	2	21	2	4	2	4	4	21	2	21	2	21	4
Creek water																
Site 1	n.d.	8.5 (1.0)	32 (11)	41 (8.3)	n.d.	36 (61)	n.d.	8.7 (1.5)	15 (0.8)	27 (10)	n.d.	11 (2)	n.d.	3.5 (0.6)	n.d.	10 (2.6)
Site 2a	n.m.	12 (1.1)	n.m.	45 (1.8)	n.m.	3.1 (0.1)	n.m.	10 (5.7)	n.m.	36 (0.7)	n.m.	12 (0.7)	n.m.	2.9 (0.3)	n.m.	5.7 (0.8)
Site 2b	n.d.	8.3 (0.5)	27 (5.7)	56 (30)	n.d.	11 (16)	n.d.	7.7 (0.8)	10 (0.4)	29 (2.3)	n.d.	19 (10)	n.d.	3.1 (0.6)	n.d.	n.d.
Site 3	n.d.	12 (2.0)	38 (4.8)	56 (4.4)	n.d.	6.3 (1.8)	n.d.	12 (1.2)	11 (0.5)	31 (6.2)	n.d.	19 (2.9)	n.d.	2.3 (0.3)	n.d.	6.1 (0.07)
Site 4	n.d.	3.8 (1.6)	14 (2.0)	25 (9.5)	n.d.	18 (15)	n.d.	4.7 (1.3)	n.d.	13 (5.2)	n.d.	13 (9.0)	n.d.	n.d.	n.d.	23.5 (24)
Site 5	n.d.	3.0 (1.2)	20 (0.8)	11 (7.3)	44 (0.0)	9.1 (6.4)	n.d.	3.2 (1.9)	n.d.	10 (6.0)	n.d.	6.0 (7.3)	n.d.	2.4 (0.2)	31 (2.1)	5.0 (0.6)
Site 6*	n.d.	2.3 (0.4)	9.3 (0.6)	4.8 (0.7)	n.d.	3.4 (1.2)	n.d.	n.d.	n.d.	8.0 (4.1)	n.d.	7.7 (2.1)	n.d.	n.d.	n.d.	n.d.
Hyporheic zone																
Push well 1	n.d.	n.m.	58 (3.7)	n.m.	n.d.	n.m.	n.d.	n.m.	23 (0.3)	n.m.	n.d.	n.m.	n.d.	n.m.	n.d.	n.m.
Push well 2	n.d.	10 (1.9)	44 (12)	48 (7.5)	n.d.	15 (0.7)	n.d.	8.1 (1.0)	10 (1.3)	28 (3.9)	n.d.	19 (2.4)	n.d.	4.3 (0.9)	n.d.	10 (0.6)
Push well 3	n.m.	3.8 (1.6)	n.m.	25 (9.5)	n.m.	5.7 (3.8)	n.m.	7.3 (0.9)	n.m.	22 (2.7)	n.m.	13 (1.2)	n.m.	2.9 (0.3)	n.m.	6.2 (0.3)
Groundwater																
Well 1	n.d.	8.9 (0.7)	85 (8.7)	40 (3.4)	n.d.	2.9 (1.3)	n.d.	n.d.	14 (5.9)	12 (1.6)	n.d.	7.3 (0.8)	n.d.	2.2 (0.2)	26 (18)	n.d.
Well 2a	n.d.	8.9 (4.2)	82 (1.1)	26 (4.8)	n.d.	n.d.	n.d.	4.8 (2.9)	22 (1.1)	18 (5.7)	n.d.	8.6 (2.6)	n.d.	n.d.	n.d.	n.d.
Well 2c	11 (3.8)	17 (3.5)	192 (33)	87 (5.3)	n.d.	3.3 (1.8)	n.d.	2.4 (0.6)	10 (0.6)	12 (1.6)	n.d.	10 (0.9)	n.d.	3.7 (0.7)	n.d.	n.d.
Well 3	9.2 (1.4)	4.0 (0.3)	31 (6.0)	19 (3.1)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[a] Mean (n=2) concentrations for creek water, hyporheic water, and groundwater. Range is given in parentheses.

Table 11. Summary of PFCs detected in project recycled water in 2005-2007.

San Jose/Santa Clara Water Pollution Control Plant Recycled Water[a]

Sample Date	PFHxS	PFOS	PFDS	PFHpA	PFOA	PFNA	PFDA	6:2 FtS	FOSA	*N*-EtFOSAA	Total PFCs
July 2005	20	341	7.7	13	113	15	4.6	n.d. (<4)	2.1	30	587
August 2005	8	258	6.1	12	103	14	4.5	5	1.7	21	488
November 2005	6.7	201	4.5	6.8	83	14	5	7.3	2.8	19	350
May 2006	n.d. (<4)	374	n.d. (<21)	5.4	120	9.5	n.d. (<21)	n.d. (<11)	n.d. (<21)	n.d. (<21)	508
June 2007	17	190	n.d. (<2)	13	180	32	7.5	n.d. (<4)	3.2	23	470

[a] tertiary treatment via dual media filtration and chloramination, followed by additional chloramination for reclaimed wastewater

The contributions of different PFCs were calculated for the 2005 baseline study and is shown in Figure 10, Figure 11, and Figure 12. PFOS and PFOA make up the majority of the PFCs for both surface and recycled water. Perfluorobutanesulfonate (PFBS) and 1H,1H,2H,2H-perfluorooctane sulfonate (6:2 FtS) appear in the recycled water but not in the surface water (note, PFBS was not measured for November surface water). The pie charts represent an average of all measurements for the sites; levels of individual PFCs and distributions were quite consistent for both recycled and surface water.

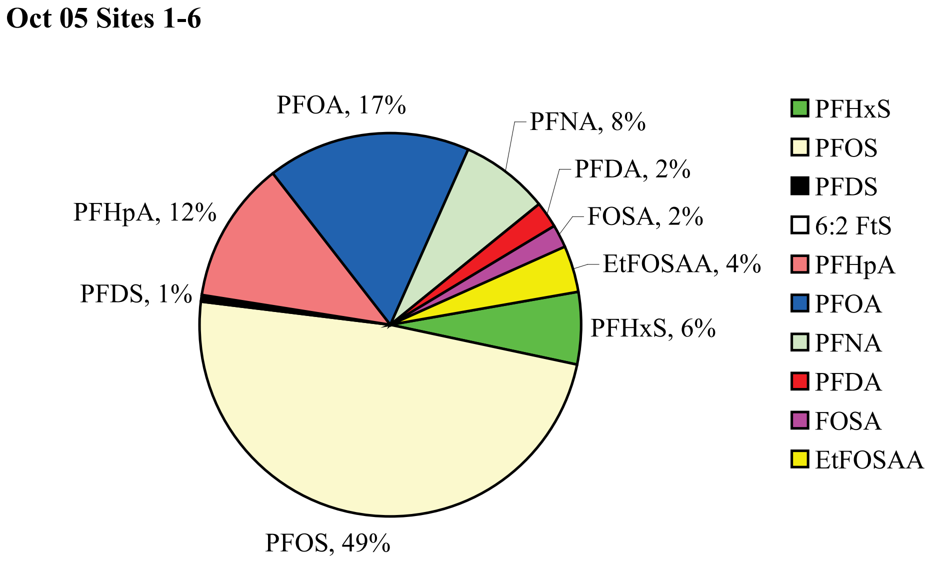


Figure 10. Percentage contributions of 11 PFCs for average of surface water sites 1-6 in October 2005.

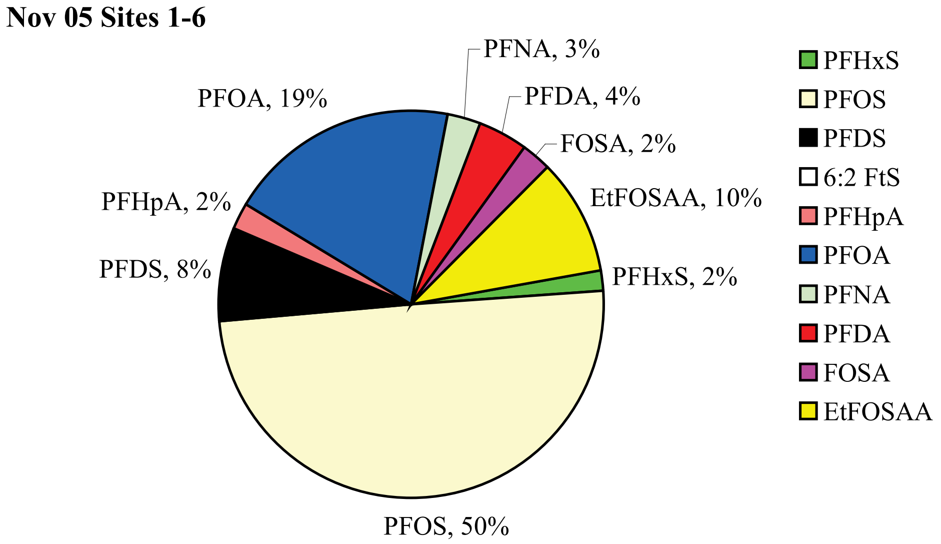


Figure 11. Percentage contributions of 10 PFCs for average of surface water sites 1-6 in November 2005.

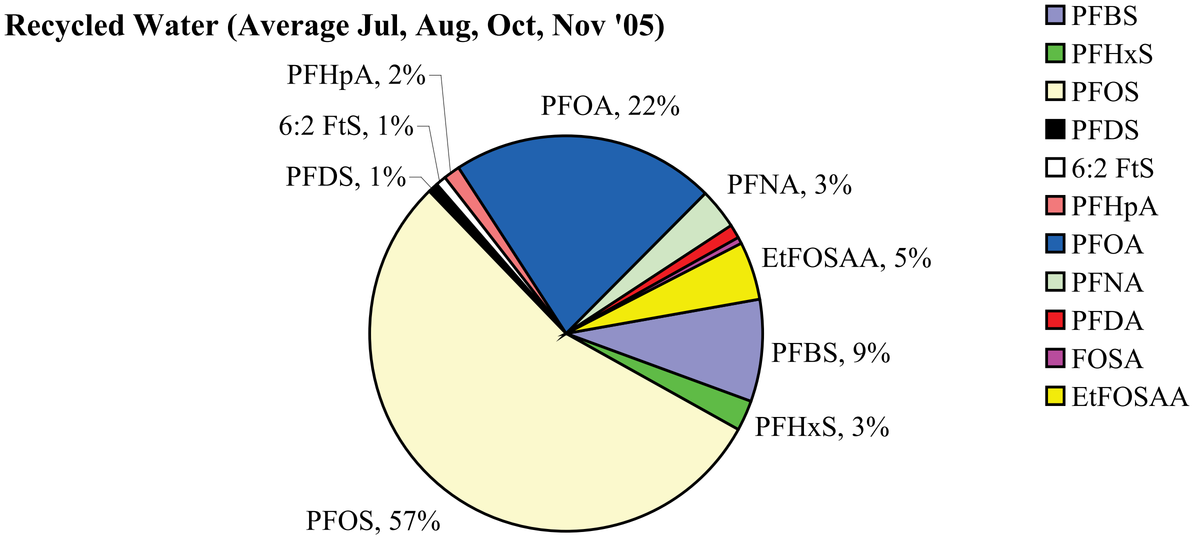


Figure 12. Percentage contributions of 10 PFCs for average of recycled water in July, August, October, November 2005.

Figure 13 shows the total PFCs plotted with distance along Upper Silver and Coyote creeks for October and November 2005. The results between the two months are consistent and show that Upper Silver Creek, the first three points, has higher levels of PFCs than Coyote creek, the lower three points. The result for the upstream control of Coyote Creek (Site 6, river mile 1.0) confirms that Coyote Creek has lower levels of

PFCs. Site 4 (river mile 1.7) is just downstream of the confluence of Silver and Coyote Creek, and shows the lower PFC levels that occur after mixing.

Further discussion of PFC occurrence, distribution, and comparison between recycled water and the creek system is provided in the publication presented in Appendix E.

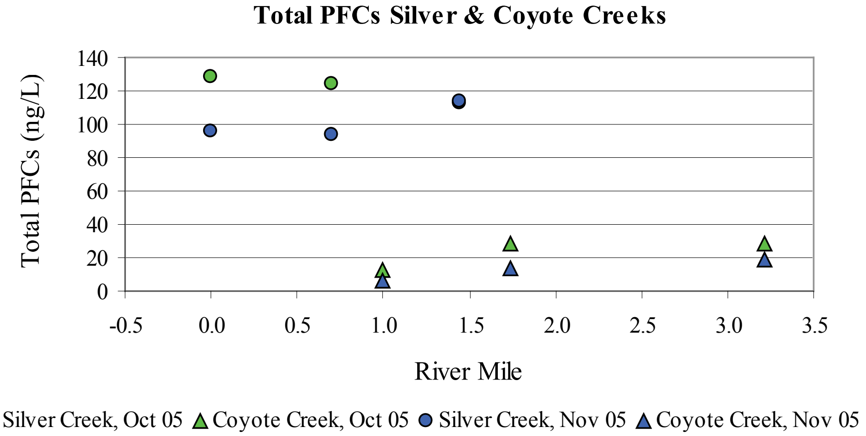


Figure 13. Total PFCs plotted with river mile along Upper Silver and Coyote Creeks. The green points indicate October 2005 results, the blue indicate November 2005 results.

<u>Summary of 2005 baseline water quality study</u>

Table 12 provides a summary of the baseline 2005 study analytical data for the recycled, surface, and ground waters at all dates and sites surveyed showing both the detections, non-detections ("n.d."), and events in which certain analytes were not measured ("n.m."). NDMA and PFCs are not included in this table as they were surveyed in slightly different months; these data may be found in Table 8 and Table 9, respectively.

Table 13 compares the creek system (surface and groundwater) to the recycled water by listing all analytes that were detected and not detected.

Table 12. Summary report of pharmaceuticals, hormones, APEMs, and other compounds monitored as part of the 2005 baseline study of the Yerba Buena Pump Station recycled water, Silver and Coyote Creeks sites 1-6, and groundwater monitoring well 3 near Coyote Creek. Sample sites are described in Table 1.

Analyte	**Yerba Buena Recycled Water**			**SW 1 (Silver Creek)**			**SW 2 (Silver Creek)**			**SW 3 (Silver Creek)**			**SW 4 (Coyote Creek)**			**SW 5 (Coyote Creek)**			**SW 6 (Coyote Creek)**			**Groundwater Well 3**		
	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05
Pharmaceuticals (ng/L)																								
Acetaminophen	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.m.	n.d.	n.m.
Caffeine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**72**	n.d.	n.d.	**19**	n.d.	n.d.	**23**	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Carbamazepine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Carisoprodol	n.d.	**217**	**195**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Gemfibrozil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ibuprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Iminostilbene	n.d.	**98**	**96**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ketoprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Naproxen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Primidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Propanolol	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.m.	n.d.	n.m.
Hormones (ng/L)																								
Estradiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Estriol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Estrone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ethynylestradiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
APEOs[1] & APEMs[2] (ng/L)																								
APEOs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Alkylphenols (nonyl-, octyl-)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
A+CAPECs[3]	**610**	**256**	**303**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Halog. APEMs[4]	**60**	**48**	**17**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Other (ng/L)																								
Bisphenol A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	**18**	n.d.
N-butyl benzenesulfonamide	**13**	**60**	**46**	**30**	**48**	**14**	**60**	**73**	**15**	**119**	**39**	**27**	**209**	**21**	**23**	**209**	**<d.l.**	**38**	**164**	**75**	**44**	n.m.	**19**	**<d.l.**
Tris(3-chloropropyl)phosphate	n.d.	**33**	**15**	**1.0**	**5.0**	**1.6**	**2.0**	**5.8**	**3.3**	**3.0**	**5.2**	**4.2**	n.d.	**2.6**	**1.5**	n.d.	**2.9**	**2.4**	n.d.	n.d.	**2.2**	n.m.	**1.0**	n.d.
Tris(2,3-dichloropropyl)phosphate	**244**	**13.4**	n.d.	**1.0E+04**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	**<d.l.**	n.d.
Oxadiazon	n.d.	n.d.	n.d.	n.d.	**12**	n.d.	n.d.	**12**	n.d.	n.d.	**3.4**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.

[1] Alkylphenol polyethoxylates (AP1EO, AP2EO, AP3EO)

[2] Alkylphenol polyethoxylate metabolites

[3] Sum of alkylphenol ethoxycarboxylates and carboxyalkylphenol ethoxycarboxylates (both metabolites of APEOs).

[4] Sum of halogenated (chlorine or bromine) alkylphenols, APEOs, and A+CAPECs

Table 13. Summary of all analytes detected and not detected in the baseline 2005 characterization of recycled water, groundwater, and creek water.

Recycled Water		Ground Water		Surface Water	
Found	**Not Found**	**Found**	**Not Found**	**Found**	**Not Found**
Carisoprodol	Acetaminophen	BPA	Caffeine	Caffeine	Acetaminophen
Iminostilbene	Caffeine	NBBS	Acetaminophen	NBBS	Carisoprodol
NDMA	Carbamazepine	Tris(3-chloropropyl)phosphate	Carisoprodol	Tris(3-chloropropyl)phosphate	Iminostilbene
A+CAPECs	Gemfibrozil	Tris(2,3-dichloropropyl)phosphate	Iminostilbene	Tris(2,3-dichloropropyl)phosphate	Carbamazepine
Halog. APEMs	Ibuprofen	PFCs	Carbamazepine	PFCs	Gemfibrozil
NBBS	Ketoprofen		Gemfibrozil		Ibuprofen
Tris(3-chloropropyl)phosphate	Naproxen		Ibuprofen		Ketoprofen
Tris(2,3-dichloropropyl)phosphate	Primidone		Ketoprofen		Naproxen
PFCs	Propanolol		Naproxen		Primidone
	Estradiol		Primidone		Propanolol
	Estriol		Propanolol		Estradiol
	Estrone		Estradiol		Estriol
	Ethynylestradiol		Estriol		Estrone
	BPA		Estrone		Ethynylestradiol
			Ethynylestradiol		NDMA
			NDMA		A+CAPECs
			A+CAPECs		Halog. APEMs
			Halog. APEMs		BPA

Baseline Analysis of Potentially Impacted Groundwater Quality

Groundwater quality was assessed alongside sampling for recycled water and surface water, and the results are presented in the previous section (sub task "Baseline Analysis of Water Quality at Coyote Creek Sampling Locations").

Task 4.1 Evaluation of Removal of Selected Trace Organics including PFCs by Nanofiltration and Reverse Osmosis Processes

One of the project objectives was to make recommendations about potential treatment options for compounds that might interfere with the use of reclaimed water for stream augmentation. Concurrent to the laboratory and field investigations of the stream flow augmentation project, a supporting laboratory study on the rejection of PFCs by nanofiltration membranes was conducted as one of the replacement tasks for augmentation using recycled water.

Rejections greater than 95% were measured for most compounds, and depended upon the solution pH (which controls the charge of the membrane) and the fouling layer. Specifically, rejections of 15 PFCs, including five perfluorinated sulfonates, nine perfluorinated carboxylates, and perfluorooctane sulfonamide (FOSA) by four nanofiltration membranes (NF270, NF200, DK, and DL) were measured. Rejections for anionic species were >95% for MW > 300 g/mol. FOSA (MW 499 g/mol), which is uncharged at the pH of deionized water (5.6), was rejected as little as 42% (DL membrane).

The effect of pH, ionic strength, and the presence of a fouling layer were all investigated. Decreasing the pH to less than 3 decreases rejection by up to 35%, effectively increasing the molecular weight cutoff (MWCO) of NF270 by >200 g/mol. Since the perfluorinated anionic surfactants studied here (except FOSA) have $pKa < 1$, the effects of pH variation on the speciation of these compounds are expected to be negligible. However, the membrane charge at pH 2.8 is neutral or even positive (compared to a negative membrane charge at neutral pH e.g. typical wastewater conditions), since the iso-electric point of the membrane is at $4 < pH < 5$. Thus at pH 2.8, the charge repulsion effect between the membrane and anionic solutes is removed from the overall balance of forces governing the rejection of the solutes. A comparison between the charged and uncharged PFCs of identical size, FOSA and perfluorooctane sulfonate (both 499 g/mol), supports this conclusion: At $5 < pH < 6$, the transmission of the uncharged FOSA (7%) is several times that of the charged PFOS (2.5%), whereas at pH 2.8, the transmission of FOSA and PFOS are nearly equal (both 30%). The effect of pH on the rejection of FOSA is much more pronounced, as would be expected from a compound with a pKa value (6.5) within the range that the pH was varied. The rejection of FOSA increases monotonically with increasing pH, from a low of 70% at pH 2.8 to a high of >99% at pH 10. Thus one possible way to increase the rejection of a contaminant of concern such as FOSA would be to increase the feed pH, since a large gain in rejection can be made for only a small shift in pH.

The effect of ionic strength on the rejection of the PFCs is much less pronounced. A 2500 mg/L NaCl equivalent increase in ionic strength had a small effect, reducing rejections <1%. This indicates that the role of increased ionic strength in reducing the charge repulsion is not significant in this range. Similar results showing a strong effect of pH and an insignificant effect of ionic strength have been shown before for other trace organic contaminants.

An alginate fouling layer increases transmission, where quantifiable, by factors of 4-8. We attribute this behavior to "foulant-enhanced concentration polarization", as has been observed previously in other membrane studies of organic contaminants (see Appendix H for further discussion).

Accumulation of PFCs on membranes was measured after the completion of rejection experiments. With the exception of FOSA, a linear correlation exists between the logarithm of sorbed PFC mass and molecular weight ($R^2 = 0.95$). This result indicates that a positive interaction takes place between the membrane surface and the perfluorinated chains, increasingly overpowering the repulsion between the membrane surface and the negative charge on the carboxylate and sulfonate groups.

Based on rejection kinetics and the extent of sorption, we infer that two different sorption processes are significant: charged species adsorb quickly to the membrane surface, whereas the uncharged FOSA absorbs within the membrane matrix in a much slower process.

Details of the experimental approach and results may be found in the research publication included as Appendix H (Steinle-Darling and Reinhard, 2008). Additional data is contained in the Ph.D. thesis of Eva Steinle-Darling.

Task 4.2 Review of the Occurrence of Emerging Contaminants in Recycled Water

As a replacement task for the augmentation using recycled water, a review of the occurrence of emerging contaminants in recycled water was conducted. PFCs were selected and agreed upon by Stanford University and SCVWD personnel as the emerging contaminants of interest for the review, given their detection in the project recycled water as well as in the site stream and groundwater. A literature review of PFC occurrence and toxicity was conducted, and the data was assessed together with PFC monitoring data from a wetland assessed by Stanford University personnel, monitoring data from the present study, and monitoring data from three other Northern California recycled waters sampled by SCVWD personnel (in addition to the Yerba Buena Pump Station water) and analyzed at Stanford University. The results are available in the publication presented in Appendix E (Plumlee et al., 2008a).

The results of PFC occurrence reported in the reviewed literature are presented in Table 1 of Appendix E, which shows measured concentrations of PFCs in wastewaters and natural waters. To summarize the monitoring work by Stanford University and SCVWD (which added to the literature bank of occurrence data in Table 1), PFCs were characterized in recycled water from four California wastewater treatment plants that employ tertiary treatment and one that treats primary sewage in a wetland constructed for both treatment and wildlife habitat. Effluent concentrations were compared with surface and groundwater from Upper Silver and Coyote Creeks. In the recycled water, 90–470 ng/l PFCs were detected, predominantly perfluorooctanoate (PFOA; 10–190 ng/l) and perfluorooctanesulfonate (PFOS; 20–190 ng/l). No significant removal of PFCs was observed in the wetland (total concentration ranged 100–170 ng/l across various treatment stages); in this case, 2-(N-ethylperfluorooctanesulfonamido) acetic acid (N-EtFOSAA), perfluorodecanesulfonate (PFDS), and PFOS were dominant. Though there is currently no direct wastewater discharge into the creeks, PFCs were found in the surface water and underlying groundwater at a total of 20–150 ng/l with PFOS and PFOA again making the largest contribution. With respect to ecotoxicological effects, PFC release via recycled water into sensitive ecosystems requires evaluation.

Task 5 Data Integration, Analysis and Reporting

As described in the work plan, a purpose of the data integration and analysis task was to assess whether groundwater protection was achieved during recycled water augmentation; however, this information is not available due to the cancellation of the augmentation. Instead, the present final report provides a summary of the project scope, methods, and baseline water quality results, as well as the findings (and supporting publications since produced) from a variety of related laboratory experiments and literature reviews.

3.2 Laboratory Investigations of Contaminant Fate

Biodegradation of NDMA

A laboratory study on the biological degradation of NDMA in sediment collected from Upper Silver Creek was performed. Details of the results and experimental approach may be found in the supporting information for the publication included as Appendix D (Plumlee and Reinhard, 2007); a summary is provided here.

Biodegradation of NDMA was observed in the microcosms containing either surface water alone or in combination with sediment (Table 14). Disappearance of NDMA (>80%) occurred more rapidly for the microcosms with sediment at 91-127 d, compared to 127-140 d in surface water. Constant NDMA concentrations in the sterile microcosms confirmed that NDMA was not lost via an unexpected pathway (e.g. volatilization, sorption to glass or septa) or via sorption to sediment, as expected from literature reports. As further evidence for biodegradation, the disappearance rate increased following the respike of the same microcosms (Table 14). This suggests the adaptation and growth of the microbial community, resulting in a greater biodegradation rate. The responsible microorganisms were not isolated; however, the degradation is likely to be cometabolic (Sharp et al., 2005; Yang et al., 2005). Bacteria having monooxygenase enzymes have been demonstrated to degrade NDMA (Sharp et al., 2005). If first-order kinetics are assumed, half-lives for NDMA biodegradation in microcosms with sediment and surface water were $t_{1/2} = 31\pm19$ (SD) d and decreased to 8±5 d following the respike. These rates are within the range of half-lives reported for NDMA biodegradation, from 4-6 d in groundcover and turfgrass soils (Yang et al., 2005), 11-39 d in soil slurries (Gunnison et al., 2000), to persistence in some soils and bog sediments (Tate and Alexander, 1976; Mallik and Tesfai, 1981).

Results show that NDMA is poorly degradable biologically, a finding that was consistent with literature reports. The conclusion of this study is that biotransformation of NDMA is not likely to be a significant process during the residence times relevant to river and groundwater transport in the Upper Silver Creek and Coyote Creek system (hours to days).

Table 14. Time to removal of NDMA for triplicate microcosms (M1, M2, and M3) containing surface water or surface water and sediment.

Treatment	NDMA Addition (100 µg/l)	Time to ≥80% Removal, d M1	M2	M3	$t_{1/2}$ (SD), d
Surface Water (n=3)	Spike 1	127	140	140	67 (12)
	Spike 2	20	76	90	12 (13)
Surface Water + Sediment (n=3)	Spike 1	91	127	127	31 (19)
	Spike 2	20	20	34	8 (5)

Direct photolysis of NDMA

The photochemical degradation of photosensitive organic pollutants in the aquatic environment plays an important role in the overall environmental fate of these compounds. Because NDMA was detected in the recycled water to be used for the stream flow augmentation, and because wastewater treatment-focused studies had shown NDMA to be photosensitive, the aqueous photolysis of seven alkyl nitrosamines was studied by irradiation in a solar simulator. Nitrosamines included *N*-nitrosodimethylamine (NDMA), *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-n-propylamine (NDPA), *N*-nitrosodi-n-butylamine (NDBA), *N*-nitrosopiperidine (NPip), and *N*-nitrosopyrrolidine (NPyr).

Details of the experimental approach and a further discussion of the results may be found in the research publication included as Appendix D (Plumlee and Reinhard, 2007). To summarize, direct photolysis at irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12-15 min for the other nitrosamines. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43$ to 0.61 for the other nitrosamines. Quantified products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98% and 79%, respectively. Indirect photolysis of nitrosamines in surface water was not observed: increasing dissolved organic carbon (DOC) slowed the NDMA photolysis rate due to light screening.

Aquatic photolysis rates in real environmental systems may be different from laboratory measurements depending upon actual solar irradiance, the light screening by the water body of interest, and the water depth. However, if the quantum yield and molar absorptivity of the chemical are known, photolysis rates in the field can be estimated for the conditions of a particular site.

Figure 14 shows the average photodecay rate constant estimated for NDMA in a nonspecific surface water with a depth of 1 m and intermediate light screening by the water (spectral slope = 0.02 and $\lambda_{280} = 0.3$, (Green and Blough, 1994)). Midday solar irradiance was modeled using SMARTS for three locations representing a range of latitudes from January to December. The predicted rates shown in Figure 14 correspond to half-lives over the year of 8-38 h in London (51° N latitude), 7-14 h in Irvine (33° N latitude, the location of the OCWD site), and 6-7 h in Ecuador (2° S latitude). If the depth of the water body is reduced to 10 cm, the half-lives (corresponding to an average rate over the depth) are reduced by a factor of approximately 10. Thus for a typical river, depending upon the depth, solar irradiation, and light screening of the water, reaching an NDMA concentration attenuated by one half-life will require (sunlit) travel times of hours to a few days. This is consistent with a report by Pehlivanoglu-Mantas and Sedlak (Pehlivanoglu-Mantas and Sedlak, 2006) for the effluent-dominated Santa Ana River (CA, USA), in which a decrease in NDMA corresponding to approximately one half-life from the upstream wastewater treatment plant effluent (24 ng/L) to <10 ng/L downstream was observed after a 10 h residence time. Gross et al. (Gross et al., 2004) report the increased attenuation of trace organic contaminants for the same river compared to the nearby Prado Wetlands; given the reduced NDMA photolysis rate expected with increasing DOC via light screening (see Appendix D) and the greater DOC typically found for wetlands over rivers, shallow rivers may also be expected to outperform wetlands with regard to NDMA attenuation.

Because biodegradation is relatively slow, aquatic photolysis of NDMA is generally expected to be more significant even at relatively low levels of solar irradiation ($t_{1/2}$ = 8-38 h at 244-855 W/m^2, 51° N latitude, 1 m depth). Based on the NDMA photodecay rates predicted in this study for a typical river, significant removal of NDMA by natural sunlight may be expected in Coyote Creek before it reaches San Francisco Bay, if recycled wastewater were to be added to this stream. However, over the short study area at Upper Silver and Coyote Creeks (Figure 3), the amount of NDMA attenuation observed would depend on light intensity and other site-specific conditions.

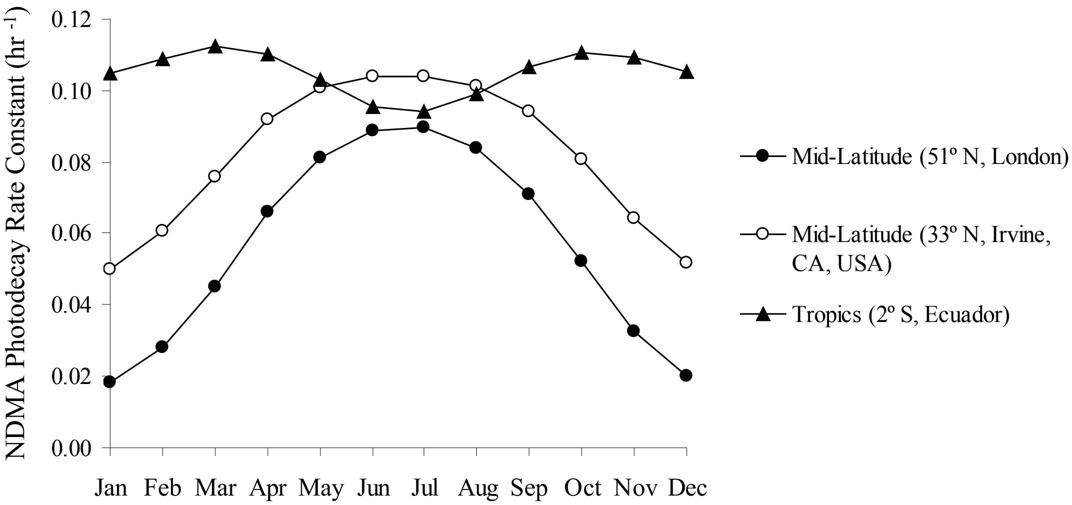


Figure 14. Average NDMA photodecay rate constants predicted for midday solar irradiance in mid-latitude and tropical zones in surface water with intermediate light screening and a depth of 1 m.

Biodegradation of APEMs

As described earlier in the report, metabolites of alkylphenol polyethoxylate compounds (APEMs; see Figure 8 for structures) were also detected in the recycled water intended for the stream flow augmentation. To explore the potential for degradation of these types of compounds by microorganisms in sediment from the site, a laboratory study on the biological degradation of nonylphenol ethoxyacetic acid (NP_1EC) in sediment collected from Coyote Creek was performed. Further details of the results and the experimental approach may be found in the publication included as Appendix G (Montgomery-Brown et al., 2008); a summary is provided here.

In this study, NP_1EC was spiked into oxic microcosms containing sediment from Coyote Creek and was monitored to evaluate the ability of this river to degrade NP_1EC (no degradation was observed under anaerobic conditions). The biological transformation pathway was elucidated by observing the appearance of products including dicarboxylated alklyphenol ethoxyacetic acids (CA_nP_1EC; where n = the number of aliphatic carbon atoms). Novel metabolites were observed that appeared to be specific to *ortho*-isomers (versus *para*-isomers) of NP_1EC. Results also suggested that dissolved oxygen availability was important in determining the dominant biodegradation pathway. Figure 15 shows the disappearance of NP_1EC over time in the spiked microcosms and the appearance of products. Overall, CA_8P_1ECs were the dominant metabolites of NP_1EC biodegradation initially, but CA_6P_1ECs became the dominant metabolites as biodegradation progressed.

Based on this study, some biotransformation of APEMs may be expected at the Coyote Creek site upon infiltration of water containing APEMs into the hyporheic and subsurface zones, particularly considering the slow travel times of groundwater. However, complete removal of APEMs is not expected, and instead, more stable forms of these compounds may be produced: Research available in the literature (Jonkers et al., 2001; Montgomery-Brown and Reinhard, 2003; Montgomery-Brown et al., 2008) shows that under aerobic conditions, shorter, relatively stable APECs (with one to three ethoxy units, i.e. AP_nECs where n = 1-3) may be formed. Under anaerobic conditions, however, biodegradation may continue to form the smaller alkylphenols (APs). Further degradation of APs under anaerobic conditions is typically not observed, but some biotransformation under aerobic conditions may occur.

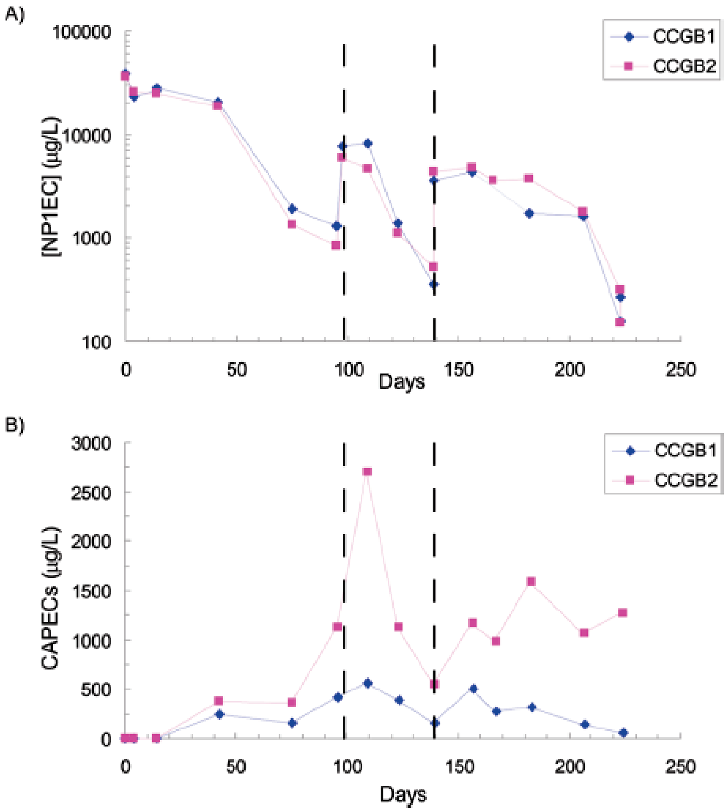


Figure 15. (A) NP1EC (log scale) and (B) CAP1EC concentrations as a function of time in the Coyote Creek microcosms (CCGB1 and CCGB2). Dashed lines indicate NP1EC respike events.

Indirect photolysis of PFCs

Because PFCs were detected in both the recycled water to be used for the augmentation and in the creek system, a laboratory investigation of PFC attenuation potential was carried out. The fluorinated portion of these compounds is generally regarded as extremely persistent, with disappearance of particular PFCs typically explained by transformation into a simpler PFC, such as PFOS or PFOA. Because biodegradation is expected to be quite slow and sorption to sediments may be negligible, attenuation by photolytic means was selected as the focus of the laboratory study. While research has suggested that PFCs are not susceptible to direct photolysis (transformation upon direct absorption of light), and this was confirmed in the present study, no research had been conducted on the potential for indirect photolysis. In the case of indirect photolysis, target compounds react with photochemically-produced reactive intermediates (such as hydroxyl radicals). Additional background and discussion of results may be found in the research publication included as Appendix G (Plumlee et al., 2008c).

To explore the possibility of indirect photolysis of PFCs, selected perfluoroalkanesulfonamides were irradiated in aqueous hydrogen peroxide solutions using artificial sunlight to simulate aquatic environmental conditions. Indirect photolysis mediated by hydroxyl radical was observed for *N*-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE), *N*-ethyl perfluorooctane sulfonamido acetate (*N*-EtFOSAA), *N*-ethyl perfluorooctane sulfonamide (*N*-EtFOSA), and perfluorooctane sulfonamide acetate (FOSAA). A proposed reaction pathway for degradation of the parent perfluorochemical, *N*-EtFOSE, to the other perfluoroalkanesulfonamides, perfluorooctane sulfonamide (FOSA), and perfluorooctanoate (PFOA) was developed (see Appendix F) and includes oxidation and *N*-dealkylation steps. As they did not undergo additional degradation, FOSA and PFOA were the final degradation products of hydroxyl radical-mediated indirect photolysis. UV-visible absorption spectra for the PFCs, showing absorbance in the UV region below the range of natural sunlight, are also reported.

Given the slow rates expected for biodegradation and limited sorption of PFCs, indirect photolysis of PFCs may be important in the determination of their environmental fate. However, the rates of indirect photolysis observed were quite slow, and thus significant rates of transformation would not be expected over the Upper Silver and Coyote Creeks study reach. Some transformation may be possible during the additional travel time to San Francisco Bay, depending upon the sunlight and reactive intermediates available to facilitate indirect photolysis of PFCs.

4.0 CONCLUSIONS AND RECOMMENDATIONS

The major conclusions of the water quality monitoring campaign and supporting laboratory investigations are presented here, followed by project recommendations.

Analysis of NDMA by SPE-LC-MS/MS

1 The analytical method developed for NDMA in support of this project (Appendix C) features a high extraction efficiency using SPE and accurate identification and quantification via LC-MS/MS at a reporting limit of 2 ng/l, below the 10 ng/l notification level specified by the California Department of Health Services, and may be applied for additional nitrosamine analyses.

Water quality comparison of recycled water and site (surface and groundwater)

1 The assessment of the microconstituent risk associated with augmenting an urban stream with recycled wastewater is complicated by the fact that different constituents may be present in different concentrations in each water. In this project, the water quality of the recycled water was better than the site water with respect to metals and microbes. However, the recycled water also contained some constituents which were not present in the creek, such as NDMA and APEMs.

2 Some constituents were present in both waters (such as PFCs, organophosphates, and NBBS) at similar or different concentrations. The concentrations in the

wastewater or at the site are likely to vary with time, and thus a more detailed evaluation of microconstituent concentration over time scales of days to months may be required to fully assess the impact of stream flow augmentation with recycled wastewater.

Perfluorochemicals in Water Reuse

1 As expected from their occurrence in wastewater and persistence during wastewater treatment, PFCs were detected in reclaimed wastewater from four California wastewater treatment plants that employ tertiary treatment (including the recycled water from the San Jose/Santa Clara Water Pollution Control Plant intended for the stream augmentation) and one that treats primary sewage in a wetland constructed for both treatment and wildlife habitat. A range of 90-470 ng/L total PFCs were detected in reclaimed wastewater, typically dominated by PFOA and PFOS. Concentrations of total PFCs in the water intended for the stream flow augmentation ranged 350-587 ng/l. Concentrations of PFOA and PFOS ranged 83-180 and 190-374 ng/l, respectively.

2 While many PFC monitoring studies focus on PFOA and PFOS, the results of the present study showed that inclusion of other PFCs in the monitoring program may identify several additional PFCs resulting in a much greater total PFC concentration.

3 Though there was no known wastewater discharge into Upper Silver and Coyote Creeks, PFCs were found in the surface water and underlying groundwater at concentrations that were similar to the wastewater, highlighting the importance of baseline system characterization for decision making and risk evaluation in water reuse for environmental enhancement.

4 With respect to ecotoxicological effects, PFC release via recycled water into sensitive ecosystems requires evaluation (see Appendix E for further details). PFCs bioaccumulate in aquatic and terrestrial organisms, and the resulting tissue concentrations constitute an internal dose which may be more ecotoxicologically relevant than the aquatic PFC concentration. One of five reclaimed wastewaters (the water intended for the augmentation in the present study) and two of six urban creek sites exceeded a threshold concentration of 50 ng/L PFOS that is viewed by some researchers as protective of trophic level IV avian species that consume organisms in equilibrium with the water.

Attenuation of NDMA and Other Nitrosamines in Surface Water

1 Results show that NDMA is poorly degradable biologically, a finding that was consistent with literature reports. Biotransformation of NDMA is not likely to be a significant process during river and groundwater transport in the Upper Silver Creek and Coyote Creek system.

2 NDMA and six other *N*-nitrosamines were found to undergo direct photolysis when exposed to simulated sunlight.

3 Irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12-15 min for the other nitrosamines. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43$ to 0.61 for the other nitrosamines.

4 Products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98% and 79%, respectively.

5 Because biodegradation is relatively slow and sorption to sediment is negligible, aquatic photolysis of NDMA is generally expected to be more significant even at relatively low levels of solar irradiation ($t_{1/2}$ = 8-38 h at 244-855 W/m^2, 51° N latitude, 1 m depth).

Biotransformation of APEMs in Creek Sediment

1 Based on this study, significant biotransformation of APEMs could be expected at the Coyote Creek site upon infiltration of water containing APEMs into the hyporheic and subsurface zones, particularly considering the slow travel times of groundwater.

2 However, literature research suggests that under aerobic conditions, relatively stable APECs may be formed. Under anaerobic conditions, biodegradation may continue to form alkylphenols (APs). Further degradation of APs under anaerobic conditions is typically not observed, but some biotransformation under aerobic conditions may occur.

3 Water quality monitoring of the surface and groundwater following stream flow augmentation with recycled water would be required to fully assess whether concentrations of APEMs, if detected, were significant following the expected attenuation and dilution with site water.

Hydroxyl-Radical Mediated Indirect Photolysis of Perfluoroalkanesulfonamides

1 In contrast to the *N*-nitrosamines, PFCs (selected perfluorooctanesulfonamides) were found to undergo *in*direct photolysis when irradiated in a solar simulator in aqueous hydrogen peroxide solutions. Indirect photolysis mediated by hydroxyl radical was observed for *N*-EtFOSE, *N*-EtFOSAA, *N*-EtFOSA, and FOSAA.

2 Final degradation products of the indirect photolysis of the perfluorooctanesulfonamides were PFOA and FOSA, which did not undergo additional degradation.

3 A proposed reaction pathway for degradation of the parent PFC, *N*-EtFOSE, to the other perfluoroalkanesulfonamides, FOSA, and PFOA was developed and includes oxidation and *N*-dealkylation steps.

4 Given the slow rates expected for biodegradation and limited sorption, indirect photolysis of PFCs may be important in the determination of their environmental

fate. However, the rates of indirect photolysis observed were quite slow, and thus significant rates of transformation would not be expected over the Upper Silver and Coyote Creeks study reach. Some transformation may be possible during the additional travel time to San Francisco Bay, depending upon the sunlight and reactive intermediates available to facilitate indirect photolysis of PFCs.

Removal of PFCs by Nanofiltration

1 Rejections greater than 95% were measured for most PFCs tested (Appendix H), and depended upon the solution pH (which controls the protonation state of the PFC) and the fouling layer.

2 If nanofiltration or reverse osmosis were viable treatment options for wastewater prior to use in stream flow augmentation, these advanced treatment processes would result in adequate removal of PFCs.

Removal of NDMA by Reverse Osmosis

1 As suggested by results obtained in a separate study for an advanced wastewater treatment facility at the time of this project (Appendix C), microfiltration (MF) of wastewater effluent is not expected to reduce NDMA concentrations and may in fact lead to NDMA formation when in combination with chlorination or chloramination used to prevent MF membrane fouling.

2 Reverse osmosis (RO) treatment of secondary effluent using thin-film composite membranes typically results in NDMA rejection of approximately 50 to 65% or less. For the overall treatment train, this rejection is an important contribution to NDMA removal. Lower rejection may be associated with changing feed conditions and fouling observed in real treatment systems.

3 UV irradiation in combination with RO treatment and in some cases, blending, allows operators to reliably maintain the residual NDMA below the 10 ng/L CA drinking water notification level.

4 If RO was a viable treatment option for wastewater prior to use in stream flow augmentation, this advanced treatment process would likely result in a significant, through incomplete, removal of NDMA.

Based on the above conclusions, we can make the following broad recommendations:

1 A study with similar objectives should be executed at a site where ecological risks associated with reclaimed water release are minimized.

2 Applicable toxicological information is needed to interpret water quality data. Limited information on PFC toxicology as it relates to aquatic environments was available (Newsted et al., 2005; Rostkowski et al., 2006), and nevertheless this information led to the significant outcome of project cancellation.

3 Source control appears to be the only feasible way to reduce the release of PFCs into the environment. Thus, steps should be taken to minimize the use of PFCs that find their way into the environment.

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GLOSSARY

APEMs	metabolites of alkylphenol ethoxylates
MF	microfiltration
NBBS	*N*-butylbenzene sulfonamide
NDMA	*N*-nitrosodimethylamine
PFCs	perfluorochemicals
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
RO	reverse osmosis
SCVWD	Santa Clara Valley Water District

APPENDICES

Appendix A: Water quality data table for constituents monitored by SCVWD

Appendix B: "Upper Silver Creek Experimental Site Exploration and Characterization" by Eduard Hoehn, 2006. Project report for Eawag, Swiss Federal Institute of Water Science and Technology.

Appendix C: Plumlee, M.H., López-Mesas, M., Heidlberger, A., Ishida, K.P., Reinhard, M., 2008. *N*-Nitrosodimethylamine (NDMA) Removal by Reverse Osmosis and UV Treatment and Analysis via LC-MS/MS. Water Res 42, 347-355.

Appendix D: Plumlee, M.H., Reinhard, M., 2007. Photochemical Attenuation of *N*-Nitrosodimethylamine (NDMA) and other Nitrosamines in Surface Water. Environ. Sci. Technol. 41, 6170-6176.

Appendix E: Plumlee, M.H., Larabee, J., Reinhard, M., 2008. Perfluorochemicals in Water Reuse. Chemosphere 72, 1541-1547.

Appendix F: Montgomery-Brown, J., Li, Y., Ding, W.-H., Mong, G.M., Campbell, J.A., Reinhard, M., 2008. NP1EC Degradation Pathways Under Oxic and Microxic Conditions. Environ. Sci. Technol. DOI: 10.1021/es702561t.

Appendix G: Plumlee, M.H., McNeill, K., Reinhard, M., 2008. Hydroxyl Radical-Mediated Indirect Photolysis of Perfluoroalkanesulfonamides, in progress.

Appendix H: Steinle-Darling, E., Reinhard, M., 2008. Nanofiltration for trace organic contaminant removal: structure, solution and membrane fouling effects on the rejection of perfluorochemicals. Environ. Sci. Technol. 42, 5292-5297.

Appendix I: Stanford University, Dr. Martin Reinhard Research Group, 2004. Technical Memorandum: Review of Available Historical Water Quality Data, Coyote Creek Streamflow Augmentation Project.

Appendix J: Streamflow Augmentation Project Upper Silver Creek and Coyote Creek Initial Study / Mitigated Negative Declaration (Draft), June 2006. Santa Clara Valley Water District.

Appendix K: Project Photographs

Appendix A

Water quality data table for constituents monitored by SCVWD

Water Quality Parameters: Streamflow Augmentation Grant Study
Project Code: 91181001-0136

Sampled			May-05	May-05	May-05	May-05	May-05	May-05	May-05	May-05	Jul-05	Jul-05	Jul-05	Jul-05	Jul-05	Jul-05	Jul-05	Jul-05	Aug-05	Aug-05	Aug-05	Aug-05	Aug-05	Aug-05	Aug-05	Aug-05	Oct-05	Oct-05	Oct-05
	units		***RW1 (Yerba Buena***	***GW3 Coyote***	***SW1***	***SW2b***	***SW3***	***SW4***	***SW5***	***SW6***	***RW1 (Yerba Buena***	***GW3 Coyote***	***SW1***	***SW2b***	***SW3***	***SW4***	***SW5***	***SW6***	***RW1 (Yerba Buena***	***GW3 Coyote***	***SW1***	***SW2b***	***SW3***	***SW4***	***SW5***	***SW6***	***RW1 (Yerba Buena***	***GW3 Coyote***	***SW1***
Herbicides and Pesticides																													
2,4,5-TP	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4-D	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aciflurfen	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Bentazon	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dalapon	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dicamba	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dinoseb	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Pentachlorophenol	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Picloram	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
3-Hydroxycarbofuran	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Aldicarb (Temik)	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Aldicarb Sulfone	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Aldicarb Sulfoxide	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Baygon (Propoxur)	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Carbaryl	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Carbofuran (Furadan)	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Methiocarb	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Methomyl	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Oxamyl (Vydate)	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Glyphosate	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
THM (502.2)																													
Bromodichloromethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	50	ND	ND	ND	ND	ND	ND	ND	62	ND	ND	ND	ND	ND	ND	ND	60	ND	ND
Bromoform	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	6	ND	ND	ND	ND	ND	ND	ND	8.7	ND	ND	ND	ND	ND	ND	ND	4	ND	ND
Chloroform	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	83	ND	ND	ND	ND	ND	ND	ND	60	ND	1	ND	ND	ND	ND	ND	66	ND	ND
Dibromochlormethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	32	ND	ND	ND	ND	ND	ND	ND	43	ND	ND	ND	ND	ND	ND	ND	33	ND	ND
Total Trihalomethanes	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	170	ND	ND	ND	ND	ND	ND	ND	170	ND	0.54	ND	ND	ND	ND	ND	160	ND	ND
VOCs (524.2)																													
1,1,1,2-Tetrachloroethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,1,1-Trichloroethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,1,2,2-Tetrachloroethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,1,2-Trichloroethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,1-Dichloroethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,1-Dichloroethene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,1-Dichloropropane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,1-Dichloropropene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,2,3-Trichlorobenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,2,3-Trichloropropane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,2,4-Trichlorobenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,2,4-Trimethylbenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,2-Dichlorobenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,2-Dichloroethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,2-Dichloropropane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,3,5-Trimethylbenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,3-Dichlorobenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,3-Dichloropropane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,3-Dichloropropene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
1,4-Dichlorobenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
2,2-Dichloropropane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
2-Chlorotoluene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
4-Chlorotoluene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Benzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Bromobenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Bromochloromethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Bromodichloromethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Bromoform	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Bromomethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Carbon Tetrachloride	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Chlorobenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Chloroethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Chloroform	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Chloromethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
cis-1,2-Dichloroethene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
cis-1,3-Dichloropropene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Dibromochloromethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Dibromomethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Dichlorodifluoromethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Diisopropyl Ether	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Ethyl tert-Butyl Ether	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Ethylbenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Hexachlorobutadiene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Isopropylbenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Methyl Ethyl Ketone (MEK, Butanone)	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Methyl Isobutyl Ketone	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Methyl tert-Butyl Ether	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Methylene Chloride	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Naphthalene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
n-Butylbenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
p-Isopropyltoluene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Propylbenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
sec-Butylbenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Styrene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
tert-Amyl Methyl Ether	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
tert-Butyl Alcohol	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
tert-Butylbenzene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Tetrachloroethene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm

Toluene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Total-Xylene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
trans-1,2-Dichloroethene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
trans-1,3-Dichloropropene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Trichloroethene	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Trichlorofluoroethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Trichlorofluoromethane	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Vinyl Chloride	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
General Water Quality																													
DOC	mg/L	1	nm	nm	3.0	3.3	3.5	2.2	1.9	2.6	nm	7.9	5.5	4.6	4.8	2.9	3.4	1.8	5.9	1.1	3.8	3.7	4.7	3.4	2.5	1.9	7.4	0.9	4.1
Total Organic Carbon	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Total Suspended Solids	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	0	4	3	9	20	8	9	6	0	nm	2	9	104	8	15	5	1	1	2
Volatile Suspended Solids	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Turbidity	NTU	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Free Ammonia as Nitrogen	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ammonia as Nitrogen	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Nitrate	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	36.60	ND	5.50	5.40	ND	ND	ND	ND	49.40	ND	5.90
Nitrate as N	mg/L	1	nm	nm	1.55	1.48	1.27	1.12	1.13	0.95	nm	nm	nm	nm	nm	nm	nm	nm	8.26	ND	1.24	1.22	ND	ND	ND	ND	11.15	ND	1.33
Nitrite	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Bicarbonate Alkalinity	mg/L	1	nm	nm	567.67	625.00	586.00	388.50	357.00	468.50	183	779	383	380	292	205	246	208	174	500	345	347	118	141	252	194	171	442	350
Carbonate Alkalinity	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	0	0	0	0	65	39	0	0	0	0	38	42	256	94	0	0	0	0	36
Hydroxide Alkalinity	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total Alkalinity	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	183	779	383	380	357	244	246	208	175	498	383	389	373	235	252	194	171	442	384
					[other analytes not measured for May]																								
Chloride	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	171	13	137	132	126	63	63	42	196	90	153	155	147	77	76	47	185	85	178
Flouride	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Phosphate	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Sulfate	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	102	96.3	81.1	79	76.1	52.6	53.2	46.7	115	69.7	84	86	80.5	57.8	57.6	40.9	115	73.4	83.5
Bromate	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Chlorate	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Perchlorate	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Conductivity	umhos	1	nm	nm	nm	nm	nm	nm	nm	nm	1150	1650	1230	1200	1100	732	751	611	1240	1230	1280	1290	1080	758	759	567	1280	1180	1270
TDS (Total Filterable Residue at 180C)	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	644	915	698	685	637	407	409	335	732	706	739	730	694	441	452	337	710	642	750
pH	pH Units	1	nm	nm	nm	nm	nm	nm	nm	nm	7	7.2	8.3	8.3	8.5	8.4	8	7.8	7.5	7.2	8.4	8.4	9.4	8.7	8.1	8	7.4	7.2	8.4
SAR (calculated parameter) - **for Groundwater ONLY**		1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Metals and Trace Compounds																													
Boron	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	486	294	303	293	268	184	198	157	492	188	286	298	274	217	216	186	443	182	300
Calcium	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	55	182	43.6	42	38.9	46.3	45.4	48.3	49.4	114	38	38.7	37.3	37.5	40.3	37.4	51.4	106	41.6
Calcium as CaCO$_3$	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	138	455	109	105	97.3	116	114	121	124	285	95	96.8	93.3	93.8	101	93.5	128	264	104
Magnesium	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	33.2	93.4	94.3	91.9	85.7	48.6	51.6	27.3	33	64	89.4	91.3	88.7	49.8	50.7	33.9	30	55.9	91.7
Hardness	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Silica	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Potassium	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	15.1	<1	2.6	2.6	3.2	2.1	2.1	1.6	14.6	<1	2.5	2.7	3.7	2.2	2.2	1.7	17.9	<1	8.3
Sodium	mg/L	1	nm	nm	nm	nm	nm	nm	nm	nm	139	72.4	101	96.5	89.7	44.6	45	31.9	151	50.8	92.7	93	87.9	46.7	48	31.4	147	49.6	104
Aluminum	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	260	320	200	240	160	ND	72	ND	160	270	160	370	77	ND	ND	ND
Iron	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	1000	ND	420	540	350	440	230	ND	1000	ND	310	550	290	840	150	ND	520	ND
Zinc	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Mercury	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Antimony	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Arsenic	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	7	7	7	3	3	ND	ND	ND	7	7	6	3	3	ND	ND	ND	8
Barium	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	230	180	190	160	110	110	ND	ND	160	180	180	150	110	120	ND	ND	150	200
Beryllium	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Cadmium	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Copper	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Lead	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Manganese	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	47.3	730	ND	ND	20.6	42.1	30.5	36.8	31.1	701	ND	ND	ND	27.3	35.9	26.2	31.6	660	ND
Nickel	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	11	23	12	18	22	11	11	ND	10	16	12	15	19	11	13	ND	13	19	12
Selenium	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Silver	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Thallium	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Total Chromium	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	11	ND	ND	ND	ND	ND	ND	ND	11	ND	ND	ND	ND	ND	ND
Hexavalent Chromium	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
UV-254	ABS	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Haloacetic Acids																													
Bromochloroacetic acid	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	26	1	1	ND	ND	1	ND	1	2	ND	ND	ND	ND	ND	ND	ND	nm	nm	nm
Dibromoacetic Acid	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	7	ND	ND	ND	ND	ND	ND	ND	1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dichloroacetic Acid	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	45	ND	ND	ND	ND	ND	ND	ND	5	ND	ND	1	1	ND	ND	1	4	ND	ND
Monobromoacetic Acid	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	2	ND	ND	ND	ND	ND	ND	ND	4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Monochloroacetic Acid	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2	ND	ND
Total haloacetic Acids (5)	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	127	ND	ND	ND	ND	ND	ND	ND	64	ND	ND	3	1	ND	ND	1	14	ND	ND
Trichloroacetic Acid	ug/L	1	nm	nm	nm	nm	nm	nm	nm	nm	70	ND	ND	ND	ND	ND	ND	ND	54	ND	ND	2	ND	ND	ND	ND	8	ND	ND
Microbes																													
E.Coli	MPN/100mL	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	500	2400	500	70	130	800	nm	nm	160	500	280	240	170	50	nm	nm	170
Fecal Coliforms	MPN/100mL	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	800	2400	3000	170	170	800	nm	nm	160	500	280	240	1100	50	nm	nm	170
Total Coliforms	MPN/100mL	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	5000	16000	>16000	9000	5000	2400	nm	nm	9000	3000	900	900	16000	900	nm	nm	900
Heterotrophic Plate Count by R2A	CFU/ml	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Cryptosporidium Oocysts	oocysts/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Giardia	cysts/L	1	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
Total # of Analytes/Parameters		156																											
Total w/o VOCs		84																											
Total w/o VOCs and Pesticides (ie if we keep orig list)		74																											

Oct-05	Oct-05	Oct-05	Oct-05	Oct-05	May-06	May-06	May-06	May-06	May-06	May-06	May-06	May-06	May-06	May-06	May-06	May-06	May-06	Jun-07	Jun-07	Jun-07	Jun-07	Jun-07	Jun-07	Jun-07	Jun-07	Jun-07	Jun-07	Jun-07	Jun-07	Jun-07
SW2b	***SW3***	***SW4***	***SW5***	***SW6***	***RW1 (Yerba Buena***	***SW1***	***SW2b***	***SW3***	***SW4***	***SW5***	***SW6***	***GW1***	***GW2c***	***GW2a***	***GW3 Coyote***	***PW1***	***PW2***	***SW 1***	***SW 2a***	***GW 1***	***GW 2a***	***GW 2c***	***PW 2a***	***GW 3***	***SW 2b***	***SW 3***	***SW 4a***	***SW 5***	***SW 6***	***RW1 (Yerba Buena***
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND	ND	nm	nm	nm	nm	ND	ND	ND	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
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ND	ND	ND	ND	ND	56	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
ND	ND	ND	ND	ND	4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
ND	ND	ND	ND	ND	76	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
ND	ND	ND	ND	ND	31	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
ND	ND	ND	ND	ND	170	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
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nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
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nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	7.0
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
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nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
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nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
4.1	4.4	3.0	3.2	2.8	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	4.7	5.3	3.0	3.2	2.8	5.9	2.0	5.4	5.9	4.2	4.0	3.6	5.4
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	4.3	4.4	2.2	2.4	1.8	3.8	1.1	4.5	5.7	3.3	3.4	2.8	4.7
5	7	6	21	6	7	0	4	3	4	7	4	nm	nm	nm	nm	nm	nm	3	2	4	1030	233	15100	2	10	79	1	9	2	1
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	1	0	1	73	15	1360	1	2	29	1	2	1	nm
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.89
<0.05	<0.05	<0.05	<0.05	<0.05	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	<0.05	<0.05	<0.05	<0.05	<0.05	0.24	<0.05	<0.05	<0.05	0.05	<0.05	<0.05	nm
<0.05	<0.05	<0.05	<0.05	<0.05	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	<0.05	<0.05	<0.05	<0.05	<0.05	0.25	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	nm
5.60	4.30	5.10	4.50	5.70	42.90	6.80	8.50	8.50	11.90	11.90	12.50	4.00	ND	ND	ND	9.50	4.20	4.20	4.10	2.10	ND	ND	3.50	ND	3.7	ND	ND	ND	ND	36.0
1.26	0.97	1.15	1.02	1.29	9.69	1.54	1.92	1.92	2.69	2.69	2.82	0.90	ND	ND	ND	2.15	0.95	0.95	0.93	0.47	ND	ND	0.79	ND	0.84	ND	ND	ND	ND	8.13
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
380	155	214	207	182	203	405	388	324	214	210	200	410	423	381	414	400	399	375	353	361	389	428	434	292	347	273	206	213	168	187
0	215	0	0	0	0	0	24	75	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	19	68	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
380	368	214	207	182	203	405	412	399	214	210	210	410	423	381	414	400	399	375	353	361	389	428	434	292	366	341	206	213	168	187
141	138	49	46	31	168	94	94	89	31	31	27	123	113	99	98	90	92	148	146	131	134	117	144	52	147	143	66	66	50	172
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.85
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.45
75.9	73.5	53.5	47.9	43.6	106	49.4	44.4	42.1	40.8	41	40.8	65.5	62.7	46.7	116	53	51.8	84.9	84.7	74.4	65.6	65.3	83.8	58.9	83.50	83.2	53.7	53.4	48	113
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	58	63	53	ND	ND	54	ND	110	25	ND	23	ND	nm
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND
1290	1190	556	651	557	1260	1110	1100	1050	595	597	563	1260	1240	1090	1470	1100	1120													
688	688	364	356	322	720	640	618	582	326	314	322	672	674	588	940	696	1120	704	686	648	670	518	580	442	660	652	382	376	332	668
8.3	9.0	8.3	8.2	8	7.5	8.3	8.3	8.7	8.1	8.1	8	7.6	7.5	7.5	8.3	7.1	7.9	8.5	8.4	7.7	7.6	7.6	8.4	7.2	8.3	8.8	8	7.8	7.8	7.5
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
298	283	170	154	128	441	203	194	178	121	121	122	250	199	204	214	234	217	294	273	236	248	212	368	180	282	279	193	186	160	449
41.7	40.2	43.3	41.7	42.3	62.6	33.7	35.4	32.8	48.1	48.9	49.7	37.7	32.8	31.4	164	59.5	60.5	41.0	39.9	36.7	41.2	33.4	58.1	77.2	39.5	39	40.5	42	39.8	56.3
104	101	108	104	106	157	84.1	88.5	81.9	120	122	124	94.3	82	78.5	409	149	151	103	99.8	91.8	103	83.5	145	193	98.8	97.5	101	105	99.5	141
92.1	89.7	40.3	39.4	30.1	36.1	93.3	94	92.1	36.5	36.1	32.5	91.1	107	85.8	83.6	169	120	91.3	89.8	94.5	111	119	180	39.5	88.6	91.6	41.7	40.3	27.8	30.5
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	246
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	23.3
3.2	3.3	1.9	2	1.7	14.6	1.9	2.3	2.3	1.9	1.8	1.7	1.8	0.6	0.7	0.7	9.6	6	2.5	2.5	1.9	1.9	1	6.3	<0.5	2.4	2.7	1.9	2.2	1.8	nm
100	94.6	35.4	34.1	25.2	135	59.6	63.9	56.8	25.7	26	23.9	88.9	59.5	71.9	64.2	62.7	60.8	112	108.0	91.0	86.9	69.5	110	51.4	105	105	56.5	55.2	43.9	149
120	110	140	720	140	ND	ND	240	120	140	ND	100	120	ND	61	ND	74000	25000	64	ND	54	9000	2200	44000	ND	170	720	ND	280	ND	ND
180	160	240	860	200	ND	ND	390	190	240	ND	180	180	ND	110	480	140000	4600	ND	ND	ND	13000	3500	77000	390	230	1100	ND	400	ND	120
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	7800	4400	ND	ND	ND	51	ND	25000	ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.44	1.63	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND
7	7	2	ND	ND	ND	8	8	7	2	ND	ND	9	3	4	4	43	13	5	4	6	4	ND	13	ND	4	ND	ND	ND	ND	ND
180	160	110	120	100	ND	180	170	170	120	130	110	210	170	130	220	940	660	170	160	130	210	180	900	ND	160	160	ND	100	ND	ND
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ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	190	65	ND	ND	ND	ND	ND	85	ND	ND	ND	ND	ND	ND	61
ND	ND	ND	ND	ND	ND	ND	ND	ND	400	ND	ND	ND	ND	ND	ND	79	68	ND	ND	ND	ND	ND	96	ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	25.3	20.3	28.6	ND	ND	ND	34	ND	ND	45.5	104	ND	861	1500	1480	ND	ND	63.9	365	315	2450	397	ND	46.3	28.8	42.6	20.9	34.5
14	14	10	14	ND	16	13	16	14	13	14	13	15	13	ND	41	1500	810	ND	ND	ND	83	43	1600	ND	ND	21	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	6	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
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ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	670	260	ND	ND	ND	54	16	660	ND	ND	14	ND	ND	ND	ND
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	ND
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.136
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
ND	ND	ND	ND	ND	ND	ND	ND	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.4
ND	ND	ND	ND	ND	2	ND	ND	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1	1.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	14.7
ND	ND	ND	ND	ND	ND	ND	ND	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.1	ND	ND	ND	ND	ND	ND	ND	ND	1.0
ND	ND	ND	ND	ND	3	ND	ND	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.7
ND	ND	ND	ND	ND	23	ND	ND	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1	1	1	ND	ND	ND	ND	ND	ND	ND	ND	27.0
ND	ND	ND	ND	ND	18	ND	ND	nm	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	6.1
3000	3000	240	500	80	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	<2
3000	3000	240	1700	80	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	<2
3000	9000	1600	9000	300	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	<2
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	450
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	<0.1
nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm	0.4

Appendix B

“Upper Silver Creek Experimental Site Exploration and Characterization” by Eduard Hoehn, 2006. Project report for Eawag, Swiss Federal Institute of Water Science and Technology.

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Upper Silver Creek Experimental Site Exploration and Characterization

Part of study:

"Attenuation of Emerging Contaminants in an Urban Stream Augmented With Recycled Water - Upper Silver Creek, San José, California"

Eduard Hoehn
Eawag, Swiss Federal Institute of Water Science and Technology
Stanford, July 26, 2006

Civil and environmental engineering Professor Martin Reinhard and student Megan Plumlee sample water in an urban creek.

http://soe.stanford.edu/research/pdf_reinhard.pdf

Summary

An experimental site of about 300 *m* (1000 *ft*) along Upper Silver Creek (a tributary to Coyote Creek, San José, California) should help to study the natural attenuation of emerging (unregulated) contaminants during a planned augmentation of the creek with recycled water. If the creek is downwelling to the hyporheic zone, sorbing of contaminants to subsurface materials will enhance natural attenuation. A loss of creek water to riverbed and subsurface materials may, however, threaten the productive ground water of the Santa Clara Valley basin. In the period between March and July 2006, the site has been instrumented with i) three wells drilled at vertical distances of up to 50 *m* (160 *ft*) from the creek, ii) two wells pushed into the creek's bed, and iii) temperature loggers in the creek and these wells. The exploration of the site included i) an assessment of the hydraulic conductivity of subsurface materials, ii) a preliminary analysis of temperature time series, iii) an interpretation of an ongoing time series of water chemical analyses, and iv) radon water analyses. A tracer experiment with rhodamine WT and bromide is planned to complement the exploration work. The existence of a hyporheic zone below the creek's bed can be inferred from the data. Flow from the creek's bed to local alluvial ground water could not be detected, although the ground water of the drilled wells is partly young and originates from the same catchment as the creek's water. From a today's perspective, a contamination of the productive aquifer with augmented water from the experimental site at Upper Silver Creek is not probable. From the composition of the ground water in a well near Coyote Creek, which is similar to that of the creek itself, some downwelling of creek water is hypothesized. The planned tracer test will give better insight into the mixing rates of recycled water with the various natural waters.

Preface

At the end of 2005, Prof. M. Reinhard arranged my sabbatical visit at Stanford University. In December 2005, the two partners, Stanford University and Santa Clara Valley Water District, submitted to the WateReuse Foundation a Research Proposal for the project “Attenuation of Emerging Contaminants in Streams Augmented with Recycled Water”. From “Schedule and Deliverables for 2006” of this proposal, I concluded that the project had started, and I proposed to Prof. Reinhard to do a field study on radon as a tracer, within this project. Upon arrival at Stanford, I realized that the field study was at an early state. Therefore, I changed my goals to contribute to the take-off of a field study that includes explicitly the exchange of water between the creek and the subsurface, see Appendix 1. An extension allows tracing emerging trace organic contaminants on their way to the subsurface, and it contributes to the district’s groundwater contamination risk assessment. This report presents the hydrogeological results of field work between March and June 2006.

Contents

1. Introduction

Water managers consider harnessing rivers as one step in a thorough multi-step treatment process of waste waters (WW). This can increase the locally available drinking water and provide more water for river habitats (Reinhard & Gurr, 2006). The release of WW with xenobiotic toxic, persistent and mobile chemicals to rivers results in a contamination risk for aquatic habitat and human water uses. Rivers have, however, a capacity to remove to some extent some of the contaminants of urban wastewater treatment plant (WWTP) discharge as the water flows through (innate "self-purification potential"). They accomplish a concentration reduction through biogeochemical processes at the air-water interface, especially in pool-riffle sequences with transient storage capacity (e.g., volatilization, photolysis, and biodegradation). At the water-sediment interface of the riverbed, biogeochemical sorption processes become important, depending on the contact time of flowing turbulent river water with the riverbed materials. In many industrialized regions, ground water recharged by rivers is used for drinking water and irrigation. A self attenuation of contaminants from WWTP in the hyporheic ground water of downwelling rivers has been found for a variety of contaminants, such as chlorinated hydrocarbons (e.g., Schwarzenbach et al., 1983), metals (von Gunten et al., 1991; Nowack et al., 1997), detergents (e.g., Ahel et al., 1996, Montgomery-Brown et al., 2003), and pharmaceuticals (e.g., Gross et al., 2004).

Recent studies have shown that most rivers flowing in flood plains and other alluvial permeable material have a zone below the riverbed, in which surface water is exchanged to a considerable extent with very young ground water (“hyporheic zone”; Stanford & Ward, 1993; Brunke & Gonser, 1997; Huggenberger et al., 1998). Rivers are downwelling and upwelling in a continuum, from the floodplain to the pool-and-riffle scale (Gonser et al., in prep.). In the hyporheic zone, flow is mostly laminar and thus the flow velocity of the water is reduced by orders of magnitude, after downwelling from the river. Compared to older alluvial ground water, we call this very young ground water “hyporheic” (Hoehn & Cirpka, 2006). The contact time of hyporheic ground water with surfaces of riverbed and aquifer materials is longer than that of river water. The natural attenuation of dissolved compounds in rivers depends on subsurface residence times of hyporheic ground water and their mixing with older ground water. The extent of natural attenuation is time-dependent because the succession of floods and periods of base flow in the rivers may result in clogging and declogging of the water-sediment interface (e.g., Schälchli, 1993).

In the industrialized and densely populated regions of the mediterranean (semi-arid) climate type like California, Israel, or southwestern Australia, districts consider the recycling of WW directly into the subsurface, or into local river systems, as a means of restoring local drinking-water supplies, and bolstering threatened riparian and aquatic habitat (e.g., Gurr & Reinhard, 2006). During the recharge of the Santa Ana River, Southern California, with tertiary-cleaned and dechlorinated WW (recycled water, RW), the concentrations of pharmaceuticals were studied along a stretch of 11 *km* (e.g., Ding et al., 1999). On this large scale, the concentrations of some contaminants dropped by two thirds and others vanished from the water completely. At distances of a few decades of *m*, however, compounds like sulphate and EDTA did not show any attenuation. Therefore, more focus is required on the study of downwelling rivers, on a smaller scale. In this work, we investigate a section with an experimental site of a few hundreds of *m* of the urban Upper Silver Creek (USC) in San José, California (Figure 1). USC is a tributary to Coyote Creek (CC), which flows to the San Francisco Bay. At the upstream end of this experimental site, the Santa Clara Valley Water District (SCVWD) plans to augment USC with tertiary-treated WW (“recycled water”, RW). The district proposes to regulate the release into USC based on the biotic standard of a warm water fishery. The release volume will be adjusted so as to prevent water temperature downstream from rising above 24 °*C* (75 °*F*). To this end, SCVWD will pump RW from the South Bay Water Recycling Plant (SBWRP) to the Yerba Buena (YB) Pump Station of SBWRP. The purpose of the augmentation is sustaining the habitat of CC by keeping the creek’s appropriate temperature for protected steelhead trout to thrive.

2. Hydrogeological Overview of the USC Site

The proposed experimental site is located at the eastern edge of Santa Clara Valley at the Silver Creek Linear Park off Yerba Buena Road, at the foot of the Yerba Buena hills. The catchment of USC extends to about 48 km^2 (18.5 *sq mi*), in an elongated valley formed by the USC fault. The natural base flow rate of USC at the YB Pump Station was estimated visually in May 2006 to be at about 0.04 m^3/sec (about 11 *gal*; details about creek discharge and gage measurements, see Appendix 2). During the rain period, this flow rate is probably higher by a factor of 100 – 1000 (e.g., April 2006). The catchment opens to the Santa Clara Valley groundwater basin (San José flood plain, southern end of San Franciscan Bay structural basin). Here USC formed a small holocene alluvial fan with stream terrace deposits (Helley & Wesley, 1994; USGS, 2006). The San José flood plain consists of an aquifer with ground water, which is extensively used (an upper and a lower aquifer zone, with a discontinous and leaky aquitard). The productive ground water flows in the San José floodplain generally in NW direction, at a hydraulic gradient of 0.3 – 0.4 per cent (Planert & Williams, 1995). The alluvial deposits at the experimental site are filled with ground water, which probably contributes to the recharge of the productive ground water (see hydrogeological cross section, Figure 2). The experimental site is located in the recharge area of the productive ground water of this aquifer (forebay zone, CRWQCBSFBR, 2003), between the YB Pump Station and the beginning of a section with flow in a concrete channel (elevation of YB Pump Station, about 70 *m* (240 *ft*) a.m.s.l.; USGS, 2001; see Figure 1). At the experimental site, USC flows in its natural bed and is flanked by a corridor of riparian forest.

3. Aquifer Testing

Three boreholes were drilled in May 2006 by SCVWD, at vertical distances from USC of maximal 50 *m* (160 *ft*; (GW1, GW2a, GW2c; hydrogeological cross section, Figure 3, technical information about wells, Table 1). Heterogeneous sequences of coarse- and fine-grained sediments prevailed from the surface to down to the top of serpentinite rock, which was found at depths of 5 - 8 *m* (16 – 26 *ft*). The wells are screened throughout water-saturated alluvium (see Figure 3) and tap ground water, which was partially confined in spring 2006 (depths to water table given in Table 2 and Figure 3). The hydraulic conductivity of the subsurface materials around the groundwater wells was assessed with Hvorslev-type slug tests. The results of this test yielded a geometric mean and standard deviation of the hydraulic conductivity values of the partly coarse- and partly fine-grained materials in the three bore holes of $K = 5 \cdot 10^2$ *gal/ft*^{2}*·day* ($2 \cdot 10^1$ *m/d*; $\mu_{\ln K} = 3$, $\sigma^2_{\ln K} = 0.003$; details, see Appendix 3). Note that the hydraulic conductivity of well 2a is lower than that of well 1 by two orders of magnitude. Thus the material around the wells is only partly permeable, and a hydraulic connection between the creek and the wells cannot be inferred from geological evidence. Without further knowledge about the elevation of USC and the top of the well casing, I assumed in Figure 3 that the creek is incised by a constant 2 *m* (7 *ft*). Under this assumption, a hydraulic gradient from the creek to the wells may not have established in April 2006. Since the water table was generally falling in spring 2006 (Table 2) and will probably fall more throughout the summer, sooner or later a hydraulic gradient from the creek to the ground water in the wells will establish. A high hydraulic gradient between the new wells in the alluvium of USC and the productive ground water of the San José flood-plain aquifer of about 4 per cent in Figure 2 corroborates the assumption of hillslope recharge towards the flood plain.

In May 2006, we pushed two stainless-steel wells of a diameter of 2” into the riverbed material, down to a depth of about 0.6 (PW1) and 0.3 m (PW2), respectively (see map

Figure 1). The wells are slotted along a section of 0.2 *m* (8”) with 6 rows of 11 openings of a diameter of about 1 *mm*. The openings cover about 0.05 per cent of the screened area. We want to sample ground water at a depth of 1’ – 2’ below the surface of the creek, to establish a hydraulic and a concentration gradient of water and its solutes between the surface water and c) the pushed wells. While PW1 required extensive purging to remove fine material from inside the well and to make it permeable, PW2 did not show any drawdown upon pumping at rates of up to 5 *L/min* (1.3 *gal/min*), and it is thus very permeable.

4. Water Temperature Time Series

The displacement of heat in water is treated in theory similarly to that of solute transport. The mixing of two waters, 1 and 2, of different temperature, T, is assessed with the mixing equations, given that the flow rates of the two waters, Q_1 and Q_2 are known (e.g., RW and USC, or USC and CC): $T_1 \cdot Q_1 + T_2 \cdot Q_2 = T_{mix} \cdot Q_{tot}$, and $Q_1 + Q_2 = Q_{tot}$. This is among the reasons, why we have to know the discharge rates of USC and CC. Furthermore, heat exchanges with the solid matrix similarly to that of sorbing solutes. This is why we have to know the behavior of heat in the hyporheic subsurface of the creek. A summary of the theory of the convective-dispersive transport behavior of heat in groundwater of granular (porous) aquifer systems is given in Hoehn & Cirpka (2006; Section 2.1. “One-dimensional analysis of heat and solute transport of infiltrating river water”). A summary of the interaction of temperature between creeks and hyporheic ground water can be drawn from Stonestrom & Constantz (2003, 2004), and Hatch et al., (2006).

Time series from HOBO® water temperature loggers, which were placed in USC, the pushed and the drilled wells, yielded insight into the flow field (duration of logger operation, see Table 3). The reasons for installing HOBOs are twofold: Temperature can be considered a tracer. By comparing the changes in surface water and groundwater, we should be able to determine, what the connection is between surface water and ground water at the experimental site. The data will show, whether the connection exists, and possibly, what the residence time is between surface water and groundwater. Furthermore, the CEQA consultants of SCVWD recommended monitoring temperature along the entire study stretch. Thus temperature is a useful tool for predicting augmentation management options.

The surface water loggers (SW1, SW2; their identification refers to positions near the pushed wells, PW1 and PW2, respectively, and is NOT identical with the sampling points for water chemistry) and the pushed well loggers (PW2, PW2) showed quasi-symmetrical daily sinusoidal patterns of water temperature. The groundwater loggers in wells GW1 and GW2a showed gradually increasing temperatures with the beginning of the warm season. From Figure 4, which shows the period of
May 13 – 23, the following can be inferred:

- The temperatures in SW1 and SW2 go in parallel.
- The temperature in well PW2 goes in parallel with SW2: maybe there is a short-cut of surface water.
- The temperature in well PW1 has the same nightly minima as PW2 and the surface water, but dampened afternoon maxima, and its maxima are somewhat delayed: this seems to be evidence for hyporheic ground water.
- The temperature in well GW2a exhibits a steeper gradient with time than that of GW1.
- The temperature change in the water of USC due to a rain event in the catchment on May 21 resulted in short-period temperature fluctuations in the two surface-water and pushed-well loggers.
- The flood that followed this rain event displaced the logger of SW2 out of the water: starting early morning of May 22, this logger recorded air temperatures rather than water temperatures.

Figure 5 is a blow-up of Figure 4, for May 20/21. From this figure, the following can be deduced:

- The delay of the afternoon maximum temperature in PW2 with respect to SW2 is about 1 - 2 hours: given a retardation of a transported temperature signal in the subsurface with respect to that of the water of a factor of 3 – 4 (Hoehn & Cirpka, 2006), a subsurface residence time for hyporheic water of at least 15 minutes would result.
- The short-term temperature fluctuations due to the rain event start at about 11am. From then on, the temperatures at SW2 are delayed from those of SW1 by about 1 hour: Maybe it was raining in the catchment only and not at the field site. If so, and under the above assumptions, a residence time of the water from SW1 to SW2 of at least ¼ hour would result for water flow from SW1 to SW2.

In Figure 6, which shows the period of May 13 – July 17, the unsystematic temperature fluctuations at the SWs and in the PWs at frequencies lower than those of the daily sinusoidal pattern represent local weather conditions – sometimes warmer, sometimes cooler. The upper end of the temperature scale, 24 *°C* (75 *°F*) is the proposed maximum temperature for warm-water fishery. At the experimental site, this temperature has not been reached in both surface-water loggers, SW1 and SW2, within the measurement period of May 13 to July 17, 2006. The daily amplitudes of the temperatures of USC at SW1 and SW2 varied at maximum by 5.4 *K* (May 7; see Figure 6; K, degree Kelvin: a temperature difference of one degree Kelvin is equivalent to that of one degree Celsius - it is used for expressing differences between two temperatures), and at minimum by 0.9 *K* (June 12). The difference between the lowest and highest extreme value was 10.3 *K* [maximum on July 7 of 23.4 *°C* (74.1 *°F*), minus minimum on May 28 of 13.1 *°C* (55.6 *°F*)]. In the pushed well, PW1, the nightly minimal temperatures of the logger started to get more and more dampened with respect to those of PW2 and the SWs, since May 2006.

In the two groundwater wells, a slightly different course of the water temperatures in June 2006 can be inferred from Figure 6: While the temperature in GW1 rose by 3.0 *K*, that of GW2a rose by 5.4 *K*. The ground water temperature at well GW2a is more susceptible to influences from the surface than that of well GW1. Both curves exhibit changes in the gradients: Future retrievals of then longer time-series will show, if the changes in the temperature gradients can be correlated with those of the SWs and PWs, or if they are artifacts. This requires a statistical analysis of the data using correlation coefficients and low-pass filtering techniques. Furthermore, a logger should be installed in well GW2c to record the temperature, for comparison.

Figure 7 is a blow-up of Figure 6, for PW1 and PW 2 in the period of June 20 – July 4, 2006. From this figure, the following can be deduced:

- One some days, the extreme temperatures of logger SW2 were lagging behind those of SW1 by up to a ½ hours, while the amplitudes remained the same. The small differences are probably due to local differences in shade and sunlight at the site where a logger is placed.
- The temperature maxima of well PW1 are delayed from those of well PW2 by 5 – 7 hours; those of the minima by up to 2 hours: This is an increase compared to the earlier observations. Furthermore, the temperature amplitudes of well PW1 decreased in the period between June 22 and 28, at about constant average temperatures. This may be due to a gradually increasing change of the water type from surface water to hyporheic ground water (settling of sediments around this well). This well is influenced by hyporheic ground water.
- The temperature minima of well PW2 lagged behind those of SW2, and were somewhat dampened. This is different from the earlier observations, where almost identical temperature courses were found. The maxima, however, still remained the same. Maybe the short-cut of water from USC to PW2, which has been concluded from the information of Figures 4 and 5, has ceased since. Influence of hyporheic ground water cannot be inferred unequivocally.

5. Major Ion Water Chemistry

Recycled, surface, and ground waters are sampled in a time series, to characterize pre-augmentation background conditions. The water analyses of July 19, August 30, and October 3, 2005, taken at sites existing previous to the instrumentation of the experimental site, revealed in general only a small temporal variability of the measured concentrations (for RW and **SW1** as examples, see Table 4; here, "RW" refers to the sampling tap of RW at YB Pump Station; "**SW**" refers to surface-water sampling points, and NOT to the position of the temperature loggers; sample identification taken from SU/SCVWD water chemistry sampling). The relative concentrations in the surface waters of some of the major geochemical compounds are different from those of USC to CC (SW4, SW5, and SW6). While this difference is on the order of a factor of about two for specific electrical conductance, and DOC, the Ca/Mg ratios varied by a factor of up to five (Table 5).

From the cationic ternary diagram of Figure 8 (SCVWD; for August 30, 2005) can be seen that all samples except RW lie on a line that is given by the variable Ca/Mg ratio (end members of this line: **SW1** and GW3). The high Ca/Mg ratios are typical for the weathering of serpentinite and dunite rocks of the Great Valley Formation and the formations of the Franciscan Group in the USC catchment (see Appendix 4). Both surface-water types, USC and CC, showed a geochemical composition that is different from that of RW (variable Ca/(Na+K) and Mg/(Na+K) (not shown) ratios; see Figure 8). RW is a more NaCl-dominated water. During augmentation, the major ions can be used for a calculation of a bimodal mixing of the natural waters with RW. Mixed waters in the creek would lie on a line in the diamond part of Figure 8, between the end members, RW and the natural waters. Maybe even a ternary mixing between RW, USC and CC waters can be assessed.

On May 2, 2006, surface water and ground water were sampled at the USC field site, and in CC and the ground water. Among the analyzed waters, the cationic composition is more different than the anionic. The relative concentrations of the major cations showed clustering among different geochemical types (see Figure 9):

- RW;
- **SW1, SW2,** SW3; GW2c;
- GW1, GW2a;
- PW1, PW2;
- SW4, SW5, SW6, PW3.

The ground water in the pushed wells was somewhat less concentrated in Na and somewhat more in Ca, and the groundwater in the drilled wells GW1 and GW2a was somewhat less concentrated in Mg and somewhat more in Na than the surface waters **SW1, SW2**, and SW3, albeit insignificantly. The composition of the ground water of well GW2c was very similar to that of the surface waters of USC, and the composition of well GW3 was similar to that of the surface waters of CC. The Ca/Mg ratio decreased gradually along the flow path from USC to CC (Table 5).

The pushed wells showed very high concentrations in Fe and Mn on May 2 – 4, 2006. A probable explanation for these high concentrations is that the wells are made of cast iron.

Iron particles formed during pushing could have resulted in an artifact. Alternatively, reducing conditions could prevail in the ground water. No values were available for either redox potential (Eh), dissolved oxygen or the reduction products of nitrogen, i.e. nitrite and ammonia. The analyses revealed low concentrations in nitrate.

6. Radon Concentrations

Radon gas exists in the subsurface, and dissolves into groundwater at a determinable rate (see Appendix 5). Radon measurements allow determining a possible connection between the surface and groundwater, and eventually residence time of water in the subsurface between infiltration of USC and the groundwater wells. On the sampling dates of May 2, and May 24, no Rn, or concentrations below detection, were found in the RW, the SW samples of USC, and in PW1 (see Table 6). In RW and the surface water, Rn has gassed out to the atmosphere. In PW1, there was either a short cut of creek water to the well, or the mixed residence time of alluvial ground water with a possible contribution of hyporheic ground water was less than 5 hours (given a detection limit of about 0.5 *Bq/L*; (SI-units: Bq/m^3, number of decays per second and m^3 of fluid; US-units: 1 *Bq/L* = 27 *pCi/L* <-> 1 *pCi/L* = 0.037 *Bq/L*). From Table 6 can be seen that more than one sample was drawn at a given date from most sampling sites. The results of Table 6 give a feeling about the high Rn variability due to sampling and preparation procedures. The Rn analysis is restricted to the ground water of the drilled wells and PW2, where concentrations above the detection limit were found.

The highest Rn concentrations were measured in the drilled wells, on May 2-4 in well GW2a (17 *Bq/L*), and on May 24/25 in well GW2c (13 *Bq/L*; Table 6). Without further knowledge, I assume that these concentrations represent steady-state conditions (i.e., mixed Rn water ages of >15 days). Given the instrumental statistical errors and the variability of the sampling and preparation, only GW1 and GW2c on May 2-4 revealed concentrations significantly below 17 *Bq/L*, eventually resulting in mixed Rn water ages of <15 days). After the rainy spring of 2006, the groundwater flow velocity might have been so much higher than three weeks later that the Rn concentrations could have increased since. In PW2, the Rn concentrations were slightly above the detection limit, at both sampling dates. This points to a small fraction of hyporheic ground water in the wells, with a residence time in the subsurface of 5 - 10 hours. This interpretation contradicts the findings of the water-temperature measurement in well PW2.

7. Planning a Rhodamine Water Tracer (RWT) Test

Purpose

A test with a tracer pulse will tell us, a) at what velocity the tracer travels (tracer residence times from the injection point to the sampling point), and b) to what extent the pulse is dispersed and diluted during flow (tracer mass loss, and tracer mass balance). The tracer may be monitored in the surface water, and in the pushed and the groundwater wells. We intend to use concomitantly Rhodamine WT (RWT) and bromide (Br^-) as tracers. RWT is hypothesized to be a proxy for the solute transport of certain trace organic solutes in a stream. Data from the RWT tracer test will be used to test this hypothesis. The RWT should thus yield tracer concentration-time breakthrough curves, a) at the SW sites of USC, and in CC, more downstream of the injection site, and b) in the PWs and (hopefully) the GWs. Bromide will be injected as a conservative tracer. The breakthrough curves of Br^- represent the flow and transport of water and yield water residence times. The breakthrough curves of both tracers allow interpreting the temporal concentration distributions statistically (μ,σ^2; see e.g., Hoehn & Santschi, 1987). We expect a retardation of RWT with respect to Br^-. The tracer fractional mass recovery rates indicates possible tracer loss and mixing ratios of surface waters with ground water.

Program

RWT (20 per cent solution) and bromide (solution of, e.g., KBr, technical grade) will be injected near the point of the planned augmentation of USC with RW (at YB Pump Station). I took the following from an analysis of Fischer et al. (1979; chap. 5.1., 5.2., and 5.4.; details, see Appendix 2):

a) The tracer masses to be injected at the USC can be compared with those of the SAR site (Lin et al., 2003), as follows: An injection of about 1/1000 of that at SAR should be sufficient (detection limit RWT: 0.1 *µg/L*; linear range: up to 1 *mg/L*; toxicity standard: 1 *mg/L*; detection limit bromide: 200 *mg/L;* toxicity standard not known to me);

b) An injection of each half of the total tracer mass will be optimal at each 0.25 the width of USC.

c) The distances between the injection point and SW1/PW1 should be sufficient for mixing;

d) The peak dilution with respect to the injection concentration are expected to be: creeks: per cent (10^{-2}); PWs: 1/10 per cent (10^{-3}); GWs: $10^{-4} – 10^{-6}$;

e) The residence times of the tracers are expected to be, in USC: minutes; in the PWs: minutes to hours; in CC: hours; and in GWs: days to weeks;

Sampling

The first 2 days (SWs, PWs): at least one automatic fluorescence logger, in USC and in a PW (PW1 is probably better suited); for the other sampling points, there should be one person to take samples. The next 10-15 days (GWs): one person should take a daily sample from each of the GWs.

8. Recommendations for Next Steps in Exploring and Characterizing the USC Experimental Site

SU and SCVWD plan a sampling date for water chemistry in August 2006, and the RWT test and a test augmentation with RW in fall 2006 (continuous augmentation planned for 2007). Before and concomitantly to this, the exploration and characterization of the USC site should be completed with the following work:

USC:

- measure flow rate, Q, at least 4 times throughout the coming year (low flow, October 2006; high flow, February/March 2007; average flow, May/June 2007; low flow August/September 2007), and establish a relationship Q vs. stage (USC water level monitored at YB Pump Station); a better option would be to have a continuously monitoring gage at the YB Pump Station;

- flow monitoring: there are miniature flow meters on the market that could measure flow velocities in open creeks, down to 0.025 *m/sec* (0.082 *ft/s*) and minimum depths of water of about 0.04 *m* (0.13 *ft*), see e.g., http://www.ott-hydrometry.de/web/ott_de.nsf/id/pa_c2_e.html
- More recent flow meters works with "side-looking" Doppler radar technology for measuring flow in Rivers, creeks & Open Channels, see e.g.,: http://www.ott-hydrometry.de/web/ott_de.nsf/id/pa_ottn6mxeqe.html.
- measure altitude above datum (sea level) of USC, best at gaging station.

Drilled Groundwater Wells:

- measure depth to water table, each time a well is operated, to establish the time series started in Table 2;
- measure the altitude above datum (sea level) of the top of the well casings, and calculate the hydraulic gradient between the creek and the wells.

Pushed Wells:

- if indications of short-cut water flow from USC to PW2 persist during the 2006 test augmentation, extract well and push it down to 2 ft and 1 - 3 ft aside of bank, for the augmentation of 2007.

HOBO® Temperature Loggers:

- avoid same name for the location of the surface-water loggers and water chemistry sampling position, which are not the same;

- install temperature logger at groundwater well, GW2c, to judge, if it is influenced by water from USC;
- retrieve logger information before and after RWT test, and before and after test and regular augmentations - do not wait with a retrieval until memory is full;
- correlate extreme values and the dampening of the general course of the temperatures from groundwater wells and pushed wells with those of USC;
- use statistical software (e.g., MATLAB) for correlation analysis and low-pass filter techniques.

Water chemical analysis

- when analyzing for Fe and Mn, filter the samples in the field, with a 0.45 μm membrane filter;
- analyze the ground waters (PWs and GWs) once for dissolved oxygen and the redox-dependent compounds, NO_2^-, and NH_4^+;
- use software for analyzing and plotting of water-chemistry data (e.g. AQUACHEM: http://www.flowpath.com/software/aquachem/aquachem_ov.htm).

Radon

- additional Rn measurements would complement the hydraulic, water temperature, water chemistry and RWT test data. It would, however, require the purchase of a Rad7 instrument with the H2O annex (for cost, see http://www.durridge.com).

9. Conclusions

Are the dimensions of the experimental site at USC suitable for an assessment of natural attenuation ?

Interpreting the results of the rain event of May 20-22 at SW1 and SW2 as temperature transport, water travel times from the YB pump station to SW2 are at least ¼ hour. This seems to me to be sufficient for the attenuation of strongly sorbing compounds only. It will be of advantage to trace the contaminants also at sites SW4 – SW6 of CC, where the residence times are longer.

Do the pushed wells tap hyporheic ground water ?

The creek has most probably a hyporheic zone. There are high chances that at least PW1 taps hyporheic ground water of a subsurface residence time of up to two hours. The interpretation of the temperature monitoring results is, however, questioned by the Rn concentrations at background. In PW2, the Rn concentrations were slightly above background and the temperature minima with respect to those of SW2 were slightly dampened. If these observations are significant, this well would also have hyporheic ground water. This is, however, not (yet) convincing. The results from chemical analyses showed a water composition in the PWs that was somewhat different from that of the SWs. As the RWT test, the test augmentation and the full augmentation will all be in the dry season, clogging effects might become of higher importance than what was found between April and July, 2006. Mixing with hyporheic ground water could increase and thus mixed residence times could be higher.

Do the GWs have creek-borne ground water ?

Probably ground water is not flowing to the drilled wells from the experimental site, to a significant extent. Well GW1 has a high hydraulic conductivity. However, the water temperature does not vary much over time, and the chemical analysis revealed a composition of this well that was different from that of the creek. There is no indication of water from the creek, although Rn in April indicated somewhat younger ground water. Well GW2a has a low hydraulic conductivity (fine-grained sediments), and the water chemistry is also different from that of the creek. Rn measurements yielded older ground water (>15 days). These facts do not point to a mixture with water from the creek. The well has highly variable water temperatures, which could indicate a fraction of young ground water, but probably not an admixture of creek water. Well GW2c has an intermediate hydraulic conductivity. The composition of this ground water is more similar to that of USC than that of the other two drilled wells. Furthermore, Rn in April indicated somewhat younger ground water. If there is downwelling to well GW2a, the residence times of the hyporheic ground water would probably be higher than 15 days. A temperature time series of this well could better assess a possible influence of creek water.

Acknowledgment

Thanks to Eawag (especially Ueli Bundi, Urs von Gunten, Rolf (RoKi) Kipfer) for making this sabbatical visit come true. At SU, I thank Prof. Martin Reinhard for hosting and giving the opportunity to contribute to the exciting project, and Megan Plumlee and Chris Gurr, without whom the project would not have taken off this spring, for their interest in my work. At SCVWD, I thank Alice Ringer for the technical organization of the instrumentation and exploration, and Alice, Henry Barrientos and the field geologist, Randy Behrens, for help during field work and for interesting technical discussions. I acknowledge valuable information from discussions on temperature time series, with Ken Bencala and Dave Stonestrom, USGS Menlo Park, and with Andy Fisher, UCSC.

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Figure Caption

Figure 1: Plan view of the Stanford University / Santa Clara Valley Water District Upper Silver Creek (USC) experimental site: Sampling positions, GW, drilled and PW pushed wells; Arrow, discharge point for recycled water at Yerba Buena Pump Station. Note purple (dark part) of line of USC at western end of figure: concrete-lined bed. North is up.

Figure 2: Generic hydrogeological cross section along Silver Creek Rd, from Yerba Buena Pump Station to Capitol Expwy. Note vertical exaggeration, factor 10. Information of Singleton Landfill, projected.

Figure 3: Hydrogeological cross section along Upper Silver Creek (USC; well logs: courtesy: SCVWD). Note vertical exaggeration, factor 25; vertical axis, *m* a.m.s.l.; dotted line, assumed elevation of USC; dash-dotted line, water table on April 14 and 20, respectively. Vertical lines adjacent to geological log: solid, full section, and dashed, screened section of well. Abbreviations refer to Unified Soil Classification System (USCS) http://www.dlwc.nsw.gov.au/care/soil/soil_pubs/soil_tests/pdfs/usc.pdf

Figure 4: Water temperature time series, May 13 – 23, 2006 (1 day = 144 units; Vertical axis is equivalent to 54 – 72 °F)

Figure 5: Water temperature time series, May 20/21, 2006 (1 day = 144 units; Vertical axis is equivalent to 60 – 65 °F)

Figure 6: Water temperature time series, May 13 – July 4, 2006 (1 day = 144 units). Note spikes in wells GW1 and GW2a = water sampling. For the series of PW1 and PW2 between July 4 and 13, 2006, see Table 3. (Vertical axis is equivalent to 54 – 75 °F: Upper end of vertical axis, 75 °F, is maximum temperature for warm-water fishery)

Figure 7: Water temperature time series, June 20 – July 4, 2006 (1 day = 144 units; Vertical axis is equivalent to 60 – 73 °F)

Figure 8: Piper diagram of major ion composition of water samples, from August 30, 2005 (courtesy: SCVWD)

Figure 9: Ternary plot of major cationic composition of water samples, from May 2 - 4, 2006. A, RW; B, **SW1**, **SW2**, and SW3; C, PW1; D, PW2; E, GW1; F, GW2a; G, GW2c; H, SW4-SW6; J, GW3.

List of Appendices

Table 1: Technical information about wells, drilled April 18 – 25, 2006: borehole diameter: 7” (0.178 *m*); well tubing inner diameter: 2” (0.05 *m*); screen size: 0.02” (0.5 *mm*; openings make up < 5 per cent of screened section of tube)

Well #	Well location	Well depth	Depth of screened section	Screen length	Hydraulic conductivity
	GPS Coo.: *Lat (N)/Long (W)*	*m*	*m*	*m*	*m/day* $(gal/ft^{2}\cdot d)$
GW1	37’17’51.767N/121’47’45.205W	7.8	3.0-7.6	4.6	$2\cdot10^{2}$ $(5\cdot10^{3})$
GW2a	37’17’53.020N/121’47’59.467W	4.9	1.8-4.9	3.1	$2\cdot10^{0}$ $(5\cdot10^{1})$
GW2c	37’17’54.055N/121’47’57.168W	6.2	2.7-5.8	3.1	$2\cdot10^{1}$ 1) $(5\cdot10^{2})$

1), n = 3 tests; $\mu_{\ln K}$=3, $\sigma_{\ln K}$=0.53

Table 2: Depth to water table of wells of Table 1, *m* (feet)

Date	GW1	GW2a	GW2c	GW3
4/20/06	1.5 (5)	3.0 (10) 1)	3.7 (12) 1)	-
5/11/06	3.0 (9.9)	3.27 (10.73)	2.51 (8.22)	-
5/23/06	1.91 (6.27)	3.28 (10.76)	3.38 (11.09)	-
7/13/06	2.11 (7.0)	3.66 (12.00)	2.81 (9.22)	-

1) values from driller’s logs: possible transient state due to skin effect following drilling

Table 3: Duration of HOBO® temperature loggers' time series

position	installation	retrieval, 05/24/06	retrieval, 07/04/06	retrieval, 07/14/06	retrieval, 07/20/06
SW1 2)	5/11/06	O.K.	O.K.	O.K.	O.K.
SW2 2)	5/12/06	O.K.	O.K.	O.K. 1)	O.K.
PW1	5/11/06	O.K.	O.K.	lost, reinstalled	O.K.
PW2	5/12/06	O.K.	O.K.	lost, reinstalled	O.K.
GW1	5/11/06	O.K.	O.K.	O.K.	O.K.
GW2a	5/12/06	O.K.	O.K.	O.K.	O.K.
GW2c	5/12/06	not launched	not launched	not launched	launched

1) additional logger "SW0" installed in period 7/4-14

2) note that the position of the logger is not identical with the sampling position for water chemistry

Table 4: Average mass concentrations and standard deviations (n=3) of major ions and other information on water chemistry information of USC at **SW1**, and RW, sampling dates: July 19, August 30, and October 3, 2005

Compound	units	RW	**SW1** 1)
DOC	mg/L	6.6±1.1	4.4±0.9
Ca^{2+}	mg/L	52±2.8	39±5.1
Mg^{2+}	mg/L	32±1.8	92.±1.5
Na^{+}	mg/L	146±6.1	99±5.7
K^{+}	mg/L	15.9±1.8	4.5±3.3
HCO_3^-	mg/L	176±6.2	359±21
SO_4^{2-}	mg/L	111±7.5	83±1.6
Cl^-	mg/L	184±13	154±23
NO_3^--N	mg/L	8.3±1.8	4.4±0.9
pH		7.3±0.26	8.4±0.06
EC	µS/cm	1223±67	1260±26

1) note that the position of the sampling position for water chemistry is not identical with the position of the temperature logger

Table 5: Relative equivalent activity1) (units: meq-%) of major ions, sampling date: May 2-4, 2006, used for the Piper diagrams, Figures 8 and 9

Compound	RW	**SW1**2)	**SW2**2)	SW3	SW4	SW5	SW6	PW1	PW2	GW1	GW2a	GW2c	GW3
Ca^{2+}	0.23	0.12	0.13	0.12	0.32	0.34	0.36	0.14	0.17	0.12	0.11	0.11	0.41
Mg^{2+}	0.23	0.60	0.57	0.60	0.45	0.43	0.40	0.65	0.60	0.52	0.55	0.63	0.38
$Na^{+}+K^{+}$	0.55	0.28	0.27	0.28	0.24	0.24	0.23	0.21	0.24	0.37	0.33	0.26	0.21
HCO_3^-	0.33	0.66	0.66	0.62	0.70	0.69	0.70	0.66	0.66	0.61	0.65	0.63	0.62
$SO_4^{2-}+NO_3^-$	0.20	0.07	0.07	0.08	0.13	0.13	0.15	0.08	0.08	0.08	0.06	0.07	0.13
Cl^-	0.47	0.26	0.28	0.30	0.17	0.18	0.16	0.26	0.26	0.31	0.29	0.30	0.25
Ca/Mg	1.0	0.20	0.23	0.20	0.71	0.79	0.90	0.22	0.17	0.23	0.20	0.17	1.1
Ca/Na+K	0.42	0.43	0.48	0.43	1.33	1.42	1.57	0.67	0.71	0.32	0.33	0.42	1.95

1), activity, molar concentration x individual activity coefficient at ionic strength of 0.01-0.02

2), note that the position of the sampling position for water chemistry is not identical with the position of the temperature logger

Table 6: Results from radon sampling

Sampling ID	Date[1)]	Rn-Conc.	σ[2)]
		[*Bq/L*][3)]	
RW	1	0.0	-
USC	1	0.12	0.08
USC	1	0.17	0.01
USC	2	0.07	0.08
PW1	1	0.25	0.21
PW1	2	0.28	0.25
PW2	1	0.61	0.38
PW2	1	0.76	0.34
PW2	2	1.1	0.30
GW1	1	10.4	1.4
GW1 4)	2	7.6	0.8
GW1 4)	2	11	0.9
GW1 4)	2	12	2.4
GW2a	1	13	2.2
GW2a	1	17	1.7
GW2a	2	10.4	1.6
GW2a	2	11	1.5
GW2c	1	10.1	1.7
GW2c	1	8.9	1.6
GW2c 4)	2	12	1.3
GW2c 4)	2	13	2.6
GW2c 4)	2	10.8	1.4
GW3 4)	1	7.8	0.2
GW3 4)	1	10.7	1.0
GW3 4)	1	11.4	1.0

Grey hue: highest concentration of sampling date, assumed steady state

1) Dates: 1, May 2-4, 2006; 2, May 24/25, 2006

2) standard deviation of n=4 individual counts (yielding instrument error)

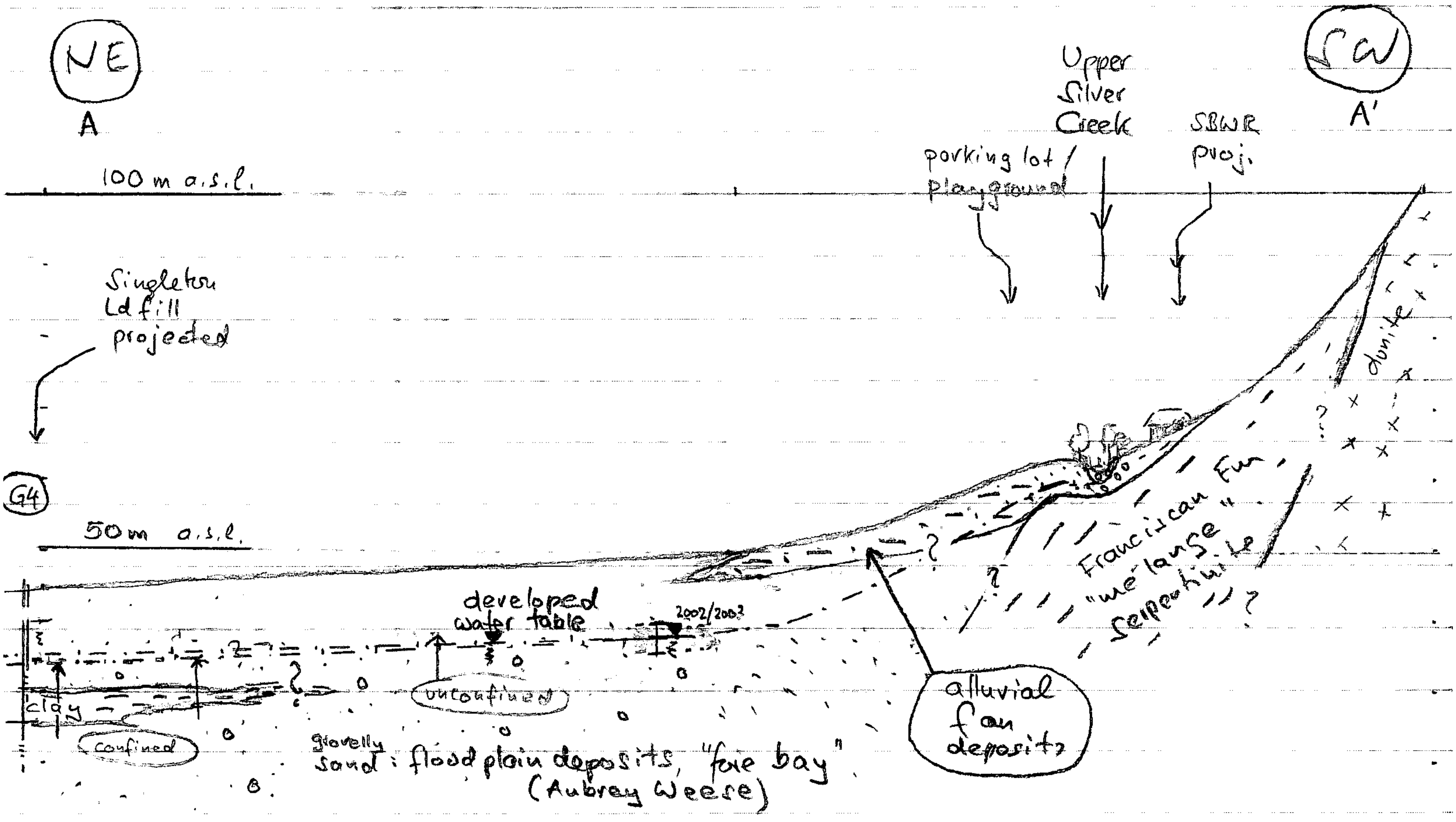
3) SI-units: *Bq/m*^{3}*,* number of decays per second and *m*^{3} of fluid; US-units: 1 *Bq/L* = 27 *pCi/L* <-> 1 *pCi/L* = 0.037 *Bq/L*;

4) n=3, GW1: 10±2.3; GW2c: 12±1.1; GW3: 10.0±1.9.

Upper Silver Creek (USC) SCVWD/SU Site

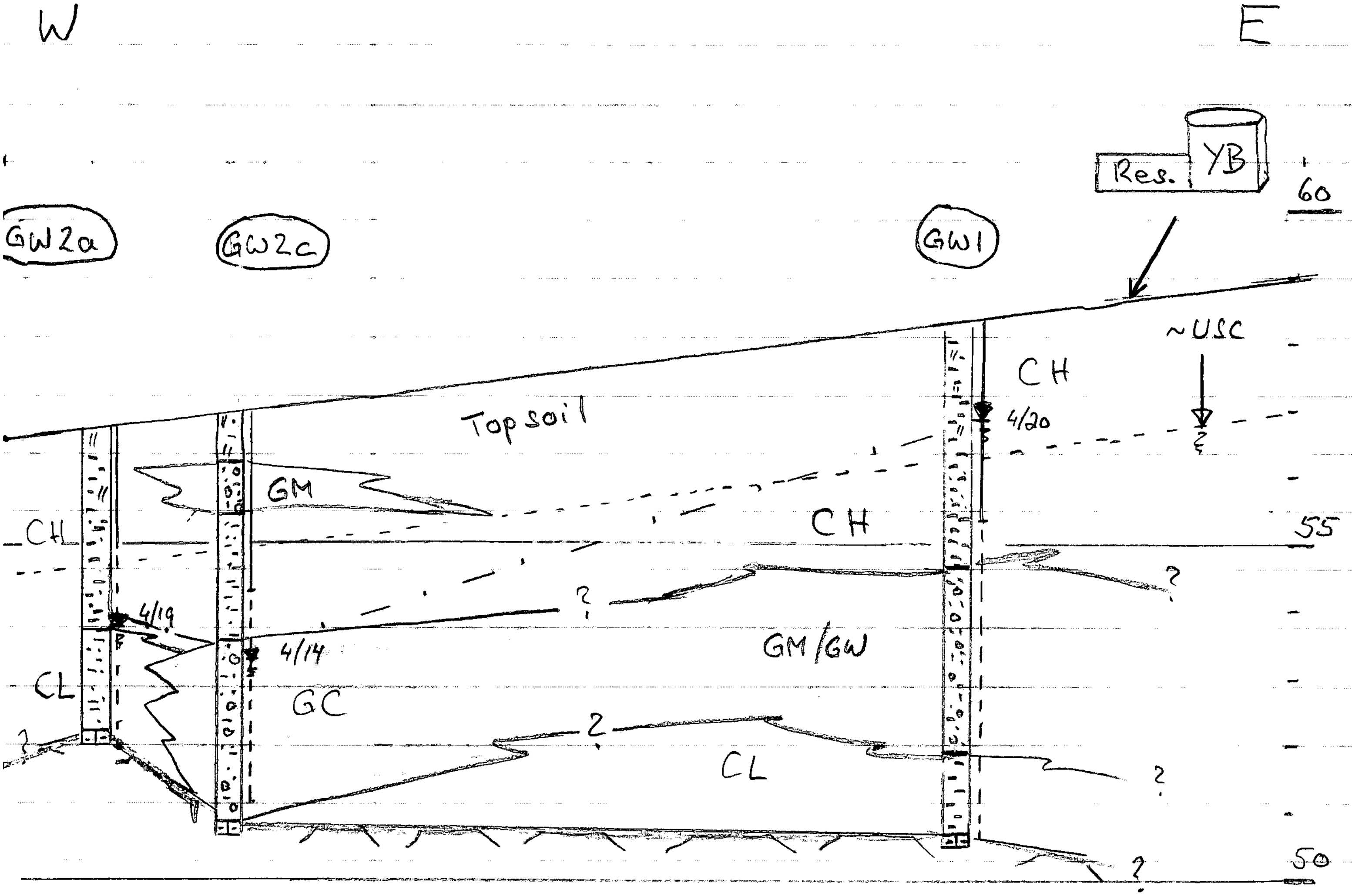
Generic hydrogeological cross-section along Silver Creek Rd, from SBWR to Capitol Expwy

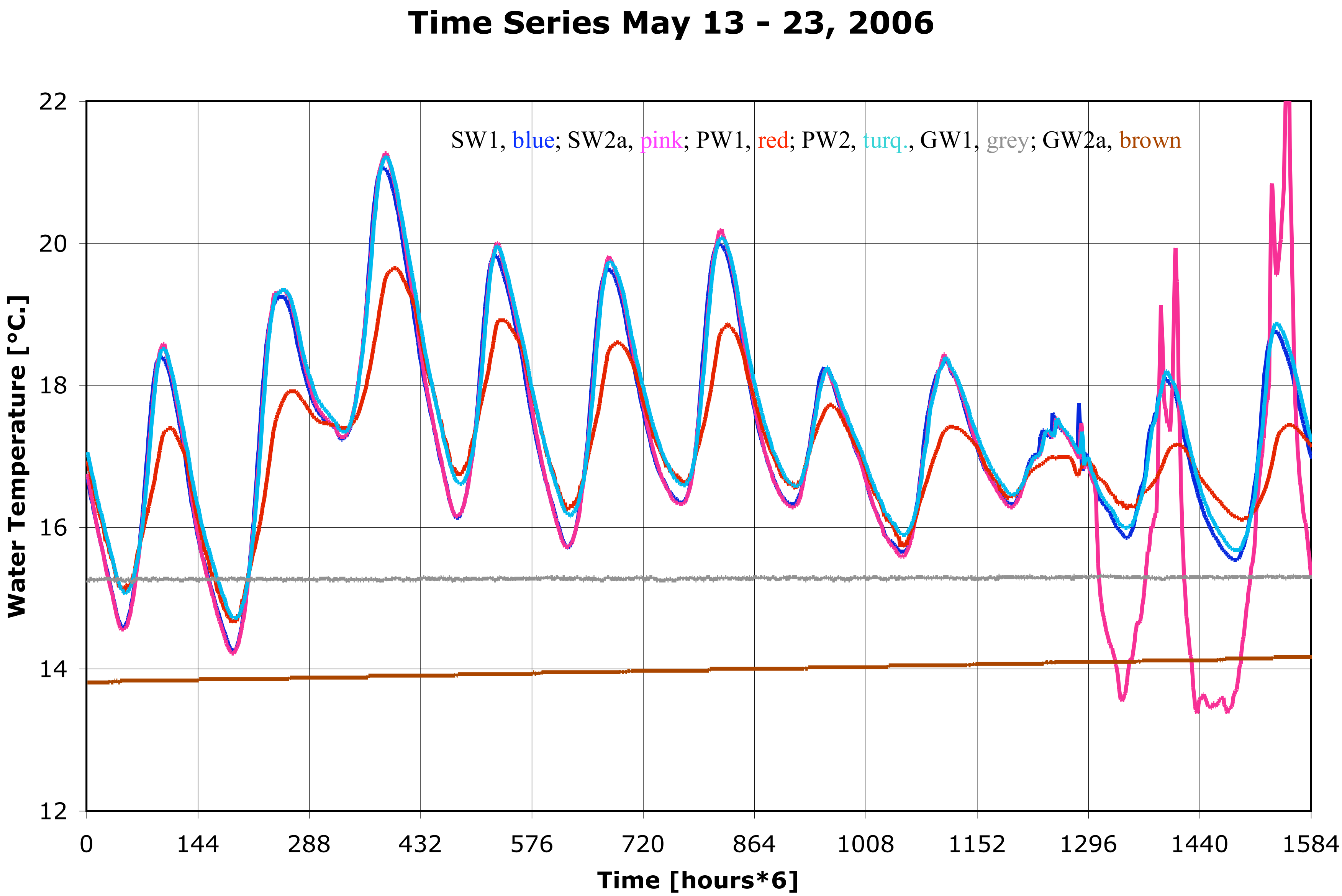
Scale 1:10'000/1000

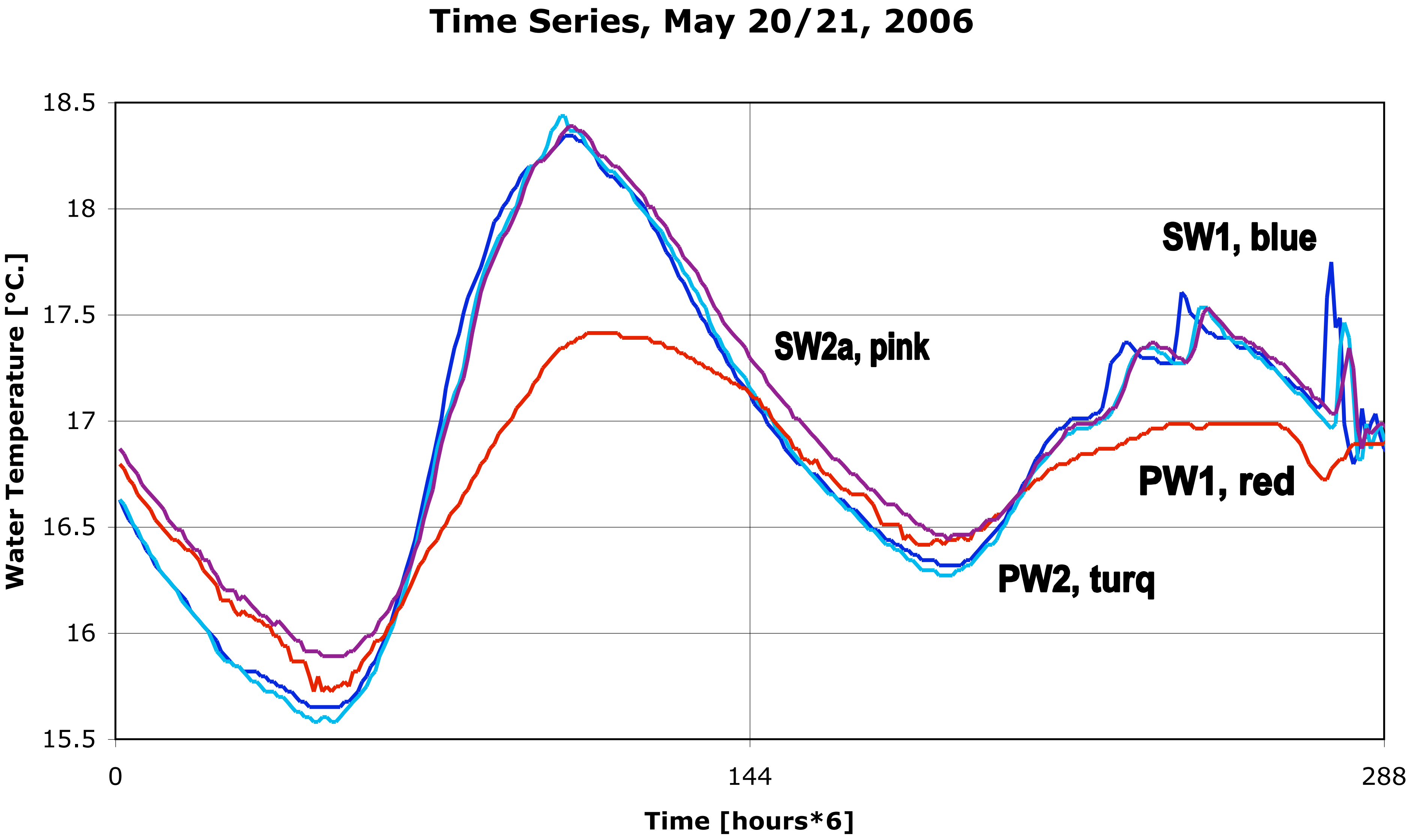


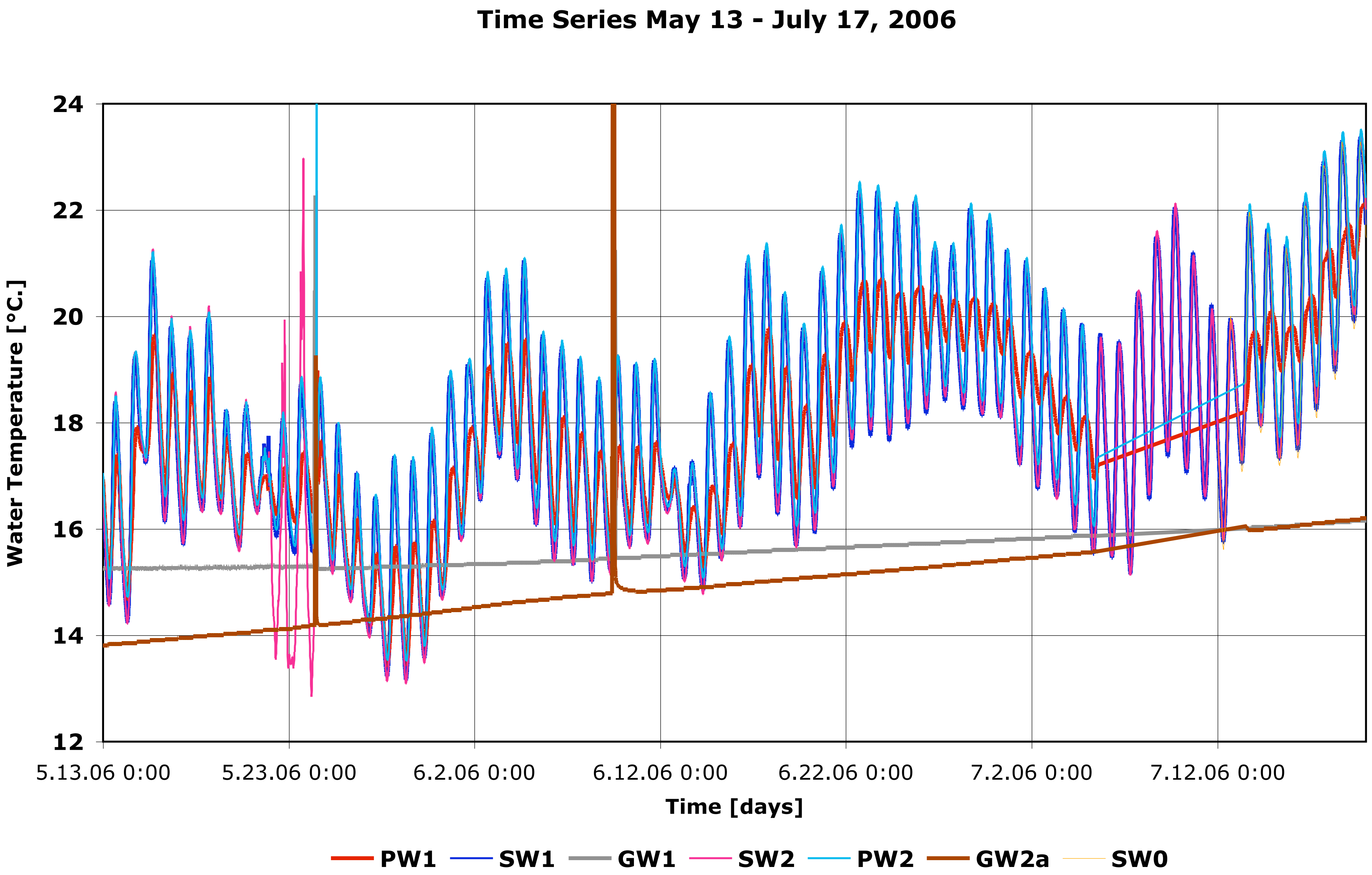
Hydrogeological cross section along Upper Silver Creek (USC)

1: 2500 : 100

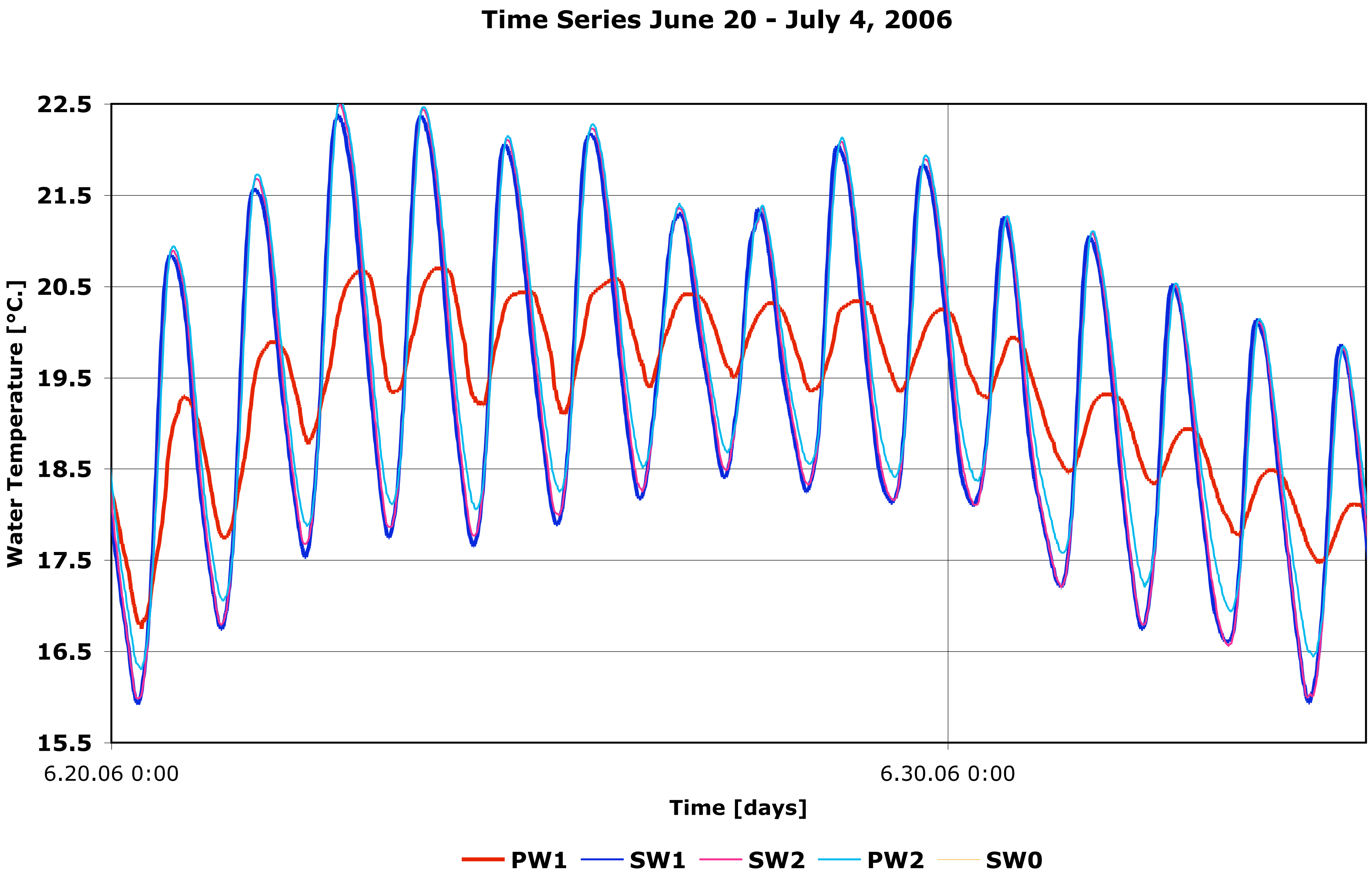



Time Series May 13 - 23, 2006
SW1, blue; SW2a, pink; PW1, red; PW2, turq., GW1, grey; GW2a, brown
Water Temperature [°C.]
22
20
18
16
14
12
0
144
288
432
576
720
864
1008
1152
1296
1440
1584
Time [hours*6]


Time Series, May 20/21, 2006
Water Temperature [°C.]
18.5
18
17.5
17
16.5
16
15.5
0
144
288
Time [hours*6]
SW1, blue
SW2a, pink
PW1, red
PW2, turq

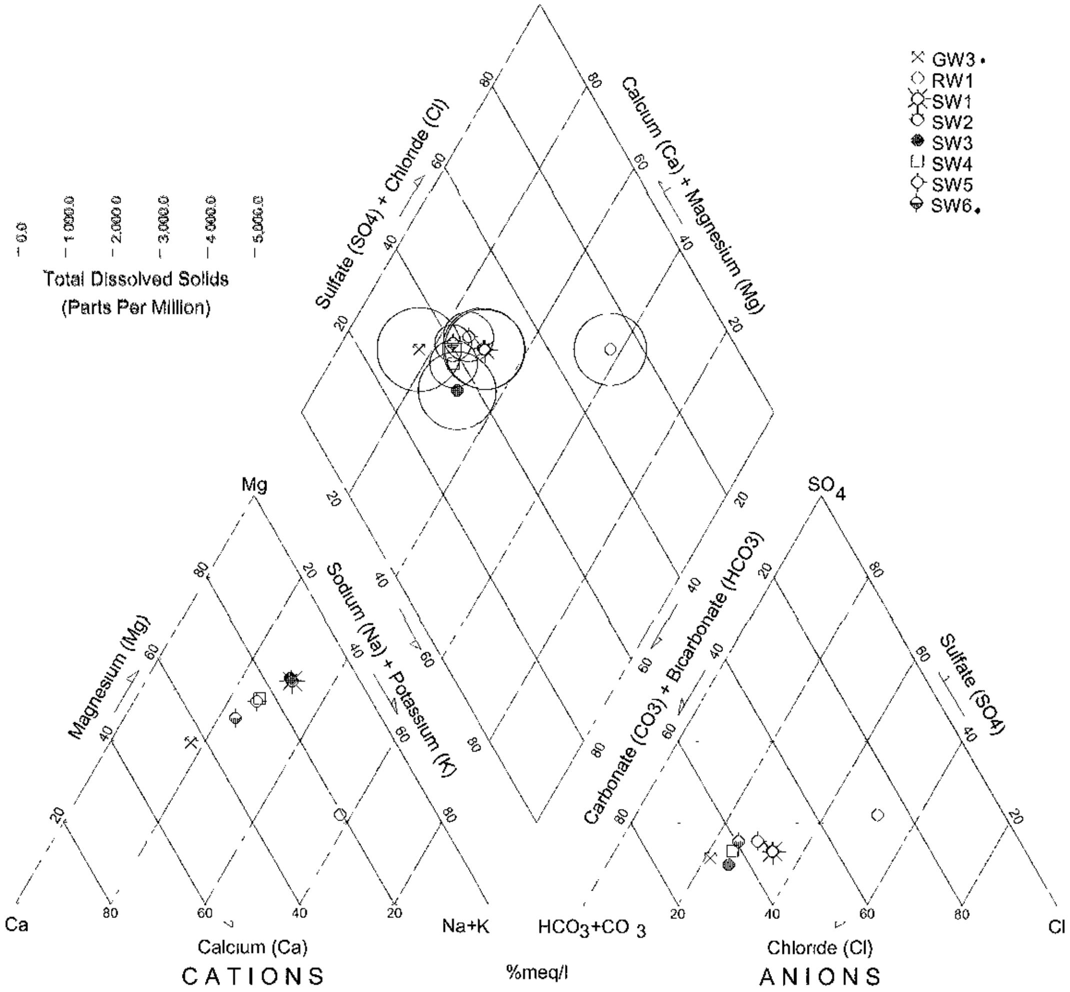


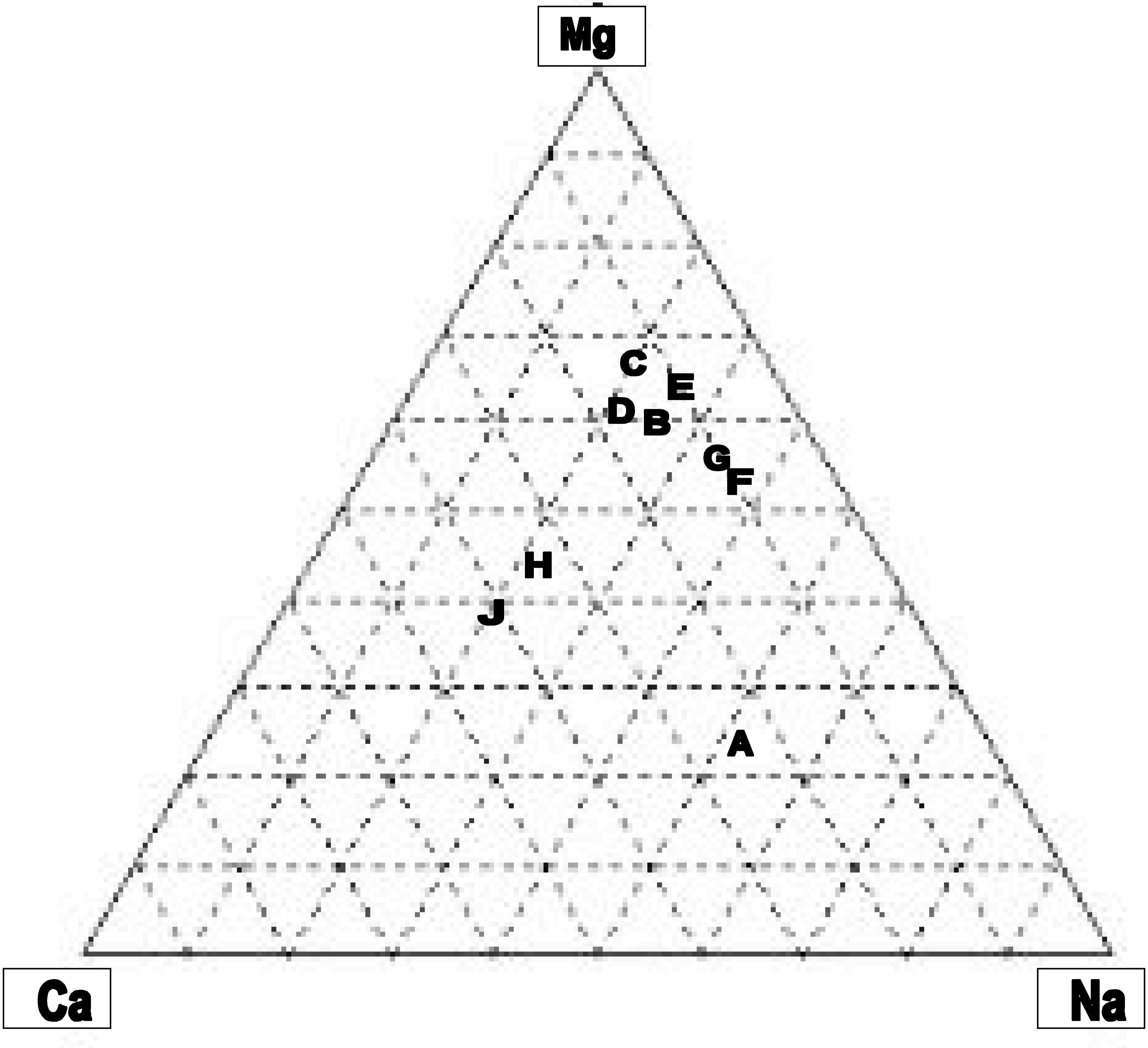
Time Series May 13 - July 17, 2006


Time Series June 20 - July 4, 2006
Water Temperature [°C.]
22.5
21.5
20.5
19.5
18.5
17.5
16.5
15.5
6.20.06 0:00
6.30.06 0:00
Time [days]
PW1
SW1
SW2
PW2
SW0

Piper Diagram

Stream Augmentation Project (Aug 05 Samples)




Mg
Ca
Na
C
E
D
B
G
F
H
J
A

Appendix 1:
Goals for scientific visit at Stanford University,
March – July, 2006

Goal 1: Before end of April

- **boreholes drilled**, (minimum) optimum number and type of wells:
    - (1) 2 shallow drilled wells
    - (1) 2 pushed wells
    - 1 deep drilled well
- wells instrumented:
    - short screened sections
    - (temperature loggers) T – transducers inserted
- wells developed.

Goal reached

Goal 2: before May 15
Slug or pumping tests in the new wells:
Q, discharge rate; ΔH, drawdown, K, hydraulic conductivity
Goal reached

Goal 3: before May 15
Analyzing the general water composition:
- ion balance (Ca, Mg, Na, K; Alk, Cl, NO3, SO4; EC, DOC),
- pH/Eh conditions (incl. O_2, Fe, Mn)

Goal reached (Eh lacking)

Goal 4: before June 15
Radon study in wells, and comparison with other data
Goal partly reached: comparison is yet lacking, due to lacking data.

Goal 4: before May 15
Salt-dilution experiment
Goal not reached, however, Br^- will be added in the RWT experiment

Goal 5: Before June 1
RW Tracer Experiment
(pilot) and full-scale injections, according to SAR Experience:
Goal not reached: postponed to August 2006 (result of meeting with SCVWD, July, 12, 2006)

Appendix 2:

Assessing flow rate of USC and base-flow recession

Knowledge of the flow rate in Upper Silver Creek (USC) is needed for i) temperature management of USC, ii) establishing mixing rates between tracers or RW and the USC water, and iii) establishing compound mass balances. SCVWD has a stream gauge at USC. The stage can be read at the following website:

1. Upper Silver Creek @ YerbaBuena Rd (Radar) (SF92-Stage)
   Info: gage height, no discharge rate; table, real time, 24 hours back;
   http://alert.valleywater.org/gagestrm.html.

Only if a good relationship is established between discharge rate and gage (Q vs gage), the continuous monitoring of gage at USC will be sufficient for the augmentation project.

Further creek gaging stations are available at the same web site
(http://alert.valleywater.org/gagestrm.html):

2. Coyote Creek @ Edenvale (SF58)
   http://waterdata.usgs.gov/ca/nwis/nwisman?site_no=11171500
   http://www.valleywater.org/wtrsuply/streamflow/sf58.htm
   Info: gage height and discharge rate; table and graph, real time, 24 hours back, and yearly statistics;
3. Coyote Creek @ AB HWY 237 A MILPITAS CA (USGS 11172175)
   http://waterdata.usgs.gov/ca/nwis/uv?11172175
   Info: gage height and discharge rate; table and graph, real time, 31 days back, and yearly statistics.

On April 16, 2006, the discharge rate at CC Milpitas was at about 12.5 m^3/s (440 cfs). On the same date, the discharge rate at CC Edenvale was at about 5.7 m^3/s (200 *cfs)*. The confluence of USC with CC is between these two stations. The discharge rates of CC at Milpitas between March 5 and April 17, 2006, are shown in Figure A2/1.

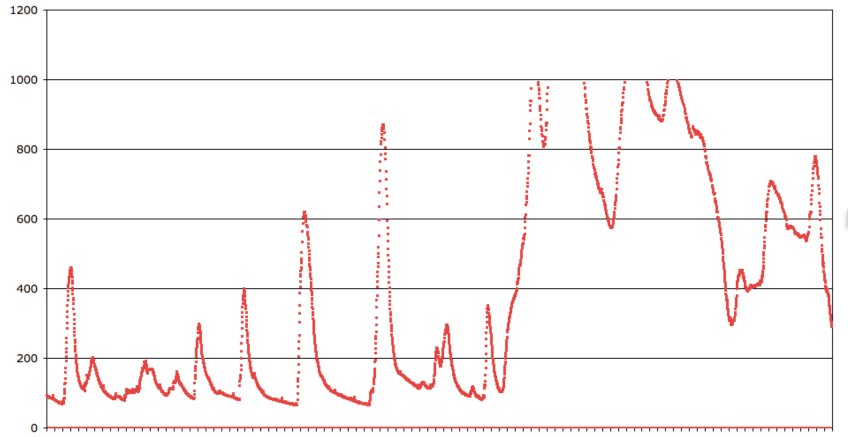


Figure A2/1: Streamflow in Coyote Creek at Milpitas, March 5 – April 17, 2006, in *cfs*. Horizontal axis: 44 days subdivided into 100 units; 1 unit, 0.44 days

For the planning of the RWT tracer test, we need to know various geometry and hydraulic parameters of the flow system of USC. To this end, the following hydraulic parameters were assessed rom Fischer et al. (1979; chap 5.1./5.2.):

depth of channel	d	~ 0.2 *m*	(0.7 *ft*);
slope of channel	S	~0.001 ;	
bottom shear velocity	$u^* = (gdS)^{1/2}$	~0.04 *m/sec*	(0.13 *ft/sec*);
average flow velocity	$\bar{u}$	~0.3 *m*/sec	(1.0 *ft/sec*);
channel width	W	~0.7 *m*	(2 *ft*);
vertical mixing coefficient, averaged over depth	$\overline{E_v} = 0.067\, du^*$	~0.001 *m²/sec*	(0.01 *ft²/sec*);
discharge rate	$Q = \bar{u}dW$	~ 0.04 *m³/sec*	(11 *gal/sec*).

For the RWT tracer experiment, we furthermore need to know a tracer injection of unit concentration and unit mass, $\dot{M}$, dilutes in the USC flow system. A maximum concentration, C_{max}, is reached at the assumed distance of well PW2 from the injection point, x = 300 *m* (1000 *ft*), according to the following relationship (Equation A2/1, taken from Fischer et al., 1979):

$$C_{max} \quad \dot{M}/\bar{u}d \cdot (4\pi\overline{E_T}\, x/\bar{u})^{-1/2} = 0.04 \text{ unit C} \qquad (A2/1).$$

The evolution of the recession base flow during the summer season (May – November), in rivers of the mediterranean climate type, which is an important parameter, can be gathered from the record of the daily mean discharge rate values of CC Edenvale, 1999 - 2005. The same data of CC Milpitas show approximately constant minimal flow rates during summer, which is probably not natural (see Figure A1/2; note log scale of vertical axis). From this figure, a recession flow constant, α, can be defined as (Equation A2/2; from Equation 6.15 in Freeze & Cherry, 1979):

$$\alpha = (\ln Q_1 - \ln Q_2)/t \qquad (A2/2),$$

where Q_1, Q_2, discharge rates at beginning (5/19) and at end (11/18) of investigation period, t. A recession-flow constant of $\alpha = 0.0054\ d^{-1}$ can be found for CC at Edenvale. The inverse of α is interpreted as the mean residence time of the creek water in the catchment, $\tau = 1/\alpha$, which is at 185 *d*. The total volume of water in the catchment, $M_{1,2} = Q_{1,2}/\alpha$, which is estimated to be at about 39 and 15 m^3 (4000 – 10'000 *gal*), for Q_1 and Q_2, respectively. Assuming that the value of α of USC is the same, given smaller discharge rates, which is probably not the case, the estimated flow rate in May of 0.04 m^3/sec relates to a minimum base flow rate at the end of the recession period of about 0.01 m^3/sec (3 *gal/sec*). This is 3 – 6 times more than what has been reported by

SCVWD. The value does include neither evaporation loss to the atmosphere nor loss due to downwelling to the subsurface.

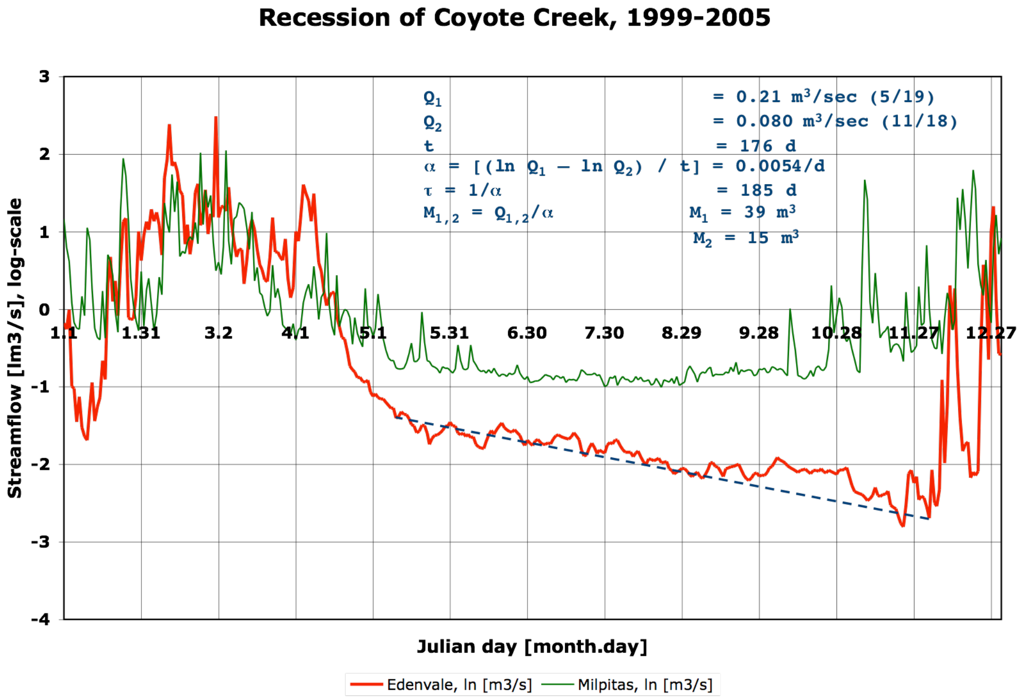


Figure A2/2: Base flow of Coyote Creek at Edenvale and Milpitas, from mean daily values, 1999 – 2005; dashed line, recession flow constant, α. Note log scale at vertical axis.

Appendix 3: Assessing hydraulic conductivity from Hvorslev-type slug tests

Hvorslev's experiment consists in the analysis of the effects of the sudden injection of a slug of a known volume of water into a piezometer well. The depth to the water table in this well is measured in a time series, as the water will flow out of the well with time. The basic idea is that the hydraulic conductivity (HC) of a formation around a well is lower the more time is required for complete head equalization, T_0. In Hvorslev's theory, the following relationship holds (Equation A3/1, Freeze & Cherry, 1979; p. 340/341):

$$T_0 = (r^2\pi) / (F \cdot K) \qquad \text{(A3/1),}$$

where r, well radius, F, piezometer shape and dimension factor, and K, HC. Assumptions for this relationship to hold are that the aquifer is homogeneous, isotropic, incompressible, and of infinite extent. The analysis of the water table receding during an experiment yields the constant relationship of Equation 2/A3:

$$(H-h) / (H-H_0) = e^{-t/T_0} = 0.37 \qquad \text{(A3/2),}$$

where H - h, water-table difference as a function of time, and $H_0 = h$ at the beginning of the experiment (in our case: well full to the well top of well casing). In the theory, the flow rate (Q) should be constant, which is, of course, not the case. However,

$T_0 = V/Q_0$, where V, volume of water added, and Q_0, inflow rate at well top of well casing. The relationship holds approximately, if a ratio L/R is >8, where L, screened section of well, and R, radius of bore hole. Under these conditions, the HC can be assessed from the theory to be (Equation A3/3):

$$K = (r^2 \cdot \ln(L/R) / (2L \cdot T_0) \qquad \text{(A3/3).}$$

The time series of the decline of the water table, after injection of water slugs are shown in Figure A3/1. In this figure, T_0 is the time at which $(H-h)/H-H_0) = 0.37$.

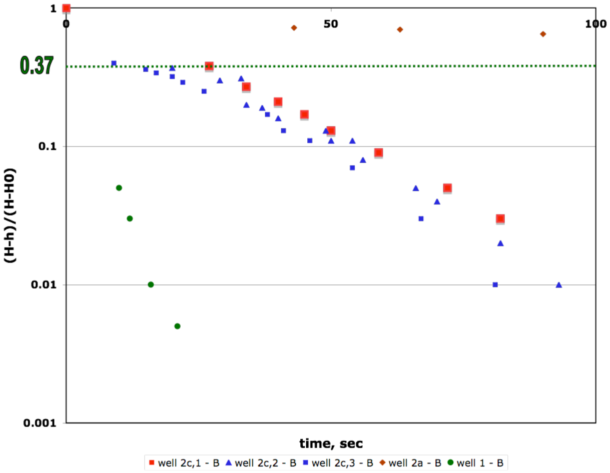


Fig. A3/1: Time-series measurements of water table in groundwater wells, after slug injection of water to top of well. Note horizontal axis located on top of figure.

Appendix 4:
Major ion composition of waters of USC experimental site

The molar Ca/Mg ratio of USC at SW1 is at 0.2 - 0.4 (ionic strength, 0.01 – 0.02; total dissolved solids, about 20 *meq/L*). In absence of primary calcite, this refers to the dissolution of dolomite and the selective weathering of mobile Mg in Mg-containing and sparingly-soluble minerals from the serpentinite rocks (hydrated magnesium(-iron)-silicates; e.g., chrysotile-asbestos, lizardite, and antigorite; Barnes & O'Neill, 1969; http://www.consrv.ca.gov/CGS/information/publications/cgs_notes/note_14/note_14.pdf). The main well-soluble normative solid magnesium phases for the resulting water can be derived from Figure A4/1: dolomite $\{CaMg(CO_3)_2\}$, magnesite or nesquehonite, $\{MgCO_3\}$ or $\{[Mg(HCO_3)(OH)\cdot 2H_2O\}$, and epsomite or kieserite, $\{MgSO_4\cdot 7H_2O\}$ or $\{MgSO_4\cdot H_2O\}$, and besides the Mg phases rock salt, $\{NaCl\}$. Buffering of the ground waters with CO_2 and dolomite results in a pH between 7 and 8, and >90 per cent of dissolved inorganic carbon (DIC) is HCO_3^-. Ground waters from these rocks are often reported to have low Eh, which was not measured here.

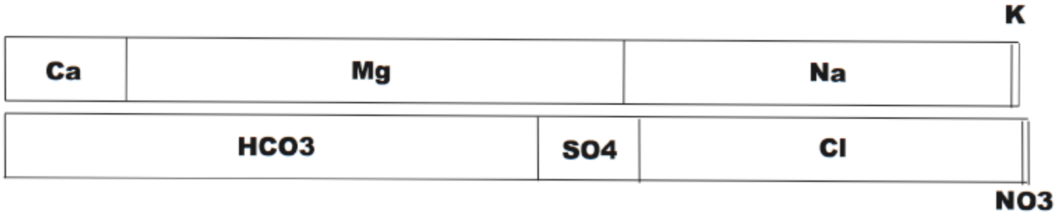


Figure A4/1: Bar diagram showing relative activities of an average of the water samples of **SW1** of Table 3 (cations: 10.1 *meq/L*; anions: 10.3 *meq/L*)

Appendix 5: Radon as a tracer for groundwater age

Radon (Rn) is a noble gas, which occurs naturally in fluid phases of the subsurface (soil gas, ground water) in small activity concentrations (here denoted as „concentrations“; SI-units: Bq/m^3, number of decays per second and m^3 of fluid; US-units: 1 Bq/L = 27 pCi/L <-> 1 pCi/L = 0.037 Bq/L;). The isotope ^{222}Rn has a half life of $\tau_{1/2}$ = 3.8 days. The radioactive mother of Rn is radium (the radioactive isotope ^{226}Ra), which is enriched on surfaces of rocks, especially poorly sorted granular material. Both radionuclides belong to the natural radioactive decay series of ^{238}U. This decay series leads to stable lead (^{210}Pb) in 10 steps. After decay of Ra, Rn enters fluid phases in that it „emanates“ from the surfaces of rock particles to the surrounding soil gas and/or ground water by recoil and diffusion processes.

Radon is measured with the DURRIDGE Rad7 instrument. This instrument consists on a semi-conductor detector in a void chamber, and a pump. The detector is shaped as an open hemisphere. On the surface of the hemisphere, a strong negative electric field is generated. Air is routed with the pump to flow above the negatively charged semiconductor chamber. A measurement unit, which is integrated in the instrument, traces the decay of ^{222}Rn. The instrument measures the Rn concentration, in that it counts the a activities of the positively charged daughter product, ^{218}Po (half life $\tau_{1/2}$ = 3.05 *min*), which are trapped from the air flow by the semi-conductor, and which impact on its surface (http://www.durridge.com). For the measurement of Rn in the water phase, the instrument is modified to „Rad7-H2O“. In this mode, Rn is purged out of the water phase of a sample bottle with a frit and transported to the instrument in a closed loop. The concentration is measured after ingrowth of the daughter nuclides.

In surface waters, Rn is outgassed to the atmosphere. At the downwelling of rivers, the hyporheic ground water becomes enriched in Rn. After 15 – 20 days (about 4 half lives of Rn), a steady-state Rn concentration establishes due to ingrowth and decay. In this short period, Rn can be used for dating very young hyporheic ground water. Rn-222 activity concentrations (here denoted as concentrations) are known to increase about exponentially with time in groundwater (Equation A5/1):

$$c(t) = c_{river} + (c_\infty - c_{river})\ [1 - \exp(\lambda t)] \qquad \text{(A5/1)},$$

in which c_{river} is the concentration in the river, λ is the radioactive decay constant ($\lambda_{Rn} = 0.183\ d^{-1}$), and c_∞ is the ^{222}Rn concentration reached within the aquifer, when ingrowth and decay of dissolved ^{222}Rn is at steady state. Equation (A5/1) can be used to estimate groundwater residence times under the following assumptions: i) on the scale of the investigations, Rn progeny (U, Th, Ra) is uniformly distributed in the aquifer; ii) the assumption of steady-state Rn concentrations is valid for the investigated groundwater flow path; iii) Rn losses due to outgassing into the unsaturated zone and atmosphere can be neglected; and iv) sorption of Rn on surfaces of aquifer materials is negligible. The value of c_∞ is specific for each aquifer as it depends on the amount of radium on the surface of the aquifer materials. Increasing radon concentrations along a flow path thus indicate an increasing radon groundwater age (Hoehn and von Gunten, 1989).

Appendix C

Plumlee, M.H., López-Mesas, M., Heidlberger, A., Ishida, K.P., Reinhard, M., 2008. *N*-Nitrosodimethylamine (NDMA) Removal by Reverse Osmosis and UV Treatment and Analysis via LC-MS/MS. Water Res 42, 347-355.

WATER RESEARCH 42 (2008) 347–355

Available at www.sciencedirect.com

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N-nitrosodimethylamine (NDMA) removal by reverse osmosis and UV treatment and analysis via LC–MS/MS

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ARTICLE INFO

Article history:
Received 30 January 2007
Received in revised form
27 June 2007
Accepted 18 July 2007
Available online 26 July 2007

Keywords:
Nitrosamines
NDMA
LC–MS/MS
Reverse osmosis
Advanced treatment

ABSTRACT

N-nitrosodimethylamine (NDMA) is a probable human carcinogen found in ng/l concentrations in chlorinated and chloraminated water. A method was developed for the determination of ng/l levels of NDMA using liquid chromatography–tandem mass spectrometry (LC–MS/MS) preceded by sample concentration via solid-phase extraction with activated charcoal. Recoveries were greater than 90% and allowed a method reporting limit as low as 2 ng/l. Using this method, the removal of NDMA was determined for the Interim Water Purification Facility (IWPF), an advanced wastewater treatment facility operated by the Orange County Water District (OCWD) in Southern California. The facility treats effluent from an activated sludge treatment plant with microfiltration (MF), reverse osmosis (RO), and an ultraviolet-hydrogen peroxide advanced oxidation process (UV-AOP). Six nitrosamines were surveyed: NDMA, *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-*n*-propylamine (NDPA), *N*-nitrosopiperidine (NPip), and *N*-nitrosopyrrolidine (NPyr). Only NDMA was detected and at all treatment steps in the IWPF, with influent concentrations ranging from 20 to 59 ng/l. Removals for RO and UV ranged from 24% to 56% and 43% to 66%, respectively. Overall, 69±7% of the original NDMA concentration was removed from the product water across the advanced treatment process and, in combination with blending, the final concentration did not exceed the California drinking water notification level of 10 ng/l. NDMA removal data are consistent with findings reviewed for other advanced treatment facilities and laboratory studies.

1. Introduction

N-nitrosodimethylamine (NDMA) is one of several *N*-nitrosamines classified as probable human carcinogens by the US Environmental Protection Agency (US EPA, 1993). NDMA received much attention as a potential drinking water contaminant after its 1998 detection in California drinking water wells (up to 3 μg/l) due to contamination from unsymmetrical dimethylhydrazine (UDMH)-based rocket fuel. Subsequent monitoring led to the discovery that NDMA was also a disinfection byproduct arising from the chlorination and chloramination of drinking water and wastewater (CA DHS, 2006). More potent than the trihalomethanes, NDMA concentrations of 20–100 ng/l typically result from the chlorination of wastewater effluent (Mitch et al., 2003). In 2002, the California Department of Health Services established a 10 ng/l

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doi:10.1016/j.watres.2007.07.022

notification level (action level) in drinking water (CA DHS, 2006).

The indirect reuse of highly treated municipal wastewater is being increasingly considered as an alternative water source for domestic and ecological applications. Consequently, the performance of secondary and advanced water treatment schemes with regard to their mitigation of potential contaminants like NDMA is an area of active research. In addition to NDMA, the EPA has listed five other nitrosamines on the Unregulated Contaminant Monitoring Rule 2 (UCMR 2) to be monitored from 2008 to 2010 (US EPA, 2006). These probable human carcinogens have been found in soil, air, plants, food, and water (Fine et al., 1977; US EPA, 2007).

A recent study found that secondary wastewater treatment achieves variable NDMA removals ranging from 0% to 75% (Sedlak et al., 2005); consequently, NDMA must be mitigated at the source or during advanced treatment. While reverse osmosis (RO) has been found to significantly remove salts, emerging contaminants (>99% for pharmaceuticals), and other compounds (Reinhard et al., 1986; Reinhard et al., 2003), the rejection of NDMA by RO is relatively low (Mitch et al., 2003), necessitating additional removal technologies such as UV treatment to meet regulatory limits. UV irradiation is the most commonly applied treatment for NDMA and has been used for drinking water, wastewater, and industrial effluents. However, it is estimated that the dose required for an order of magnitude reduction in NDMA is 10 times that for equivalent virus removal in a drinking water system, highlighting the expense of such an approach for adequate treatment (Mitch et al., 2003). While a variety of UV photolysis studies under different laboratory conditions show NDMA half-lives on the order of minutes (Ho et al., 1996; Stefan and Bolton, 2002; Sharpless and Linden, 2003), there are fewer reports for online UV treatment systems, in which other factors like path length, lamp choice, and light screening may play a role (Sharpless and Linden, 2003). In one such report from an Ohsweken drinking water plant in Ontario, Canada, NDMA was discovered in the water above the Ontario limit of 9 ng/l. Laboratory, pilot tests, and finally full-scale implementation of UV irradiation removed NDMA to below detectable levels (Jobb et al., 1994).

For the detection of NDMA in wastewater and drinking water, some existing methods are based on continuous liquid–liquid extraction followed by gas chromatography (Raksit and Johri, 2001; Mitch et al., 2003; Richardson, 2003). These methods are labor intensive, require large volumes of toxic solvents, and achieve low recoveries. Grebel et al. (2006) recently developed a solid-phase microextraction method for NDMA and other nitrosamines, which requires a conveniently short analysis time but does not achieve detection limits in the 1–10 ng/l range required for drinking water. While some methods utilizing solid-phase extraction (SPE) have achieved recoveries of only 30–60% (Mitch et al., 2003), other techniques show >80% recovery and generally rely on gas chromatography coupled to mass spectrometry (GC–MS) (Ontario Ministry of the Environment, 2003; Charrois et al., 2004) or tandem mass spectrometry (GC–MS/MS) (Munch and Bassett, 2004). Recently, Zhao et al. (2006) developed a method for nitrosamine analysis using liquid chromatography–tandem mass spectrometry (LC–MS/MS), also coupled to SPE for sample concentration.

The objectives of the present study were to assess NDMA removal efficiencies during microfiltration (MF), RO, and UV treatment at an advanced wastewater treatment facility, and to develop a simple SPE–LC–MS/MS technique for analysis of NDMA and other nitrosamines given in Table 1. The method combines the extraction efficiency of SPE with the convenience and selectivity of LC–MS/MS detection. The selectivity of the technique is due to the detection of multiple specific mass spectral fragmentations ("transitions") (Budde, 2001). Findings are compared to literature reports of both laboratory and treatment plant data in an effort to provide a useful summary of NDMA removal via advanced wastewater treatment processes, with particular emphasis on rejection data for RO.

2. Experimental

2.1. *Materials*

Chemicals, sources, and purities were as follows: methanol and acetonitrile, HPLC grade from Fisher Scientific (Fair Lawn, NJ, USA); acetone UltimAR from Mallinckrodt Chemicals (Phillipsburg, NJ, USA); neutralized activated charcoal from Sigma (St. Louis, MO, USA); NDMA, *N*-nitrosopiperidine (NPip), *N*-nitrosodiethylamine (NDEA), and *N*-nitrosodi-*n*-propylamine (NDPA) from Supelco (Bellefonte, PA, USA); *N*-nitrosomethylethylamine (NMEA) and *N*-nitrosodi-*n*-butylamine (NDBA) from Ultra Scientific (North Kingstown, RI, USA); *N*-nitrosopyrrolidine (NPyr) from Aldrich (St. Louis, MO, USA), and NDMA-d6 99.8% from CDN isotopes (Pointe-Claire, Canada). Glass fiber filters were obtained from Whatman (Florham Park, NJ, USA). Teflon 1/8″ tubing, weights, tube adaptors, and a 16-port vacuum manifold for performing SPE sample loading were purchased from Supelco. Extract-Clean SPE 8 ml cartridges, frits, and syringe adapters (for connecting SPE cartridges in-series) and the SPE vacuum manifold were purchased from Alltech (Deerfield, IL, USA). Strata Phenyl SPE cartridges were from Phenomenex (Torrance, CA, USA). Milli-Q water was generated using a Synergy 185 Millipore with Simpak2 purifying system (Billerica, MA, USA).

2.2. *Site description and sample collection*

Water samples were obtained from different stages throughout the IWPF (Fig. 1), also known as Interim Water Factory 21, a now-decommissioned advanced wastewater treatment plant operated by the OCWD in Southern California. This facility reclaimed effluent from the Orange County Sanitation District (OCSD) secondary sludge plant to potable standards for injection into a coastal aquifer as a hydraulic seawater barrier. Advanced treatment at the IWPF included the following: disinfection by chlorination, MF (Siemens), RO (Hydranautics ESPA2 composite polyamide membranes), and an ultraviolet-hydrogen peroxide advanced oxidation (UV-AOP; Trojan Technologies UVPhox) system of six reactors each equipped with 72 low-pressure, high-intensity UV

Table 1 – Multiple reaction monitoring (MRM) transitions, optimized operating parameters, and instrument detection limits for selected nitrosamines

Nitrosamine	Transitions (*m/z*)[a] (Primary) (Secondary)	Precursor ion	Product ions	DP (V)	CE (V)	CXP (V)	IDL (μg/l)
NDMA	75 > 43 75 > 58	75 $[M+H]^+$	43 $[M+H-NHOH]^+$ 58 $[M+H-OH]^+$	31	23	6	2
NDMA-d6	81 > 46 81 > 64	81 $[M+H]^+$	46 64	31	25	2	na
NMEA	89 > 61 89 > 43	89 $[M+H]^+$	61 43	26	17	2	2
NDEA	103 > 75 103 > 47	103 $[M+H]^+$	75 47	21	15	8	2
NDPA	131 > 89 131 > 43	131 $[M+H]^+$	89 43	16	15	8	2
NDBA	159 > 103 159 > 57	159 $[M+H]^+$	103 57	16	15	6	2
NPyr	101 > 55 101 > 83	101 $[M+H]^+$	55 83	21	23	10	6
NPip	115 > 69 115 > 41	115 $[M+H]^+$	69 41	21	21	8	25

DP = declustering potential (determines fragmentation); CE = collision energy (determines fragmentation); CXP = collision exit potential; IDL = instrument detection limit.

[a] Primary transition used for quantitation, secondary transition for confirmation.

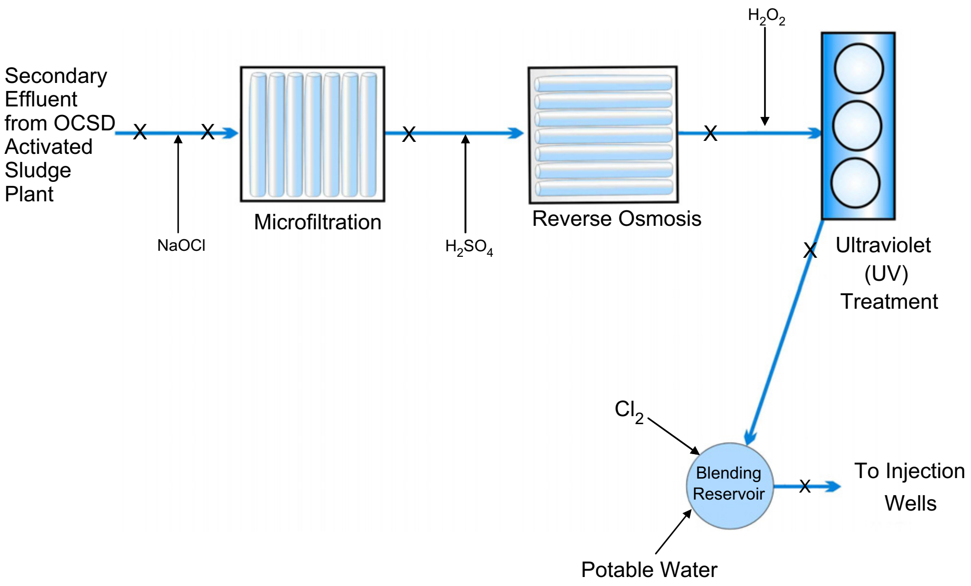

Fig. 1 – Process schematic of the Interim Water Purification Facility (IWPF), with sampling points indicated by “X”. OCSD = Orange County Sanitation District.

lamps. Though the system was dosed with sodium hypochlorite (NaOCl) prior to MF, chloramines were formed due to the high ammonia concentration. Operators maintained a total residual chlorine of 3–5 mg/l in the MF feed water (free chlorine, <0.1 mg/l). Hereafter, this disinfection step will be referred to as chloramination. Flux over the sampling period was 20.4 gfd (recovery, 89%) for MF and 12 gfd (recovery, 85%) for RO. The pH of the RO feed and permeate was measured at 7–8 over the sampling period. UV-AOP was operated at a flow rate of 5.1 MGD, a typical energy input of 0.4–0.5 kWh/kgal, and hydrogen peroxide was dosed at 3 mg/l with a contact time of ~53 s. Before well injection, the product water was blended with potable water (to increase product flow) and disinfected using chlorine gas.

Grab samples of the reclaimed water were taken at each of the locations indicated in Fig. 1 on May 24, June 14, and July 26, 2006. The samples (3–5 l per site) were collected in 1 l glass amber bottles (I-CHEM; Rockwood, TN, USA) and sodium thiosulfate (100 mg) was added to samples to quench chlorine. Samples were packed on ice and shipped to Stanford University, where they were filtered through 0.2 μm nylon membranes (Supelco), acidified to pH 2.3 using sulfuric acid (Sigma), and kept at 4 °C until analyzed using the SPE–LC/MS–MS method described.

2.3. *LC–MS/MS*

A liquid chromatograph from Shimadzu (LC-10AD VP) with a Shimadzu SIL-10AD VP autosampler (Columbia, MD, USA) connected to a triple quadrupole mass spectrometer (API3000) from Applied Biosystems (Foster City, CA, USA) was used for analysis of the nitrosamines given in Table 1. A volume of 50 μl of sample was injected at a flow rate of 0.15 ml/min onto a 50 mm × 2.1 mm Targa Sprite C18 column (5 μm pore size, Higgins Analytical, Mountain View, CA, USA) equipped with a C18 Guard Column (Higgins Analytical). The mass spectrometer was operated in multiple reaction-monitoring transition mode at an optimized voltage for each transition in positive-ion mode. To select the MS/MS parameters, standards of NDMA, NDMA-d6, and the other tested nitrosamines were injected in continuous-flow mode and the declustering potential, collision energy, and collision cell exit potential were optimized for each transition. The nebulizer, curtain, and collision gas flows were 6, 6, and 5 au, respectively, and the ion spray voltage was operated at 5000 V with a source temperature of 375 °C. A dwell time of 150 ms was used per ion pair monitored. The nebulizer and drier gas were generated by a Parker-Balston Zero Air Generator (Haverhill, MA, USA) and nitrogen for the curtain and collision gas was generated by a Parker-Balston N_2-4000 Generator. The deuterated compound NDMA-d6 (110 μg/l) was added as an internal standard to sample extracts and nitrosamine standards at a ratio of 0.3 internal standard volume/sample volume.

Deuterated internal standards that elute with the analyte of interest allow a correction for the ion suppression effect but with the disadvantage of losing sensitivity since ion suppression still occurs (e.g. Miao and Metcalfe, 2003). Ion suppression is produced by the co-elution of the target analyte and organic compounds present in the matrix which compete for ionization at the source (Pat et al., 2002). To prevent ion suppression of NDMA, the method was optimized to chromatographically resolve NDMA and the matrix components, which were observed to produce ion suppression. A natural surface water (Upper Silver Creek, San José, CA, USA) was used as a representative matrix.

2.4. *SPE method development*

A variety of sorbents and elution solvents were tested to optimize the SPE method for NDMA (see Supplementary information for details). The recovery of NDMA from Milli-Q water and surface water (Upper Silver Creek) at environmentally relevant concentrations (100 ng/l), the effect of sample pH, filtration pore size, extract evaporation technique, and the presence of an additional cartridge in-series (Strata Phenyl) were evaluated.

To test the applicability of the optimized NDMA SPE method to other similar nitrosamines, a method recovery test was performed by extracting and analyzing 500 ml of Milli-Q water ($n = 6$) and surface water ($n = 6$) spiked with 100 ng/l each of six nitrosamines. The nitrosamines included NMEA, NDEA, NDPA, NDBA, NPyr, and NPip (structures given in Fig. 2); all but NPip are included in UCMR 2.

Different SPE cartridges commonly recommended for the extraction of trace organic compounds were tested in order to evaluate the adsorption of NDMA, if any. A single water sample may be extracted for multiple compounds with different properties by placing appropriate SPE cartridges in-series, with the second cartridge extracting compounds that sorb negligibly to the first. For extraction of NDMA, it is therefore important to verify that it has no affinity for the first cartridge. Results of these tests with several commercial SPE cartridges are summarized in the Supplementary information.

2.5. *Quantification*

Nitrosamine standards consisted of a mixed standard solution in Milli-Q water which contained NDMA and the six other tested nitrosamines. The instrument detection limit (IDL) for each nitrosamine was determined as the lowest injected standard that gave a signal-to-noise ratio of at least three and an accuracy of 70–130%. The SPE method was evaluated by determining the recoveries and relative standard deviation (RSD) of spiked samples processed through the entire analytical method (SPE, elution, concentration). Method detection limits (MDLs) were calculated using the known extraction recovery, concentration factor, and IDL.

Calibration standards from 0.1 to 200 μg/l nitrosamines were injected before and after sample groups and were analyzed using linear regression with inverse weighting (1/x). Satisfactory r^2 values were obtained for all nitrosamines (0.98–0.99). Blanks processed through the entire method were also analyzed with each sample set. Nitrosamine identification and quantification were made for samples with a signal-to-noise ratio of at least three and a minimum of two transitions eluting at the expected retention time.

3. Results and discussion

3.1. *LC–MS/MS method optimization*

For all nitrosamines, the precursor ion detected was the $[M+H]^+$ ion. The most abundant transition was used for quantitation and a second transition was used for qualitative confirmation. Few additional product ions were observed due to the low molecular weight of the compounds. NDMA showed an adduct of molecular weight 92, suspected to be due to the presence of ammonium in the mobile phase, which fragmented into mass 75 (the $[M+H]^+$ ion) and was used as an

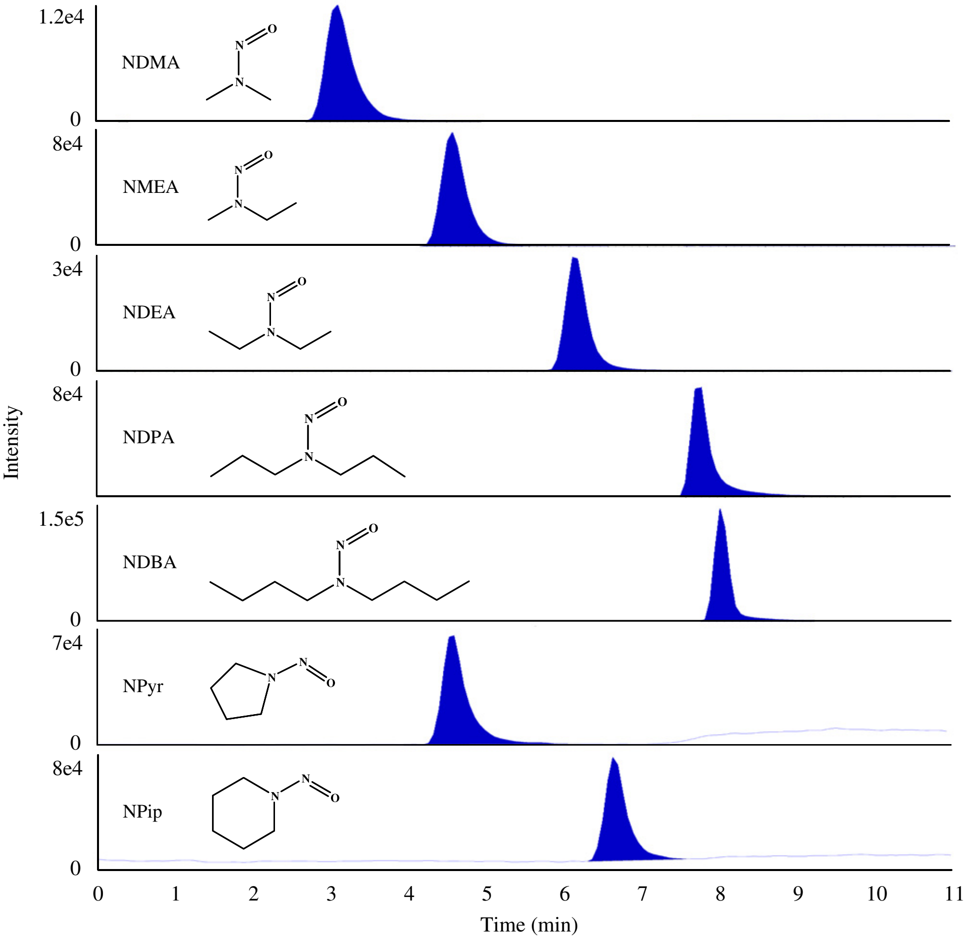

Fig. 2 – Molecular structures and typical LC–MS/MS chromatogram for seven nitrosamines (100 μg/l standard) showing the major (quantitation) transition for each nitrosamine.

additional qualifier transition. The optimized mass spectrometry parameters and IDLs are given in Table 1. Precision expressed as % RSD was evaluated by injecting each calibration standard six times; for all nitrosamines, the RSD was less than 15% for all standards at or above the IDL. For NDMA, the IDL was found to be 2 μg/l, and ranged between 2 and 25 μg/l for the other nitrosamines (Table 1) for a 50 μl injection volume. One of the benefits to LC-based analyses over GC is the fact that samples may be directly injected as an aqueous aliquot. This is a major advantage for laboratory studies or for environmental and wastewater samples in which the analyte concentration exceeds the IDL. For example, NDMA concentrations in industrial effluent from circuit board manufacturers have been measured as high as 105 μg/l, well above the NDMA IDL reported here. Department of Defense and aerospace testing facility superfund sites also regularly show high μg/l-range NDMA concentrations due to contamination from the use of UDMH-based rocket fuel (Mitch et al., 2003). Therefore, these types of samples may be injected directly onto the column without prior extraction into an organic solvent.

A mobile phase consisting of methanol and 2 mM ammonium acetate in water resulted in optimal retention time and peak shape. It was noted that if standards of NDMA were prepared in solvents other than water, the compound was not retained well by the column. The final conditions for the mobile phase were as follows: 10–45% methanol over 4 min, to 100% methanol at 5 min, held until 10 min, and finally returned to 10% methanol at a flow rate of 0.15 ml/min. The total run time was 11 min. The nitrosamines were eluted in order of increasing chain length; compounds present in the matrix, which were observed to cause ion suppression of NDMA, were chromatographically separated from the analytes, eluting at 1–2 min while NDMA eluted at 3.1 min and the other nitrosamines between 4 and 8 min (Fig. 2).

3.2. *SPE recovery and method detection limit*

In a preliminary evaluation, activated charcoal showed the highest adsorption capacity for NDMA among alternative sorbents. While other methods rely on more than one sorbent (Charrois et al., 2004; Zhao et al., 2006), high NDMA recoveries were achieved here using only activated charcoal. Under typical SPE conditions (1 g of charcoal packed into an 8 ml SPE cartridge) and a loading rate <5 ml/min, the retention efficiency of NDMA from the water sample to the sorbent was greater than 98%. Glass fiber filters inside the packed cartridge below the frit were required to prevent loss of the fine charcoal during sample loading. The charcoal was not allowed to dry before elution in order to retain some water in the extract. A recovery of 99.9±1.5% NDMA was achieved for spiked Milli-Q water (30 μg/l) with an elution of 2 ml of acetonitrile, followed by 2 ml of methanol and finally 2 ml of acetone (each two times and drained completely under vacuum in between each addition). The elution solvents were evaporated from the extract at 37 °C in a sand bath, leaving 1–3 ml water for injection onto the LC–MS/MS.

When the SPE technique was tested using natural surface waters spiked with environmentally relevant concentrations (100 ng/l) of NDMA, 90±11% recovery was obtained by sample pH adjustment to 2.3, filtration with either 0.2 or 0.45 μm filters, sample loading with activated charcoal alone or in-series with an additional SPE cartridge, and extract evaporation using a 37 °C sand bath. Additional details on the sorbent selection, elution optimization, and NDMA recovery tests are provided in the Supplementary information.

Spiked samples (100 ng/l) were processed through the entire analytical method to determine the recoveries and MDLs for all nitrosamines. The calculated MDL for the combined SPE–LC–MS/MS technique depends upon the IDL of the LC–MS/MS, the SPE percent recovery, and the concentration factor (ratio of volume loaded to volume of concentrated extract). For NDMA, mean recoveries were 90±11% and 105±5% in surface water and Milli-Q water, respectively. The recoveries of the other tested nitrosamines were variable, with higher recoveries achieved for shorter alkyl-chain lengths. The mean recoveries in Milli-Q water were 86±6%, 66±13%, 26±10%, and 5±4% for NMEA, NDEA, NDPA, and NDBA, respectively, and 104±8% and 142±5% for the cyclic nitrosamines NPip and NPyr. The results were inversely correlated with the octanol-water partition coefficient (log-K_{ow}), suggesting that the strongly sorbing nitrosamines were not eluted as effectively from the activated charcoal. In the case of 1000 ml water samples concentrated to 1 ml extracts, the optimal MDLs using the SPE–LC–MS/MS technique are 2 ng/l for NDMA, NMEA, and NDEA, and 4, 6, and 24 ng/l for NPyr, NDPA, and NPip, respectively.

3.3. *Nitrosamines in advanced water treatment*

NDMA was detected in the secondary effluent and at all sampling points throughout the IWPF advanced treatment train (Table 2). A range of 20–59 ng/l NDMA was determined for the secondary effluent (input to the advanced treatment) prior to chloramination, which is consistent with a recent survey of wastewater treatment plants showing a median concentration of 80 ng/l NDMA in untreated wastewater and variable removals of 0–75% for secondary (biological) treatment (Sedlak et al., 2005). While NDMA is expected to form following wastewater chlorination or chloramination, there are other sources (Najm and Trussell, 2001; Mitch et al., 2003). Sources of NDMA to the IWPF are known point sources, domestic wastewater, industrial sources (OCSD, 2002; Sedlak et al., 2005), and potentially the use of polymeric coagulants in the water treatment (Park et al., 2005). Fig. 3 shows the cumulative percent removal of NDMA through the advanced treatment stages (MF, RO, and UV) at the IWPF. A mean of 69±7% of the NDMA was removed overall, but this reached 90±3% following blending. Final product water concentrations were below the California 10 ng/l notification level (Table 2).

The other nitrosamines surveyed (NMEA, NDEA, NDPA, NPip, and NPyr) were not detected above MDLs (6, 8, 21, 82, and 15 ng/l, respectively) estimated based upon the IWPF sample volumes extracted (typically 500 ml). NDBA was also not detected, perhaps due to the low extraction recovery. While only NDMA was found in the present study, it is clear that the nitrosamine family may come under increasing scrutiny as wastewater contaminants and disinfection byproducts. Schreiber and Mitch (2006) monitored the effluent from four wastewater treatment plants and the nearby effluent-impacted Quinnipiac River (CT, USA) for nitrosamines including NDMA, NMEA, NDEA, NPyr, NPip, and *N*-nitrosomorpholine (NMOR), detecting only NDMA and NMOR in the effluents and river. Like NDMA, NPyr and NDBA have been observed to form during chloramination (Hwang et al., 2004; Sedlak and Kavanaugh, 2006). Recently, Zhao et al. (2006) developed an SPE–LC–MS/MS method for nitrosamines with similar detection limits to those presented in this study. The authors found NDMA, NPyr, NPip, and *N*-nitrosodiphenylamine in a drinking water distribution system and found that the concentrations increased with residence time, suggesting that these nitrosamines are formed as a result of disinfection.

Table 2 – Concentrations of NDMA measured over 3 months for the IWPF, an advanced wastewater treatment facility featuring MF, RO, and UV-AOP treatment

Treatment stage	NDMA concentration±1 SD (ng/l)[a]		
	May-06	Jun-06	Jul-06
2° Effluent	20±5	59±14	36±1.0
Chloraminated 2° effluent/pre-MF	18±11	37±14	39±2.4
Post-MF/pre-RO	18±0.04	57[b]±5.2	45±5.2
Post-RO/pre-UV	14±2.4	41[b]±7.9	20±6.7
Post-UV	7.6±0.8	14[b]±1.0	11±3.3
Post-blending	2.3±0.9	4.5±2.2	–

[a] $n=2$ extractions.
[b] $n=3$ extractions.

3.3.1. *Microfiltration*

As expected, MF was not effective in removing NDMA. The small NDMA molecule easily passes through the MF membrane. In fact, the NDMA concentration increased (by 5–56%), which is consistent with communications from advanced treatment facilities (Mitch et al., 2003) and findings by Sedlak and Kavanaugh (2006) for three advanced treatment facilities showing increases of 0–32%. The authors attribute the increase to NDMA formation as a result of chlorination performed prior to MF to prevent MF membrane fouling. In this case, chloramination was performed prior to MF, which produces significantly more NDMA than chlorination (Najm and Trussell, 2001; Mitch and Sedlak, 2002a, b).

3.3.2. *Reverse osmosis*

The percent removal of NDMA by RO (Hydranautics ESPA2, composite polyamide) at the IWPF was found to be fairly variable, with a range of 24–56%. Periodic measurements by OCWD have shown a similar RO performance, at 11% and 50% removal. Fig. 4 provides a comparison of the results from this study and others, including field (wastewater treatment monitoring) and laboratory work, summarizing the performance of thin-film composite RO membranes and UV treatment for NDMA removal. A report from the WateReuse Foundation (Sedlak and Kavanaugh, 2006) showed RO rejection of NDMA for the Groundwater Replenishment System Pilot Facility (GWRS-Pilot, OCWD) at approximately 45–65% for thin-film composite membranes (Fig. 4). Other advanced treatment plants monitored as part of that study showed a range of 10–70% rejection of NDMA via RO. With the exception of a recent laboratory study (Steinle-Darling et al., 2007), there are no reports in the peer-reviewed literature concerning RO rejection of NDMA; however, a review by Mitch et al. (2003) cites 50% removal (their personal communication, L. McGovern)

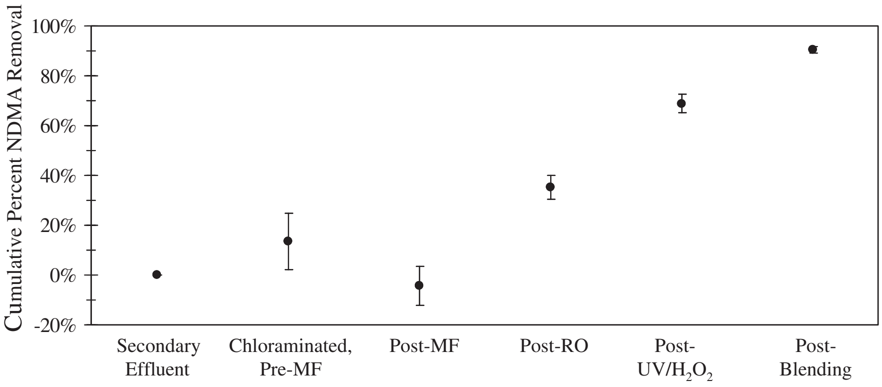

Fig. 3 – Cumulative percent NDMA removal through stages of advanced treatment at the IWPF and blending. Error bars represent one standard deviation of mean removals ($n = 3$) over 3 months.

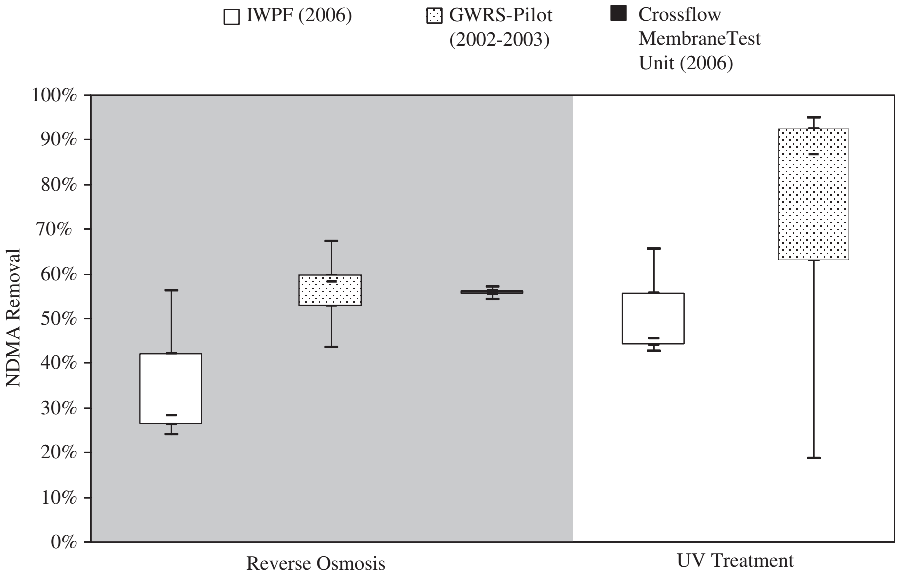

Fig. 4 – Summary of RO and UV treatment removal efficiencies for NDMA for the present study (IWPF 2006; ESPA2 RO membranes) and others as standard box plots, including results from the Groundwater Replenishment System Pilot Facility (GWRS-Pilot; thin-film composite RO membranes) at OCWD (Sedlak and Kavanaugh, 2006) and a laboratory investigation using ESPA3 RO membranes (Steinle-Darling et al., 2007). Boxes represent the inner quartile range (25–75 percentile), outer whiskers represent the data range or 1.5 times the inner quartile range, and the median is indicated inside the box.

for thin-film composite RO membranes, in agreement with the data shown here. A National Water Research Institute (NWRI) report showed quite low rejections for a variety of membranes (DOW/Filmtec BW30: 17.7%; Hydranautics ESPA2: 19.2%; Hydranautics LFC1: 15.8%; Koch/Fluid Systems TFC-HR: 21.3%; Osmonics cellulose acetate: 5.9%), but the bench-scale system lacked a cross-flow component representative of real systems and the authors note that the removal of poorly rejected compounds, like NDMA, was impacted by this design difference (Rodriguez et al., 2004). A recent result by Steinle-Darling et al. (2007) is included in Fig. 4, showing 55.8±1.3% removal for NDMA in deionized water using a cross-flow, bench-scale system with ESPA3 (Hydranautics) membranes. As may be expected, these laboratory results show less measurement variability than do the field studies, but they generally agree. Importantly, Steinle-Darling et al. (2007) show that while a rejection near 56% may be expected under pure water (deionized) conditions, the rejection of NDMA will decrease with changing feed characteristics and membrane fouling due to concentration polarization. This may explain NDMA rejections of <50% measured in actual treatment facilities such as the IWPF and GWRS-Pilot (Fig. 4).

3.3.3. *UV treatment*

UV treatment of NDMA resulted in removals of 43–66% for the IWPF. This range is consistent with performance found for GWRS-Pilot (Sedlak and Kavanaugh, 2006), as shown in Fig. 4. While UV treatment at the IWPF was performed in combination with H_2O_2, this is not expected to enhance NDMA destruction (Mitch et al., 2003; Sharpless and Linden, 2003). In addition to blending the final product water with potable water, the advanced treatment effluent was chlorinated. Although there is some debate over whether NDMA may be reformed from degradation products when a chlorination or chloramination step follows UV treatment (Mitch et al., 2003), final concentrations measured in this study did not appear to increase following the chlorination and blending of product water, and ranged from 2 to 5 ng/l, below the 10 ng/l notification level. The lack of significant NDMA formation may be explained by the choice of chlorination over chloramination, and by the fact that the upstream RO treatment is expected to nearly completely remove NDMA precursors (Sedlak and Kavanaugh, 2006).

Currently, UV treatment is the most accepted method for removal of NDMA. While RO may not be as effective for NDMA as it is for pharmaceuticals (Reinhard et al., 1986, 2003), it nevertheless contributes to removal. In fact, RO in combination with UV treatment may be necessary for adequate and reliable NDMA removal. In the case of the present study, 59–75% was removed across RO and UV treatment together. In combination with blending performed to increase product flow, the final product water (reclaimed wastewater) met potable standards at NDMA concentrations of non-detect or below the 10 ng/l CA notification level.

4. Conclusions

Many communities already rely on water recycling to meet their freshwater needs, and more water agencies are working to expand their reclamation of wastewater for this purpose. Consequently, the fate of wastewater-derived contaminants like NDMA in the environment and in wastewater treatment must be evaluated. The present study reports NDMA removal efficiencies for advanced wastewater treatment in an actual facility operated by the OCWD featuring MF, RO, and UV-AOP, with nitrosamines measured using a developed LC–MS/MS analytical method. Results of other field and laboratory studies have also been reviewed. In summary,

- The described method for NDMA features a high extraction efficiency using SPE and accurate identification and quantification via LC–MS/MS at a reporting limit of 2 ng/l, below the 10 ng/l notification level specified by the California Department of Health Services, and may be applied for additional nitrosamine analyses.
- Contaminated industrial effluents or other waters having concentrations of nitrosamines above the LC–MS/MS instrument detection limit (2 μg/l for NDMA and 2–25 μg/l for other tested nitrosamines) may be directly injected (no pre-concentration) and as water, in contrast to GC-based techniques.
- NDMA was detected in the secondary effluent of the OCSD (20–59 ng/l) and throughout the advanced treatment at the IWPF. Of the other nitrosamines monitored (NMEA, NDEA, NDPA, NPip, NPyr), none were detected above the 6–82 ng/l method detection limits.
- MF of wastewater effluent is not expected to reduce NDMA concentrations and may in fact lead to NDMA formation when used in combination with chlorination or chloramination to prevent MF membrane fouling.
- RO treatment of secondary effluent using thin-film composite membranes typically results in NDMA rejection of approximately 50–65% or less. For the overall treatment train, this rejection is an important contribution to NDMA removal. Lower rejection may be associated with changing feed conditions and fouling observed in real treatment systems.
- UV irradiation in combination with RO treatment and, in some cases, blending allows operators to reliably maintain the residual NDMA below the 10 ng/l CA drinking water notification level.

Acknowledgment

This research was funded by the Santa Clara Valley Water District (CA), the California Department of Water Resources, Nanyang Technological University (Singapore), the National Science Foundation Graduate Research Fellowship program, and WaterCAMPWS (under Director Vern Snoeyink), a Science and Technology Center of the National Science Foundation (CTS-0120978). Any opinions, findings, conclusions, and recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the sponsoring agencies.

Appendix A. Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.watres.2007.07.022.

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Supplementary Information for

N-NITROSODIMETHYLAMINE (NDMA) REMOVAL BY REVERSE OSMOSIS AND UV TREATMENT AND ANALYSIS VIA LC-MS/MS

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Submitted to
Water Research
January 30, 2007

SPE Sorbent Selection and Elution Optimization

For the optimization of SPE for NDMA, neutralized activated charcoal purchased from Sigma (St. Louis, MO, USA), Zeolite CBV780 obtained from Zeolyst (Valley Forge, PA, USA), and two types of Black Carbon (Black Pearls 1300A73 and 460) from CABOT (Boston, MA, USA) were tested as possible sorbents. Davisil Silica (300Å) from Grace Davison (Columbia, MD, USA) was also included as a control. At pH 6.0, 1 g of the adsorbent was added to 1 l of Milli-Q water spiked with 30 µg/l NDMA and mechanically shaken in a closed bottle for 24 h. Disappearance of NDMA from the solution was monitored.

The loss of NDMA from water using the various sorbents is given in Table SI 1. The activated charcoal showed the highest capacity for adsorption compared to the other sorbents. Adsorption increased rapidly with time of contact, then slowed after 1 h with the maximum adsorption achieved after 5 h for both pH 7 and 8. Over a larger pH range of 2.5 to 9, the effect of pH on adsorption was not found to be significant. When 1 g of charcoal was packed into an 8 ml SPE cartridge and loaded with 1 l of 30 µg/l NDMA in Milli-Q water at a flow rate < 5 ml/min using a 16-port vacuum manifold from Supelco (Bellefonte, PA, USA), the retention efficiency of NDMA from the water sample to the sorbent was greater than 98%. This increase in adsorption compared to the prescreening test was likely due to the greater degree of contact between the water sample and the adsorbent, as facilitated by the low flow rate and packed cartridge. However, extracting a 500 ml sample at such a low flow rate required several hours to complete.

Since activated charcoal showed the highest capacity for NDMA adsorption, the selection of elution solvents and volume was based on this sorbent. The activated charcoal was washed with water at pH 2, 9 and 5.5 to remove interferences (for later sample analyses, the charcoal was washed with water at the same pH as the water sample of interest). The charcoal (1 g) was packed into an empty SPE cartridge and water spiked with 30 µg/l NDMA was loaded as before. Glass fiber filters were placed inside the packed cartridge below the frit to prevent loss of the fine charcoal during sample loading. Following sample loading, the charcoal was not allowed to dry before elution in order to retain 1 to 3 ml water in the extract. As shown in Table SI 1, the results of several tested solvent combinations showed that elution with 2 ml of acetonitrile, followed by 2 ml of methanol and finally 2 ml of acetone (all of them two times and drained completely under vacuum in between each addition) achieved nearly 100% recovery. The extract was evaporated at 37ºC in a sand bath, removing the volatile solvents (the presence of which would interfere with chromatography) and leaving 1 to 3 ml water for injection onto the LC-MS/MS.

Performance of NDMA Extraction In-Series with Additional SPE Cartridge

The NDMA extraction method was tested to determine whether the placement of an additional SPE cartridge in-series upstream of the packed activated charcoal cartridge would have any negative impact on the recovery of NDMA. The SPE cartridges C18, CN (Alltech; Deerfield, IL, USA), Isolute ENV+ (IST; Cambridge, U.K.), Supelclean Envi-Carb (Supelco), and Strata X (Phenomenex; Torrance, CA, USA) were conditioned with 4 ml of methanol, followed by 4 ml of acetonitrile and 4 ml of distilled water and then loaded with 1 l of distilled and Milli-Q water at pH 6 spiked with NDMA. A blank was prepared for each cartridge. The water was loaded at a flow rate < 10 ml/min and the product water collected following passage through the cartridge was analyzed to assess the extraction ratio. Adsorption of NDMA to commercial SPE cartridges was less than 5%, showing that the method may indeed be modified to include the simultaneous extraction of NDMA and other trace organics by placing SPE cartridges in-series, without compromising the recovery of NDMA. Well-sealed connections between cartridges were required to ensure balanced loading and draining.

Recovery Test for Trace NDMA Concentration

To verify the extraction for natural waters at environmentally relevant concentrations, NDMA was also spiked into a representative surface water (Upper Silver Creek, San José, CA, USA) at a low concentration (100 ng/l) and 500 ml was extracted using the optimized method. For this test, sample pH, filtration pore size, extract evaporation technique, and the presence of an additional cartridge in-series (Strata Phenyl; Phenomenex) during sample loading were all tested in triplicate for their effect on the recovery of NDMA and differences between the recoveries were assessed using the two-sided t-test. For calculation of recovery, the same mass of NDMA was spiked into a Milli-Q water aliquot as a reference and analyzed in the same manner as the sample extracts.

As shown in Table SI 2, there was no significant difference between the 0.2 and 0.45 μm filtration and no effect of performing the NDMA SPE in-series with a Strata Phenyl cartridge. However, adjusting the sample pH to 2.3 led to an increase in recovery from 66±7% (mean of treatments C and D) to 90±11% (mean of treatments A and B). Higher recoveries were also observed when sample extracts were evaporated by 37°C heat rather than by nitrogen bubbling. Nitrogen evaporation led to losses and consequently is not recommended for this method. In summary, method recoveries of 90±11% for surface water at environmentally relevant concentrations of NDMA were obtained by: sample pH adjustment to 2.3, filtration with either 0.2 or 0.45 μm filters, sample loading with activated charcoal alone or in-series with an additional SPE cartridge, and evaporation to 1 to 3 ml water (removal of organic solvent) using a 37°C sand bath. The water-based extract is injected onto the LC-MS/MS following addition of internal standard.

Table SI 1. Performance of Selected Adsorbents and Elution Solvents.

Adsorbent	**% NDMA Adsorption**[a]
Charcoal Activated	61
Davisil Silica	< 0.5
Black Pearls 1300A73	<1
Black Pearls 460	20
Zeolite CBV780	5

Elution Solvents	**% NDMA Recovery**[b] **(RSD)**[c]
2 ml acetonitrile, 3 times 2 ml methanol, 3 times	90.7 (3.8)
2 ml acetonitrile, 2 times 2 ml methanol, 2 times 2 ml acetone, 2 times	99.9 (1.5)
2 ml acetonitrile, 3 times 2 ml methanol, 3 times	90.7 (3.8)
1 ml acetonitrile, 2 times 2 ml acetone, 4 times	80.2 (4.2)
1 ml acetonitrile, 2 times 1 ml methanol, 2 times 1 ml acetone, 2 times	70.0 (5.6)

[a] As removal from 1 l water spiked with 30 μg/L NDMA.

[b] As removal from 1 l water spiked with 30 μg/L NDMA and loaded through a solid phase extraction reservoir packed with 1 g activated charcoal.

[c] RSD = relative standard deviation (n = 2).

Table SI 2. Recovery of ng/l Levels of NDMA from Surface Water as a Function of Sample Preparation.

Recovery Test: 100 ng/l NDMA in 500 ml Surface Water

	Treatment[a]	Mean Recovery[b]	Standard Deviation
A	0.2 µm, pH 2.3; cartridges in-series[c]	88%	14%
B	0.2 µm, pH 2.3; charcoal	93%	9%
C	0.2 µm; charcoal	64%	10%
D	0.45 µm; charcoal	68%	1%

Concentration Test: Evaporation of Spiked Extract

	Treatment	Mean Recovery	Standard Deviation
E	37°C heat on sand bath	116%	25%
F	Nitrogen	73%	8%

[a] Sample filtration pore size, sample pH adjustment, sorbent utilized for SPE.

[b] n=3 (A,B,E,F); n=2 (C,D).

[c] Strata-phenyl and charcoal cartridges connected in-series, as for multiple compound extraction.

Appendix D

Plumlee, M.H., Reinhard, M., 2007. Photochemical Attenuation of *N*-Nitrosodimethylamine (NDMA) and other Nitrosamines in Surface Water. Environ. Sci. Technol. 41, 6170-6176.

Environ. Sci. Technol. **2007**, *41,* 6170−6176

Photochemical Attenuation of *N*-Nitrosodimethylamine (NDMA) and other Nitrosamines in Surface Water

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The aqueous photolysis of seven alkyl nitrosamines was studied by irradiation in a solar simulator. Nitrosamines included *N*-nitrosodimethylamine (NDMA), *N*-nitrosomethylethylamine (NMEA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-*n*-propylamine (NDPA), *N*-nitrosodi-*n*-butylamine (NDBA), *N*-nitrosopiperidine (NPip), and *N*-nitrosopyrrolidine (NPyr). Direct photolysis at irradiations of 765 W/m^2, representing Southern California midsummer, midday sun, resulted in half-lives of 16 min for NDMA and 12−15 min for the other nitrosamines. The quantum yield for NDMA was determined to be $\Phi = 0.41$ and $\Phi = 0.43-0.61$ for the other nitrosamines. Quantified products of NDMA photolysis included methylamine, dimethylamine, nitrite, nitrate, and formate, with nitrogen and carbon balances exceeding 98 and 79%, respectively. Indirect photolysis of nitrosamines in surface water was not observed; increasing dissolved organic carbon (DOC) slowed the NDMA photolysis rate because of light screening. Removal of NDMA measured in tertiary treated effluent flowing in a shallow, sunlit engineered channel agreed with photolysis rates predicted based on the measured quantum yield and system parameters. Because biodegradation is relatively slow, aquatic photolysis of NDMA is generally expected to be more significant even at relatively low levels of solar irradiation ($t_{1/2} = 8-38$ h at 244−855 W/m^2, 51° N latitude, 1 m depth).

Introduction

Given the high demand for freshwater, rivers and reservoirs that receive wastewater effluent are also often relied upon as a freshwater resource. The effluent is likely to contain trace organic contaminants, some of which may be carcinogens, toxins, or endocrine disruptors. *N*-nitrosodimethylamine (NDMA) is a dialkyl-*N*-nitrosamine frequently detected in municipal wastewater effluent and reclaimed wastewater at concentrations of 20−100 ng/L (*1*, *2*), as well as in drinking water at lower concentrations. It is formed as a disinfection byproduct of chlorination and chloramination (*1*) and has been classified as a probable human carcinogen by the U.S. Environmental Protection Agency (*3*). While the potential for ecotoxicological impact has not been thoroughly investigated at environmentally relevant concentrations, in vitro bacterial and mammalian cell studies have shown NDMA to be a mutagen and in vivo studies have also shown genetic effects (*4*). In addition to NDMA, other nitrosamines have recently been detected in effluent-impacted rivers (*5*) and in a drinking water distribution system (*6*).

Nitrosamines resist acidic and basic hydrolysis (*7*, *8*) and field and microcosm studies of NDMA have established that it does not readily sorb to sediments and is slow to biodegrade in soils, sediments, and surface water (*9*−*13*). Nitrosamines are photosensitive, however, and currently UV irradiation is the most commonly applied treatment method for NDMA removal in wastewater and drinking water (*1*). The majority of NDMA photolysis studies employ UV irradiation (*7*, *14*−*18*), and quantum yields of $\Phi = 0.28-31$ have been reported for neutral pH (*15*−*17*).

Information regarding kinetics, quantum yields, and products for NDMA photolysis under environmental conditions is lacking. In addition to a UV absorption band at $\lambda =$ 230 nm (corresponding to a $\pi \rightarrow \pi^*$ transition), NDMA can absorb in the range of natural sunlight due to a weaker absorption band at $\lambda = 330$ nm ($n \rightarrow \pi^*$ transition) (*14*, *19*). In general, the photochemistry of an $n \rightarrow \pi^*$ transition state differs from a $\pi \rightarrow \pi^*$ excitation and can lead to a distinct quantum yield and products (*20*). To predict the photochemical fate of NDMA, it is important to know whether the photolysis of NDMA in the natural environment is as effective without UV irradiation or compared to other attenuation mechanisms. If the photochemistry of NDMA in the natural environment is like that observed with UV light, the photodegradation will give a known suite of products including dimethylamine, methylamine, nitrite, nitrate, formaldehyde, and formate (*14*). Quantum yields for other dialkyl nitrosamines such as *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-*n*-butylamine (NDBA), and *N*-nitrosopiperidine (NPip) have been determined for the vapor phase or in an organic solvent (*7*), but they have not been determined in water for either UV or natural irradiation.

To predict the rate of aquatic photolysis in the environment, the rate of light absorption by a compound of interest can be calculated from absorbance and irradiance spectra and converted into transformation rates by multiplying by the quantum yield (*21*). Predicted rates are sensitive to factors such as latitude, season, depth of water, and concentration of chromophoric dissolved organic matter (cDOM), and they can be modeled using these inputs (*21*, *22*). In addition, indirect mechanisms of photolysis are often important in natural systems (*21*, *23*, *24*) because of the presence of photosensitizers and quenchers, but this has not yet been investigated for nitrosamines.

The objectives of this study were to determine rates of direct and indirect photolysis and quantum yields for NDMA and six other nitrosamines under conditions of simulated natural sunlight. Structures and occurrence information for the selected nitrosamines, most of which are listed on the EPA's Unregulated Contaminant Monitoring Rule 2 (UCMR 2) (*25*), are given in Table S1 in the Supporting Information (SI). Given its recent attention as a drinking and wastewater contaminant, NDMA was selected for additional study. Photodegradation products reported for UV irradiation were identified for simulated sunlight. From the measured quantum yield, expected aquatic photolysis rates for NDMA were calculated for a range of representative environmental conditions and for a 1 m deep, sunlit channel fed with tertiary treated reclaimed wastewater by the Orange County Water District (OCWD).

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10.1021/es070818l CCC: $37.00

Experimental Section

Materials and Methods. Information regarding chemicals and materials and a more detailed description of the analytical methods can be found in the SI. Briefly, NDMA and the other nitrosamines were analyzed by high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) using a C18 column with methanol and 2 mM ammonium acetate as the mobile phase, according to the method described by Plumlee et al. (*2*). 50 μL samples were directly injected without preconcentration, with instrument detection limits of 2 μg/L for NDMA and 2−25 μg/L for the other nitrosamines. The method was adapted to include dimethylamine and methylamine. 4-nitroanisole (PNA) was analyzed using HPLC based on the method described by Dulin and Mill (*26*). Nitrate, nitrite, and formate were measured using ion chromatography.

Photolysis Apparatus and Procedure. Solutions of nitrosamines were irradiated using an Atlas Suntest CPS+ photosimulator (Chicago, IL) equipped with a 1.1 kW xenon arc lamp according to the method described by Lin and Reinhard (*27*). The lamp was fitted with special glass filters to block the transmission of wavelengths below 290 nm to simulate natural sunlight (passing wavelength, 290 nm $< \lambda < \sim$800 nm). Nitrosamines included NDMA, *N*-nitrosomethylethylamine (NMEA), NDEA, *N*-nitrosodi-*n*-propylamine (NDPA), NDBA, NPip, and *N*-nitrosopyrrolidine (NPyr). The factory specified photosimulator intensity was verified by comparing the measured photolysis rate of NDMA to the rate predicted given the quantum yield. Sample solutions were kept in capped quartz tubes (Quartz Scientific, Fairport, OH) and placed horizontally in a constant temperature (20.0 ± 1.7 °C) water bath 25 cm directly below the photosimulator lamp, and an additional tube covered in aluminum foil was placed in the photosimulator to serve as a control. Each sample tube ($n = 2-4$) represented a replicate photolysis experiment.

For direct and indirect photolysis experiments, initial concentrations of nitrosamines were spiked to 100 μg/L (1.3 μM for NDMA, and 0.6−1.1 μM for the other nitrosamines) with the exception of NPip, which was spiked to 1000 μg/L (8.8 μM) due to its higher detection limit. Direct photolysis tests in Milli-Q water (pH 6, unadjusted) were performed at 765 W/m^2, which is equivalent to midday, midsummer sun in California (*27*), and used alongside actinometry to determine nitrosamine quantum yields. To assess the potential for indirect photolysis, nitrosamines were irradiated (n = four test tubes per nitrosamine) in filtered (0.45 μm) surface water (absorbance spectrum given in Figure S1, SI) with photosimulator intensity reduced to 250 W/m^2 to slow the rapid nitrosamine photolysis and compared to irradiation of nitrosamines in Milli-Q water (n = four test tubes). To assess light screening by DOC, NDMA (200 μg/L) was irradiated in solutions of increasing concentrations of Aldrich humic acid (0−35 mg C/L), also at 250 W/m^2. The test tubes were simultaneously irradiated, one at each concentration. The uncertainty in the photodecay rate at a given concentration was calculated as the standard error in the slope (rate) of the linear regression instead of from variation of the mean of multiple rates. This error estimate does not take into account the effect of test tube position in the photosimulator, which typically resulted in a greater relative standard deviation of 5−10% of the measured rate.

To test the effect of oxygen, additional experiments were performed for some nitrosamines by bubbling Milli-Q water solutions with either oxygen or helium to purge oxygen. To monitor the products resulting from the photochemical decay of NDMA, 500 μg/L NDMA (6.7 μM) was spiked into Milli-Q water, and expected products were monitored over 1 h.

Determination of Quantum Yield. The quantum yield (Φ) of a photochemical reaction describes the moles of reactant transformed per moles of photons absorbed (*21*). An environmental quantum yield, Φ_c, representing the averaged value over the wavelength range at which the nitrosamine absorbs sunlight, was calculated using the following equation (*26*, *28*):

$$\Phi_c = \Phi_a \left(\frac{k_p^c \sum I_0(\lambda)\epsilon^a(\lambda)}{k_p^a \sum I_0(\lambda)\epsilon^c(\lambda)} \right) \qquad (1)$$

where Φ_a is the known quantum yield of the actinometer; k_p^c and k_p^a are the rates of photolysis for the chemical and actinometer, respectively; $\epsilon^a(\lambda)$ and $\epsilon^c(\lambda)$ are the extinction coefficients for the actinometer and chemical, respectively; and $I_0(\lambda)$ is the solar irradiance. Chemical actinometry, in which a calibrated photochemical reaction is used to quantify light intensity, was performed using the binary actinometer PNA/pyridine described by Dulin and Mill (*26*). Φ_a for PNA is reported to be

$$\Phi_a = 0.44[pyr] + 0.00028 \qquad (2)$$

and was thus determined from the known experimental molar concentration of pyridine. The actinometer half-life was adjusted to match that of NDMA, requiring 981 mg/L pyridine (12.4 mM) and 1.2 mg/L PNA (7.8 μM). Rates of photolysis were determined by monitoring the disappearance of the nitrosamine and PNA, which have similar absorption spectra, and calculated from the slope of the linear regression using

$$\ln\left(\frac{C_0}{C_t}\right) = k_p t \qquad (3)$$

where C_0 and C_t are the chemical or actinometer concentrations at time zero and at time t, respectively, and k_p is the rate of photolysis for the chemical or actinometer. Irradiation data ($I_0(\lambda)$) for the lamp with UV filters, simulating natural sunlight, was obtained from the photosimulator manufacturer. The molar extinction coefficients, $\epsilon(\lambda)$, were determined from measured ultraviolet/visible (UV−vis) spectra of each nitrosamine and the actinometer at known concentrations. The total absorbance of the reaction solutions were maintained below 0.02 to minimize light absorption by the system (*29*), except the absorbance of the actinometer solution reached a maximum of 0.08.

Calculation of Solar Irradiance and Expected Photolysis Rate. Global horizontal irradiance at the earth's surface over the wavelength range 280−2279 nm was calculated using SMARTS (Simple Model for the Atmospheric Radiative Transfer of Sunshine, v. 2.9.5) (*30*) for midlatitude and tropical locations so that the expected NDMA aquatic photolysis rate could be calculated for a range of environmental conditions. Inputs to SMARTS included geographical position, season, date and time, and specific parameters such as ozone abundance, atmospheric gases, and aerosol model. For the purposes of this nonspecific irradiance prediction, representative or average inputs recommended by SMARTS developers were assumed, and water (non-Lambertian) was selected as the surface.

SMARTS was also used to calculate the irradiance at Orange County Water District (OCWD) Water Factory 21 (WF-21) for June 23−30, 2000, 33° N latitude. During this time, OCWD monitored NDMA in the influent and effluent of a sunlit, open channel receiving Orange County Sanitation District (OCSD) tertiary treated effluent (*31*). In addition to geographical position and time, inputs to the SMARTS model included air temperature and relative humidity. These parameters were determined for the site on the June 2000

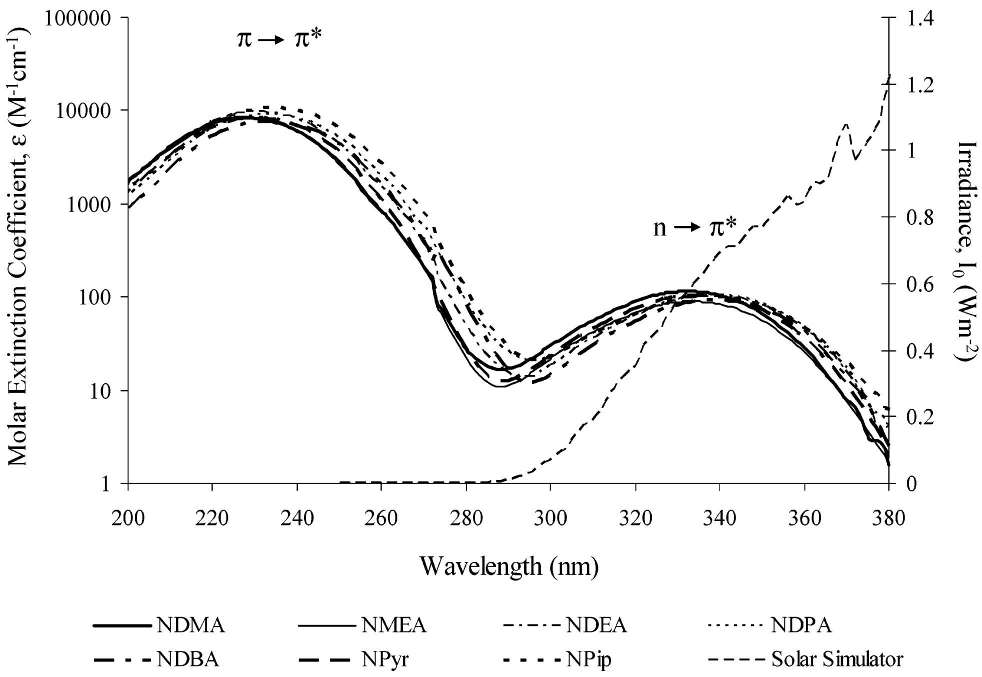

FIGURE 1. Absorption spectra for selected nitrosamines in Milli-Q water. Irradiance of the photosimulator used for photolysis experiments is shown on the secondary *y* axis.

dates from the California Irrigation Management Information System (CIMIS) online database (*32*) for an Irvine monitoring station located just 17 miles from OCWD WF-21. The database also reports total irradiance, which was used to adjust the SMARTS irradiance calculated for each wavelength and thus allowed a correction for cloud cover. Other required inputs included total ozone column and turbidity, which were estimated from historical data available from the Royal Netherlands Meteorological Institute (KNMI) Global Ozone Monitoring Experiment (GOME) (*33*) and using recent Irvine weather reports of visibility, respectively. An "urban" model was selected as the aerosol model.

Given irradiance data predicted by SMARTS, expected rates of NDMA photolysis were calculated assuming a particular water depth and light screening by the water body and using the quantum yield and molar absorptivity of the compound of interest (*21*) using equations S1 and S2 (SI). The photolysis rates at nonspecific midlatitude and tropical locations were determined for water body depths of 10 cm and 1 m, and intermediate light screening by the water body was assumed. This was calculated using a spectral slope of 0.02 and $\lambda_{280} = 0.3$; a smaller spectral slope and greater reference absorbance correspond to increased light screening by the water body (*34*). An approximate channel depth was used (~ 1.1 m) for OCWD, and the UV–vis absorbance of a 2006 water sample taken from a similar stage in the treatment train was collected to determine the light screening (spectral slope = 0.03 and $\lambda_{280} = 0.1$). Rates of NDMA photodegradation were also predicted for the solar simulator experiment performed with increasing concentrations of Aldrich humic acid. The UV–vis absorbance of each solution was measured to determine the light screening, and the depth used was the inner diameter of the horizontally placed sample tubes (1.5 cm). Irradiance data (millieinsteins cm^{-1} d^{-1}) was provided by the manufacturer of the solar simulator.

Results and Discussion

UV-Visible Absorption Spectra. In agreement with literature reports (*14*, *19*), the UV–vis absorption spectra for NDMA and the other nitrosamines (Figure 1) show two absorption bands with maxima near 230 and 330 nm corresponding to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The nitrosamine absorption band near 230 nm is below the range of natural sunlight, but the less intense band at 330–340 nm overlaps with the irradiance spectrum of natural sunlight and of the photosimulator (Figure 1) and thus is responsible for the photodecay of nitrosamines in the environment. The nitrosamine absorption spectra are quite similar, which can be expected due to the structural similarity of the homologues. The molar absorptivity maxima measured for the seven nitrosamines are given in Table S2 of the SI.

Direct Photolysis and Quantum Yield. The rates of direct photolysis and quantum yields for NDMA and the other nitrosamines are reported in Table 1. All dark controls showed stable nitrosamine concentrations, confirming no unexpected loss pathways. Photolysis is quite rapid for all nitrosamines, resulting in half-lives less than 20 min for the irradiation conditions of the photosimulator. Stefan and Bolton (*14*) found zero-order kinetics for NDMA at concentrations of 0.01–1 mM (0.74–74 mg/L) and first-order kinetics at concentrations less than 0.01 mM; all rate measurements reported here were performed at less than 0.01 mM, and first-order kinetics were indeed observed.

Nitrosamine quantum yields are 10–100 times larger than that of some other photosensitive environmental contaminants, such as the pharmaceutical naproxen ($\Phi = 0.04$) (*24*) and the surfactant metabolite nonylphenol ($\Phi = 0.003$) (*23*). The quantum yield for NDMA measured in the present study for sunlight, $\Phi = 0.41 \pm 0.02$, is similar to that measured for UV photolysis studies ($\Phi \sim 0.3$) (*16–18*). Also using UV light, Ho et al. (*7*) report pH-dependent broadband quantum yields between 0.11 (>pH 7) and 0.27 (<pH 4); however, the discrepancy between this and the quantum yields reported at neutral to slightly alkaline pH ($\Phi \sim 0.3$) has been noted (*17*) and attributed to calculation error. Though the quantum yields of NDMA photodegradation for UV and natural light indicate a similar efficiency of transformation upon light absorption, a greater rate of NDMA photolysis is expected for UV irradiation because NDMA absorbs more light in the UV range ($\epsilon_{227\ \mathrm{nm}}/\epsilon_{332\ \mathrm{nm}} \sim 70$) and intensity of UV irradiation during water treatment is high.

Indirect Photolysis and Effect of Humic Acid and Oxygen. Irradiation experiments performed in surface water showed that the presence of cDOM or other photochemically

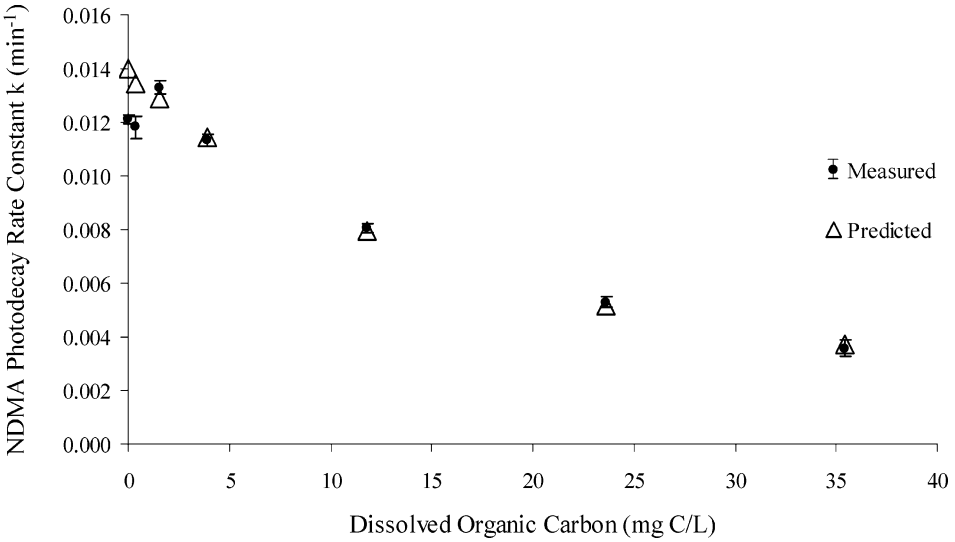

FIGURE 2. Measured and predicted NDMA photodecay rates ($[NDMA]_0 = 200\ \mu g/L$, pH 6, irradiation 250 W/m^2) with increasing DOC concentration. Error bars on measured rates are the standard error of the slope (rate).

TABLE 1. Direct Photolysis Rate Constants and Quantum Yields for Seven Nitrosamines

nitrosamine	direct photolysis[a] rate constant k_p (min^{-1}) ± SD	r^2	half life (min) ± SD	quantum yield (Φ) ± SD
NDMA	0.040 ± 0.002	0.995−0.998	16 ± 0.8	0.41 ± 0.02
NMEA	0.049 ± 0.003	0.964−0.999	15 ± 0.8	0.61 ± 0.03
NDEA	0.045 ± 0.004	0.994−0.999	15 ± 1	0.43 ± 0.04
NDPA	0.050 ± 0.004	0.974−0.994	14 ± 1	0.46 ± 0.04
NDBA	0.048 ± 0.001	0.997−0.998	15 ± 0.3	0.52 ± 0.01
NPyr	0.055 ± 0.006	0.981−0.995	14 ± 1	0.55 ± 0.06
NPip	0.057 ± 0.002	0.851−0.892	12 ± 0.5	0.51 ± 0.02

[a] Experiments performed at an irradiation of 765 W/m^2 in Milli-Q water (pH 6). Initial nitrosamine concentrations were 100 μg/L except $[NPIP]_0$= 1000 μg/L. Means and range of r^2 values are reported for $n = 3$ rate measurements, with k_p normalized by the rate of PNA decay in each experiment.

produced reactive intermediates (PPRIs) did not enhance nitrosamine photolysis via an indirect sensitization, as has been observed for some other organic contaminants. In fact, the rapid nitrosamine decay tended to be slower in the presence of DOM, indicative of light screening. In nearly all cases the rate difference was too slight to be statistically significant for the tested surface water (P value < 0.05, two-sided t test), except for NDEA (13% rate decrease) and NDBA (7% rate decrease). To rule out a possible effect of the pH difference between Milli-Q (pH 6) and the surface water (pH 8.5), NDMA photolysis in Milli-Q water at pH 8.5 was also measured and was not significantly different. To further investigate the importance of light screening, NDMA was irradiated in the presence of a range of DOC concentrations using Aldrich humic acid dissolved in Milli-Q water. Increasing DOC concentration led to a decrease in the photodecay rate (Figure 2) rather than an enhancement via indirect photolysis, as confirmed by the agreement of the measured and predicted photodecay rates calculated using the light screening factor measured for each DOC solution.

A preliminary investigation for NDMA, NMEA, NDEA, and NDPA showed that oxygen (oxygen-sparged compared to helium-sparged solutions) did not significantly enhance or slow the rapid nitrosamine photolysis rate. An increase in the quantum yield under oxygen saturation was not expected for the nitrosamines under simulated sunlight conditions: Although the excited $\pi \rightarrow \pi^*$ transition state of NDMA reacts with oxygen, the $n \rightarrow \pi^*$ transition (induced by absorbance near $\lambda_{max} \sim 330$ nm in the range of natural sunlight) does not (*16*).

Photolysis Products. Several products including methylamine, dimethylamine, nitrate, nitrite, and formate were produced from NDMA photodegradation under simulated sunlight. Methylamine and nitrite were the dominant nitrogen-containing species, and relatively little formate was produced compared to the other products. A complete nitrogen mass balance was maintained throughout the experiment, and the products observed accounted for 80−90% of the carbon from NDMA (Figure 3). An additional product, formaldehyde, is also expected but was not monitored. It may account for the remaining carbon.

The products observed in the present study as well as formaldehyde have been detected in NDMA photolysis studies using UV light (*1*, *14*). The similarity between products observed for natural and UV light is consistent with a study of other nitrosamines by Chow et al. (*19*) for acidic conditions and with computational predictions by Peláez et al. (*35*), in which products resulting from excitation of the $\pi \rightarrow \pi^*$ transition band are also produced for the $n \rightarrow \pi^*$ excitation. Pathways for product formation from NDMA to dimethylamine or methylamine have been described elsewhere (*14*−*16*, *36*), and are influenced by NDMA concentration, dissolved oxygen, and pH. Lee et al. (*15*) report that high NDMA concentration and acidic conditions favor the formation of dimethylamine, and note that at NDMA concentrations expected in wastewater, methylamine is the major expected amino product with only trace amounts of dimethylamine generated.

Extrapolation to Environmental Conditions. Aquatic photolysis rates in real environmental systems may be different from laboratory measurements depending upon actual solar irradiance, the light screening by the water body of interest, and the water depth. However, if the quantum yield and molar absorptivity of the chemical are known,

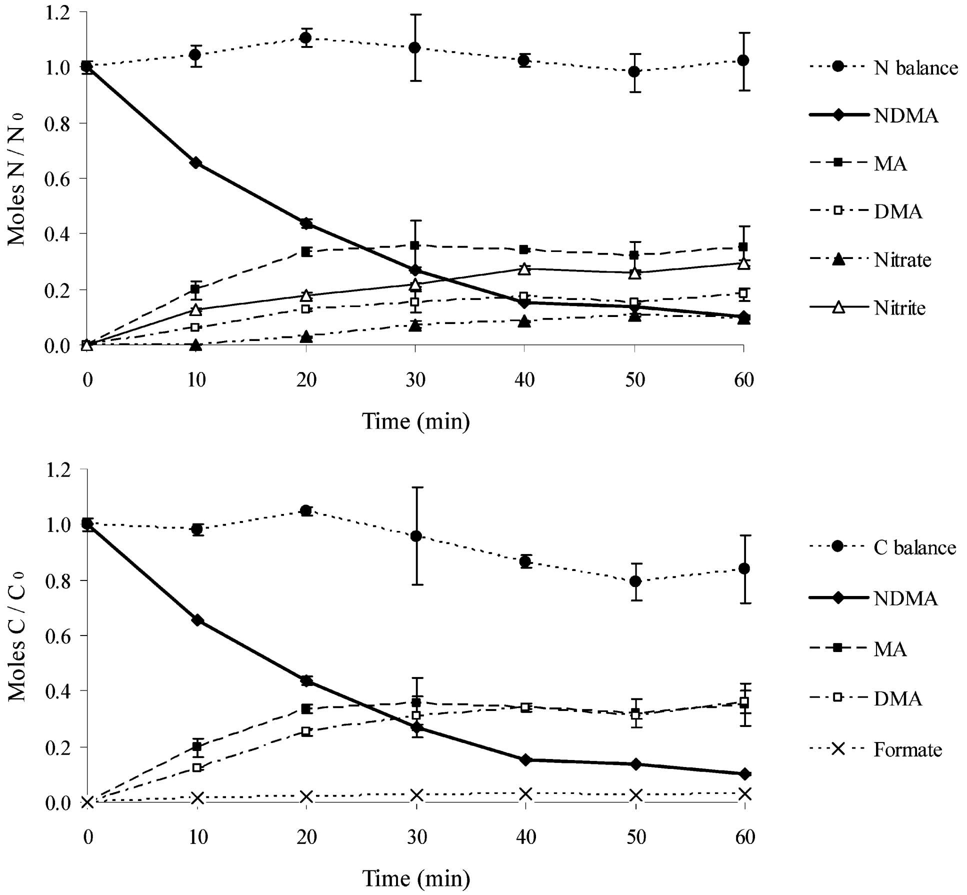

FIGURE 3. NDMA disappearance ([NDMA]$_0$ = 500 μg/L, pH 6), nitrogen and carbon balances, and product formation during irradiation (765 W/m^2) using simulated sunlight. Error bars = 2SD.

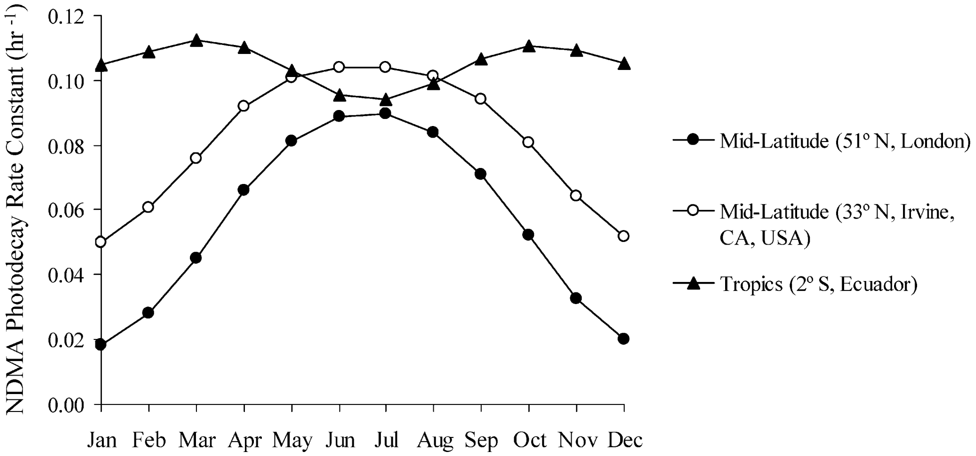

FIGURE 4. Average NDMA photodecay rate constants predicted for midday solar irradiance in midlatitude and tropical zones in surface water with intermediate light screening and a depth of 1 m.

photolysis rates in the field can be estimated for the conditions of a particular site. Figure 4 shows the average photodecay rate constant estimated for NDMA in a nonspecific surface water with a depth of 1 m and intermediate light screening by the water (spectral slope = 0.02 and λ_{280} = 0.3, ref *34*). Midday solar irradiance was modeled using SMARTS for three locations representing a range of latitudes from January to December. The predicted rates shown in Figure 4 correspond to half-lives over the year of 8–38 h in London (51° N latitude), 7–14 h in Irvine (33° N latitude, the location of the OCWD site), and 6–7 h in Ecuador (2° S latitude). If the depth of the water body is reduced to 10 cm, the half-lives (corresponding to an average rate over the depth) are reduced by a factor of approximately 10. Thus for a typical river, depending upon the depth, solar irradiation, and light screening of the water, reaching an NDMA concentration attenuated by one half-life will require (sunlit) travel times of hours to a few days. This is consistent with a report by Pehlivanoglu-Mantas and Sedlak (*37*) for the effluent-dominated Santa Ana River (CA), in which a decrease in NDMA corresponding to approximately one half-life from the upstream wastewater treatment plant effluent (24 ng/L) to <10 ng/L downstream was observed after a 10 h residence time. Gross et al. (*38*) report the increased attenuation of

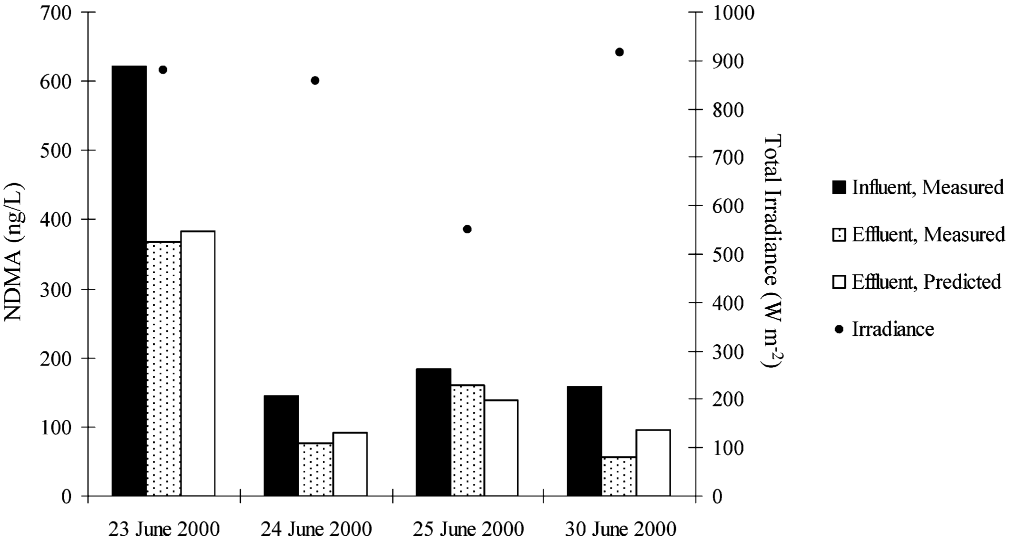

FIGURE 5. NDMA concentration in tertiary treated wastewater in sunlit channels (83 min residence time) measured by OCWD at WF-21 in June of 2000 (*31*). Predicted effluent concentrations, calculated from the modeled solar irradiance at the site and expected photodecay rate, are also shown.

trace organic contaminants for the same river compared to the nearby Prado Wetlands; given the reduced NDMA photolysis rate expected with increasing DOC via light screening (Figure 2) and the greater DOC typically found for wetlands over rivers, shallow rivers may also be expected to outperform wetlands with regard to NDMA attenuation.

In addition to estimating the removal of trace organics in rivers and wetlands, it may be useful to predict the natural photolysis expected in engineered systems. Using historical data obtained from OCWD for tertiary treated effluent in a series of shallow, sunlit channels at WF-21 in June of 2000 (*31*), NDMA photolysis rate was modeled and compared to measured influent and effluent concentrations. If the major loss of NDMA for surface water systems is through direct photolysis, as may be expected from the relative unimportance of biodegradation, sorption, and indirect photolysis, then the effluent concentrations should be predicted by the photolysis model. Figure 5 presents the monitoring data collected by OCWD. From influent and effluent samples taken approximately according to the channel residence time (1 h 23 min), a mean of 41 ± 22% removal was observed for four different days. The measured effluent concentrations agree with those predicted by the model (Figure 5), indicating that direct photolysis is the primary attenuation mechanism. Predicted effluent concentrations were calculated from expected photolysis rates determined using the solar irradiance for each of the monitored days in June, the estimated light screening by the water, and channel depth (~1.1 m). June 25 had the lowest irradiance (likely a cloudy day), resulting in a lower percent removal of NDMA. Excluding the cloudy day, the mean NDMA half-life in the engineered channels was 1.4 ± 0.5 h.

Biodegradation half-lives reported for NDMA range from 4 to 6 days in groundcover and turfgrass soils (*11*), 11−39 days in soil slurries (*13*), to persistence in some soils and bog sediments (*9*, *39*). These rates agree with our data for surface water microcosms ($t_{1/2}$ = 31 ± 19 (SD) *d*; see SI). While these results indicate that NDMA biodegradation is slow ($t_{1/2} \sim$ days) compared to photolysis, biodegradation in a natural or artificial system will make a significant contribution to overall attenuation under certain circumstances. One such example is groundwater recharge systems, which exclude light and are likely to have long residence times. Without adequate mixing, average photolysis rates in surface water systems will be greatly reduced for water bodies in which a significant fraction of the NDMA-contaminated water occurs below the photic zone. However, even at depth and for relatively low levels of solar irradiation, the predicted half-life for NDMA ($t_{1/2}$ = 8−38 h over 1 m depth at 244−855 W/m^2, 51° N latitude, Figure 4) is significantly shorter than that predicted for biodegradation in surface water.

Acknowledgments

This research was funded by the Santa Clara Valley Water District (CA), the California Department of Water Resources, the WateReuse Foundation, and the National Science Foundation Graduate Research Fellowship program. We thank Andy Heidlberger for assistance in the laboratory, Kristopher McNeill (University of Minnesota) for helpful comments, and Greg Woodside (Orange County Water District) for providing the NDMA WF-21 data. Any opinions, findings, conclusions, and recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the sponsoring agencies.

Supporting Information Available

Describes the calculation of aquatic photolysis rates and results of NDMA biodegradation in surface water microcosms. Also provided are details of the chemicals, materials, and analytical methods as well as a table summarizing nitrosamine structure and occurrence. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review April 6, 2007. Revised manuscript received June 28, 2007. Accepted June 29, 2007.

ES070818L

Supporting Information for:

Photochemical Attenuation of *N*-Nitrosodimethylamine (NDMA) and Other Nitrosamines in Surface Water

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Environmental Science & Technology

01 June, 2007

No. of Pages: 10

No. of Figures: 1

No. of Tables: 3

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Materials

Methanol and acetonitrile (HPLC grade), sodium nitrate, and sodium nitrite were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Ammonium acetate was purchased from Mallinckrodt (Phillipsburg, NJ, USA). *N*-nitrosodimethylamine (NDMA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-n-propylamine (NDPA), and *N*-nitrosopiperidine (NPip) were purchased from Supelco (Bellefonte, PA, USA). *N*-nitrosomethylethylamine (NMEA) and *N*-nitrosodi-n-butylamine (NDBA) were purchased from Ultra Scientific (North Kingstown, RI, USA). *N*-Nitrosopyrrolidine (NPyr), 4-nitroanisole (PNA), dimethylamine hydrochloride, sodium azide, and humic acid (sodium salt) were purchased from Aldrich (St. Louis, MO, USA), and NDMA-d_6 99.8% from CDN isotopes (Pointe-Claire, Canada). Methylamine hydrochloride and formic acid were purchased from Sigma (St. Louis, MO, USA). Pyridine was obtained from MP Biomedicals (Solon, OH, USA). Helium (99.9%) and oxygen (99.6%) were purchased from Praxair (Santa Clara, CA, USA).

Upper Silver Creek (San Jose, CA, USA) surface water (dissolved organic carbon, 1.8 mg/L; pH 8.5; nitrate, 6.1±0.7 mg/L measured at site prior to experiments) used for indirect photolysis experiments and microcosm preparation and secondary effluent from the Orange County Sanitation District (OCSD) were collected using 1 L glass, amber bottles (I-CHEM; Rockwood, TN, USA) and filtered with 0.45 μm nylon membranes from Supelco (Bellefonte, PA, USA).

Milli-Q water was generated using a Synergy 185 Millipore with Simpak2 purifying system (Billerica, MA, USA).

Calculation of Aquatic Photolysis Rate

The rate of aquatic photolysis in the environment may be predicted from solar irradiance and the known quantum yield as follows (1):

$$k_p^c(\lambda) = \Phi_i k_a(\lambda) \tag{S1}$$

$$k_a(\lambda) = \frac{I_0(\lambda)\varepsilon_i(\lambda)(1-10^{-\alpha_D(\lambda)z_{mix}})}{z_{mix}\alpha(\lambda)} \tag{S2}$$

where $k_p^c(\lambda)$ is the first-order direct photolysis rate constant; Φ_i is the quantum yield of compound i; $k_a(\lambda)$ is the specific rate of light absorption; $I_0(\lambda)$ is the incident solar irradiation; $\varepsilon_i(\lambda)$ is the molar extinction coefficient of compound i; $\alpha(\lambda)$ is the beam attenuation coefficient of the water body; $\alpha_D(\lambda)$ is the apparent attenuation coefficient (where $\alpha_D(\lambda) = D(\lambda)\alpha(\lambda)$; $D(\lambda)$ is the distribution function for light scattering in the water body, and is approximately 1.2 for nonturbid, shallow waters) and z_{mix} is the mean depth.

Analyses

UV-Visible (UV-Vis) absorption spectra of nitrosamine solutions prepared in replicate or triplicate were measured in Milli-Q water using a UVIKON UV-Vis spectrophotometer (Bio-Tek Instruments, Inc.; Winooski, VT, USA) or a Cary 50 UV-Vis spectrophotometer (Varian, Inc.; Palo Alto, CA, USA). NDBA was measured in 10% methanol due to its low solubility in water; increasing methanol concentration led to a shift in the absorption peaks.

Analysis of PNA was performed using an Agilent (Santa Clara, CA, USA) 1100 Series HPLC system equipped with an autosampler and UV-Vis detector based on the method described by Dulin and Mill (2). Reverse-phase chromatographic separation was performed using an Alltech

(Nicholasville, KY, USA) Adsorbosphere HS C18 column (length, 250 mm; inner diameter, 4.6 mm; film thickness, 5 μm) with 60/40 acetonitrile/water as the mobile phase. A PNA stock solution was prepared in acetonitrile from which calibration solutions were prepared in Milli-Q water over a range of 0.125 to 2 mg/L PNA.

Nitrosamines analysis was performed by directly injecting water samples onto a high performance liquid chromatography-tandem mass spectrometer (HPLC-MS/MS) using the method described by Plumlee et al. (3). Instrument detection limits were 2 μg/L for NDMA and 2 to 25 μg/L for other tested nitrosamines. Samples (50 μL) were injected on a Shimadzu (Columbia, MD, USA) HPLC system equipped with a SIL-10ADvp autosampler and a LC-10ADvp pump, with detection via a Sciex API 3000 triple-stage quadrupole MS (Applied Biosystems, Foster City, CA, USA) operated in multiple reaction-monitoring (MRM) transition mode. Precursor-product transitions, declustering potential, collision energy, and collision cell exit potential for each nitrosamine are given in Plumlee et al. (3). Chromatographic separation was carried out using a Higgins Analytical (Mountain View, CA, USA) reverse-phase C18 column (length, 40 or 75 mm; inner diameter, 2.1 mm; film thickness, 5 μm) and a HAIPEEK C18 guard column (Higgins Analytical). Methanol and 2 mM ammonium acetate buffer in Milli-Q water were used as the mobile phase at a flow rate of 0.15 mL/min using the following program: 10% methanol to 45% methanol over 4 min, to 100% methanol at 5 min, held until 10 min, and finally returned to 10% methanol (3). A mixed stock solution of the nitrosamines was prepared in Milli-Q water and diluted to obtain calibration standards over a range of 0.1 to 1000 μg/L. Samples and standards were prepared for LC-MS/MS analysis by adding NDMA-d_6 (110 μg/L) as an internal standard at a ratio of 0.3:1 internal standard volume/sample volume. Ion suppression tests were carried out to confirm that nitrosamine signals were not being suppressed in the surface water or humic acid solutions by matrix materials which may compete for ionization. All photosensitive samples and standards were protected from light before analysis.

For the product study, nitrogen and carbon balances were determined by converting NDMA and its products to moles of nitrogen or carbon and normalizing by the initial nitrogen or carbon moles of NDMA. Nitrate, nitrite, and formate were analyzed using ion chromatography and dimethylamine and methylamine were analyzed alongside NDMA using LC-MS/MS. To determine the MRM transitions of methylamine and dimethylamine, standard solutions were infused into the MS and operating parameters were optimized. In both cases, significant fragmentation of the parent compounds were not observed due to their low molecular weights. The ionized parent compound was instead monitored (32.1 and 46.1 for methylamine and dimethylamine, respectively) for quantitation. For dimethylamine, however, the transitions 46.1/31.1 and a weak 46.1/30.3 were observed and thus used for confirmation. Instrument detection limits for methylamine and dimethylamine were approximately 80 and 40 μg/L, respectively. Using the same chromatographic method as for the nitrosamines, methylamine eluted at 1.9 min and dimethylamine at 2.0 min.

NDMA Biodegradation in Microcosms

To assess NDMA biodegradation in surface water and sediment, triplicate aerobic microcosms were prepared using creek water or 10:1 creek water and sediment ($f_{oc} = 0.30\%$; Huffman Laboratories, Golden, CO, USA) collected from Upper Silver Creek (San Jose, CA, USA). Sediment was sieved to remove particle sizes above 1.168 mm. Microcosms were prepared in 100 mL glass serum bottles (Supelco; Bellefonte, PA, USA) and sealed with rubber septa. For both treatments, one set of microcosms (abiotic) was sterilized with sodium azide. All microcosms were prepared in triplicate, except a duplicate set of Milli-Q water microcosms to serve as a control. Microcosms were spiked with 100 μg/L NDMA (1.3 μM) and respiked after a significant fraction or all of the NDMA was degraded. A blank microcosm which was not spiked was also prepared and sampled similarly. Resazurin was added to all microcosms as an oxygen indicator, and oxygen was bubbled into the microcosms periodically to maintain aerobic conditions. Microcosms were stored at room temperature in the dark on a shaker at 150 rpm and small volumes (120 μL) were taken from the overlying water using a sterilized syringe to monitor disappearance of NDMA. Sample aliquots were centrifuged and 100 μL was taken for analysis.

Biodegradation of NDMA was observed in the microcosms containing either surface water alone or in combination with sediment (Table S3). Disappearance of NDMA (>80%) occurred more rapidly for the microcosms with sediment at 91-127 d, compared to 127-140 d in surface water. Constant NDMA concentrations in the sterile microcosms confirmed that NDMA was not lost via an unexpected pathway (e.g. volatilization, sorption to glass or septa) or via sorption to sediment, as expected from literature reports. As further evidence for biodegradation, the disappearance rate increased following the respike of the same microcosms (Table S3). This suggests the adaptation and growth of the microbial community, resulting in a greater biodegradation rate. The responsible microorganisms were not isolated; however, the degradation is likely to be cometabolic (4, 5) and bacteria having monooxygenase enzymes have been demonstrated to degrade NDMA (5). If first-order kinetics are assumed, half-lives for NDMA biodegradation in microcosms with sediment and surface water were $t_{1/2}$ = 31±19 (SD) d and decreased to 8±5 d following the respike. These rates are within the range of half-lives reported for NDMA biodegradation, from 4-6 d in groundcover and turfgrass soils (4), 11-39 d in soil slurries (6), to persistence in some soils and bog sediments (7, 8).

Figures and Tables

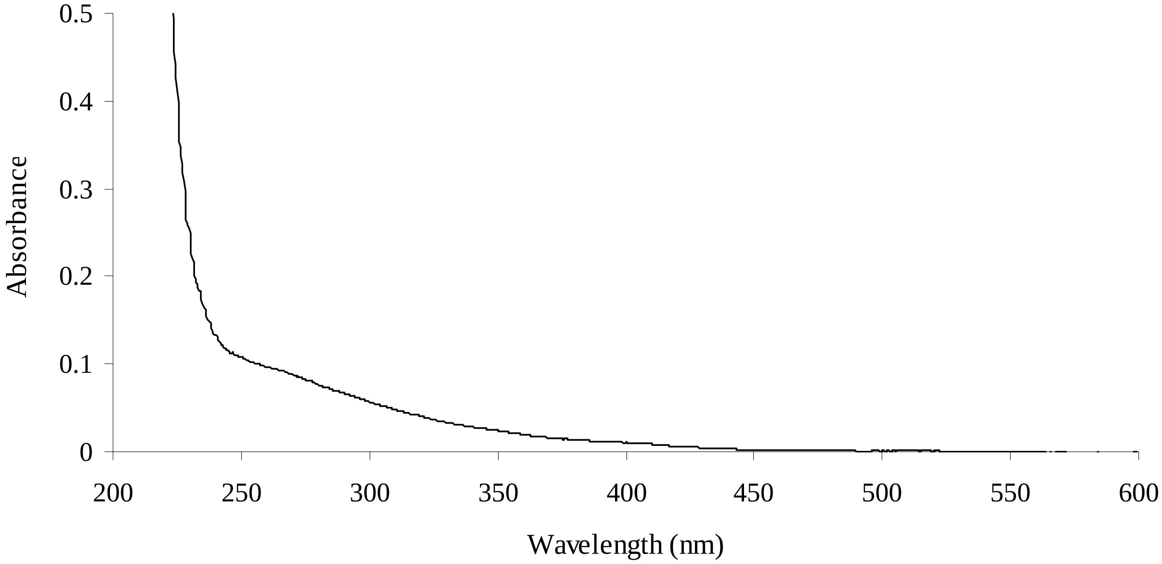


Figure S1. UV-visible spectrum of surface water used in indirect photolysis experiments.

Table S1. Structures and descriptions of selected *N*-nitrosamines.

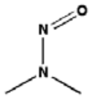
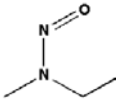
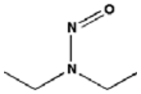
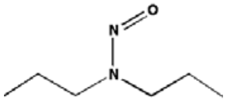
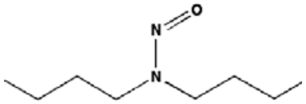
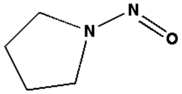
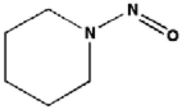
Nitrosamine	**Structure**	**Sources and Reported Occurrence**
N-Nitrosodimethylamine (NDMA)		May originate from reactions of nitrogen-containing precursors in the environment, foods, or during wastewater disinfection (9-11). Typical concentrations range from 1-10 ng/L in drinking water (12), 20-100 ng/L in wastewater effluent (3, 13) and <10-35 ng/L in rivers receiving wastewater discharge (14, 15). Increasing concentrations detected in a drinking water distribution system at 52-108 ng/L (16).
N-Nitrosomethylethylamine (NMEA)		Found in tobacco smoke and food, not known to be produced commercially (17).
N-Nitrosodiethylamine (NDEA)		Found in drinking water wells at 0.01 μg/L and DI water at 0.33 to 0.83 μg/L. Found in wastewater from chemical plants at 0.07 and 0.24 μg/L (18).
N-Nitrosodi-n-propylamine (NDPA)		Detected in wastewater from chemical plants, rubber, cheese, alcohol, cigarette smoke, and herbicides including trifluralin (18).
N-Nitrosodi-n-butylamine (NDBA)		Detected in a variety of products including soybean oil, cheese, smoked/cured meats, and cigarette smoke; also found in coke facility effluent water (18).
N-Nitrosopyrrolidine (NPyr)		Found in nitrite-preserved or contaminated foods and associated vapors and tobacco smoke; reported in wastewater from chemical factories at 0.09 – 0.20 μg/L (18). Increasing concentrations detected in a drinking water distribution system at 18-71 ng/L (16).
N-Nitrosopiperidine (NPip)		Found in cigarettes, meats, fish (due to use of sodium nitrite as a preservative) (18). Increasing concentrations detected in a drinking water distribution system at 33-118 ng/L (16).

Table S2. Molar absorptivity maxima measured for seven nitrosamines at two absorption bands.

Nitrosamine	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$)
NDMA	227	8462	332	115
NMEA	227	8203	334	90
NDEA	230	9729	337	102
NDPA	232	9094	339	104
NDBA	234	7701	339	93
NPyr	230	8465	335	106
NPip	234	10815	339	105

Table S3. Time to removal of NDMA for triplicate microcosms (M1, M2, and M3) containing surface water or surface water and sediment.

Treatment	NDMA Addition (100 μg/l)	Time to ≥80% Removal, d			$t_{1/2}$ (SD), d
		M1	M2	M3	
Surface Water (n=3)	Spike 1	127	140	140	67 (12)
	Spike 2	20	76	90	12 (13)
Surface Water + Sediment (n=3)	Spike 1	91	127	127	31 (19)
	Spike 2	20	20	34	8 (5)

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Appendix E

Plumlee, M.H., Larabee, J., Reinhard, M., 2008. Perfluorochemicals in Water Reuse. Chemosphere 72, 1541-1547.

Chemosphere 72 (2008) 1541–1547

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Perfluorochemicals in water reuse

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ARTICLE INFO

Article history:
Received 16 January 2008
Received in revised form 17 April 2008
Accepted 18 April 2008
Available online 10 June 2008

Keywords:
PFOS
PFOA
Reclaimed wastewater
Wetland
Toxicity

ABSTRACT

Faced with freshwater shortages, water authorities are increasingly utilizing wastewater reclamation to augment supplies. However, concerns over emerging trace contaminants that persist through wastewater treatment need to be addressed to evaluate potential risks. In the present study, perfluorinated surfactant residues were characterized in recycled water from four California wastewater treatment plants that employ tertiary treatment and one that treats primary sewage in a wetland constructed for both treatment and wildlife habitat. Effluent concentrations were compared with surface and groundwater from a creek where recycled water was evaluated as a potential means to augment flow (Upper Silver and Coyote Creeks, San Jose, CA). In the recycled water, 90–470 ng/l perfluorochemicals were detected, predominantly perfluorooctanoate (PFOA; 10–190 ng/l) and perfluorooctanesulfonate (PFOS; 20–190 ng/l). No significant removal of perfluorochemicals was observed in the wetland (total concentration ranged 100–170 ng/l across various treatment stages); in this case, 2-(*N*-ethylperfluorooctanesulfonamido) acetic acid (*N*-EtFOSAA), perfluorodecanesulfonate (PFDS), and PFOS were dominant. Though there is currently no wastewater discharge into the creeks, perfluorochemicals were found in the surface water and underlying groundwater at a total of 20–150 ng/l with PFOS and PFOA again making the largest contribution. With respect to ecotoxicological effects, perfluorochemical release via recycled water into sensitive ecosystems requires evaluation.

1. Introduction

With ecosystems increasingly stressed by the shortage of freshwater, treated wastewater effluent is a promising water resource for the augmentation of water-starved environments. Historically, release of treated wastewater to surface water has been commonplace given the lack of alternatives. Water recycling, however, requires consideration of a complex set of benefits and risks at sites where a natural source (rain, groundwater, rivers) is replaced or augmented with tertiary effluent. Considerations include ecological effects and contamination of potable aquifers with potentially harmful organic contaminants.

Perfluorochemicals represent one such group of contaminants. They are used in a variety of materials such as food packaging, paints, and lubricants (Kissa, 1994) and have been detected in wastewater (Alzaga and Bayona, 2004; Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006; Loganathan et al., 2007), surface water (Hansen et al., 2002; Moody et al., 2002; Boulanger et al., 2004; Boulanger et al., 2005; Simcik and Dorweiler, 2005; Rostkowski et al., 2006; Sinclair et al., 2006; Skutlarek et al., 2006; McLachlan et al., 2007; So et al., 2007), groundwater (Moody et al., 2003; Schultz et al., 2004), drinking water (Harada et al., 2003; Skutlarek et al., 2006; Paustenbach et al., 2007), and rain (Loewen et al., 2005; Scott et al., 2006). Table 1 summarizes the aquatic occurrence of two commonly detected perfluorochemicals, perfluorooctanoate (PFOA) and perfluorooctanesulfonate (PFOS).

Laboratory studies demonstrate that mammals readily absorb PFOA and PFOS during oral and inhalation exposures. They tend to distribute to the blood serum and the liver and can cross the blood-brain and placental barriers (Lange et al., 2006). Although research shows that PFOA, perfluorononanoate (PFNA), and PFOS are not estrogenic (Maras et al., 2006), high doses of PFOA and PFOS lead to mortality while lower doses result in hepatotoxic, immunotoxic, neurotoxic, and behavioral effects (Lange et al., 2006). When present in a mixture, PFOS may enhance the toxicity of other compounds by increasing cell membrane permeability (Hu et al., 2003; Jernbro et al., 2007). Perfluorochemicals bioaccumulate and have been detected in biota around the world, including fish, seals, minks, albatross, bald eagles, polar bears, and humans (Giesy and Kannan, 2002; Schultz et al., 2003). Typical concentrations of PFOA and PFOS in the serum of non-occupationally exposed humans are 3–35 and 7–82 μg/l, respectively (Hansen et al., 2001; Kannan et al., 2004). These levels are concerning given that adverse effects have been observed in rats at levels (370 μg/l PFOA) which differ from humans by less than a safety factor of 100 (Butenhoff et al., 2004; Lange et al., 2006). Wildlife monitoring studies for high trophic levels report PFOS concentrations of 8–242 μg/l serum in ringed seals (Kannan et al., 2001a), 3–34 μg/l

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doi:10.1016/j.chemosphere.2008.04.057

Table 1

Summary of perfluorochemical occurrence in wastewater, freshwater, and drinking water

Site and location	PFOA (ng/l)	PFOS (ng/l)	Other perfluorochemicals detected	Source of perfluorochemicals[a]	References
Wastewater effluent					
2 WWTPs (Catalonia, Spain)	<100–4300	n.m.	PFDA (50-8170)	Domestic and industrial influents	Alzaga and Bayona, 2004
WWTP (Iowa City, Iowa, USA)	22	26	*N*-EtFOSAA (3.6 ng/l)	Domestic influent (no known manufacturing or industrial perfluorochemical source)	Boulanger et al., 2005
10 WWTPs (USA)	3–97	1–130	PFBS, PFHxS, 6:2 FtS, PFHxA, PFNA, PFDA, FOSA	Domestic, industrial, and commercial influents	Schultz et al., 2006
6 WWTPs (New York, USA)	58–1050	3–68	PFHxS, PFNA, PFDA, PFUnDA, 8:2 FTCA, 8:2 FTUCA	Domestic, industrial, and commercial influents	Sinclair and Kannan, 2006
Reclaimed wastewater, 4 WWTPs (California, USA)	12–185	20–187	PFHxS, PFDS, PFHxA, PFHpA, PFNA, PFDA, 6:2 FtS, FOSA, *N*-EtFOSAA	Domestic, industrial, and commercial influents	present study, 2007
Surface water					
Tennessee river (Decatur, AL, USA) upstream and downstream of fluorochemical manufacturing facility	Upstream: <25; Downstream: <25–513	Upstream: 17-53; Downstream: 30–140	n.m.	Fluorochemical manufacturing facility	Hansen et al., 2002
Etobicoke Creek (Toronto, Ontario, Canada) upstream and downstream of fluorochemical spill over time	Upstream: n.d.-33; downstream: n.d.-10 600	Upstream: n.d.; downstream: n.d.-995 000	PFHxS	Accidental spill of aqueous film-forming foams (AFFFs)	Moody et al., 2002
Lake Erie and Lake Ontario (USA), urban and remote locations	27–50	21–70	*N*-EtFOSAA (4.2–11 ng/l), FOSA (0.6–1.3 ng/l), PFOSulfinate (n.d.-17 ng/l)	Not stated	Boulanger et al., 2004
River (Iowa City, Iowa, USA)	8.7	23	*N*-EtFOSAA (1.2 ng/l)	Wastewater effluent	Boulanger et al., 2005
"Remote" lakes (Lake Superior, Minnesota, USA; Voyageurs National Park lakes, Canada)	0.1–0.7	n.d.-1.2	PFHxA, PFHpA, PFNA	Atmospheric deposition	Simcik and Dorweiler, 2005
"Urban" waters (3 lakes in Minneapolis and Minnesota River in Minnesota, USA)	0.5–19	2.4–47	PFHxA, PFHpA, PFNA, PFDA	Urban location, runoff, and wastewater discharge	Simcik and Dorweiler, 2005
Lake Michigan (USA)	0.3–3.4	0.9–3.1	PFHpA	Non-atmospheric sources	Simcik and Dorweiler, 2005
Streams, lake in Shihwa and Banweol industrial areas, South Korea	0.9–62	2.2–651	PFBS, PFHxS, FOSA, PFHxA, PFHpA, PFDA	Local industrial sources	Rostkowski et al. (2006)
Surface waters of New York state, USA	<0.5–7.4	<0.8–756	PFHxS	Industrial and municipal wastewater effluent	Sinclair et al., 2006
Rhine river, Moehne river, and their tributaries (Germany)	2–48 (Rhine); 11–33 900 (Moehne)	2–26 (Rhine); 2–5900 (Moehne)	PFBS, PFBA, PFPnA, PFHxA, PFHpA	Superficial run-off from waste materials applied to agricultural areas upstream; wastewater discharge	Skutlarek et al., 2006
Tributaries of the Pearl and Yangtze Rivers (China)	0.85–260	<0.01–99	PFBS, PFHxS, FOSA, PFHxA, PFHpA, PFNA, PFDA, PFUnA	Industrial and municipal wastewater effluent	So et al., 2007
European rivers including Po, Rhine, Danube, Elbe, Oder, Seine, and Loire	200 (Po River) <0.65–23 (other rivers)	n.m.	PFHxA, PFHpA, PFNA	Fluoropolymer manufacturing facilities present in Po watershed; wastewater effluent is a likely source for the other rivers	McLachlan et al., 2007
Constructed wetland receiving reclaimed wastewater (California, USA)	9–14	19–29	PFHxS, PFDS, PFHxA, PFHpA, PFNA, PFDA, FOSA, *N*-EtFOSAA	Wastewater effluent	Present study, 2007
Upper Silver and Coyote Creeks (San Jose, CA, USA)	8–36	5–56	PFHxS, PFDS, PFHxA, PFHpA, PFDA, FOSA, *N*-EtFOSAA	Urban location, runoff, and atmospheric deposition	Present study, 2007
Groundwater					
Wurtsmith air force base (Michigan, USA)	8000–105 000	4000–110 000	PFHxS, PFHxA	Past fire-training exercises using AFFFs	Moody et al., 2003
Wurtsmith (Michigan, USA) and Tyndall (Florida, USA) Air Force Bases	3000–6 570 000	4000–2 300 000	4:2 FtS, 6:2 FtS, 8:2 FtS	Past fire-training exercises using AFFFs	Schultz et al., 2004
Monitoring wells near Upper Silver and Coyote Creeks (San Jose, CA, USA)	n.d.-18	19–87	PFHxS, PFDS, PFHxA, PFHpA, PFDA, FOSA, *N*-EtFOSAA	Infiltration from overlying urban stream, possibly other sources	Present study, 2007
Rainwater					
Winnipeg, Manitoba, Canada	n.d.	0.6	FTCAs, FTUCAs	Degradation from volatile fluorotelomer alcohols and other precursors	Loewen et al., 2005

Table 1 (*continued*)

Site and location	PFOA (ng/l)	PFOS (ng/l)	Other perfluorochemicals detected	Source of perfluorochemicals[a]	References
4 urban sites (2 USA, 2 Canada) and 5 rural/remote sites (2 USA, 3 Canada)	<0.1–89 (urban); <0.1–10 (rural)	n.m.	TFA, PFPrA, PFBA, PFPnA, PFHxA, PFHpA, PFNA, PFDA, PFUnA, PFDoA, FTCAs, FTUCAs	Degradation from volatile fluorotelomer alcohols	Scott et al., 2006
Drinking water					
Japan (four cities)	n.m.	0.1–51	n.m.	Sourced from Tama River	Harada et al., 2003
Ruhr area (Germany)	n.d.-519	n.d.-22	PFBS, PFBA, PFPnA, PFHxA, PFHpA	Sourced from rivers contaminated by land application of waste materials, see above	Skutlarek et al., 2006
Outside the Ruhr area (Germany), Paris (France), Hampshire (Great Britain)	n.d.-4 (outside Ruhr); n.d. (Paris, Hampshire)	n.d.-6 (outside Ruhr); n.d. (Paris, Hampshire)	PFPnA, PFHxA	Not stated	Skutlarek et al., 2006
West Virginia, USA measured over 1984–2004	58-4800	n.m.	n.m.	Sourced from groundwater contaminated by nearby Dupont facility	Paustenbach et al., 2007

[a] Known or suggested by authors of study.

blood in albatross (Kannan et al., 2001b), and 0.8–74 μg/l serum in red panda (Dai et al., 2006). Morikawa et al. (2006) report both the serum and aquatic concentrations of PFOS for turtles collected in a Japanese river, reporting 2–486 μg/l in the serum and 3–37 ng/l in the nearby water.

Because of the persistence of perfluorochemicals in wastewater treatment (Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006) and their expected bioaccumulation, the occurrence of these compounds must be considered in wastewater and wastewater reclamation, especially where humans or wildlife may be exposed. To this end, a range of perfluorochemicals (Fig. 1) were determined in recycled water and in two unique water recycling operations: a wetland constructed using wastewater for both treatment and habitat creation, and an urban stream evaluated for flow augmentation using recycled water. Results are interpreted based on literature evaluations of perfluorochemical toxicity.

2. Experimental

Reclaimed wastewater was collected in June 2007 from four California (USA) wastewater treatment plants (WWTP 1, 2, 3, and 4) that produce tertiary treated effluent for landscape irrigation and other reuse purposes. Grab samples were collected following tertiary treatment.

Water samples were also collected from a constructed wetland (California, USA) that receives primary treated wastewater

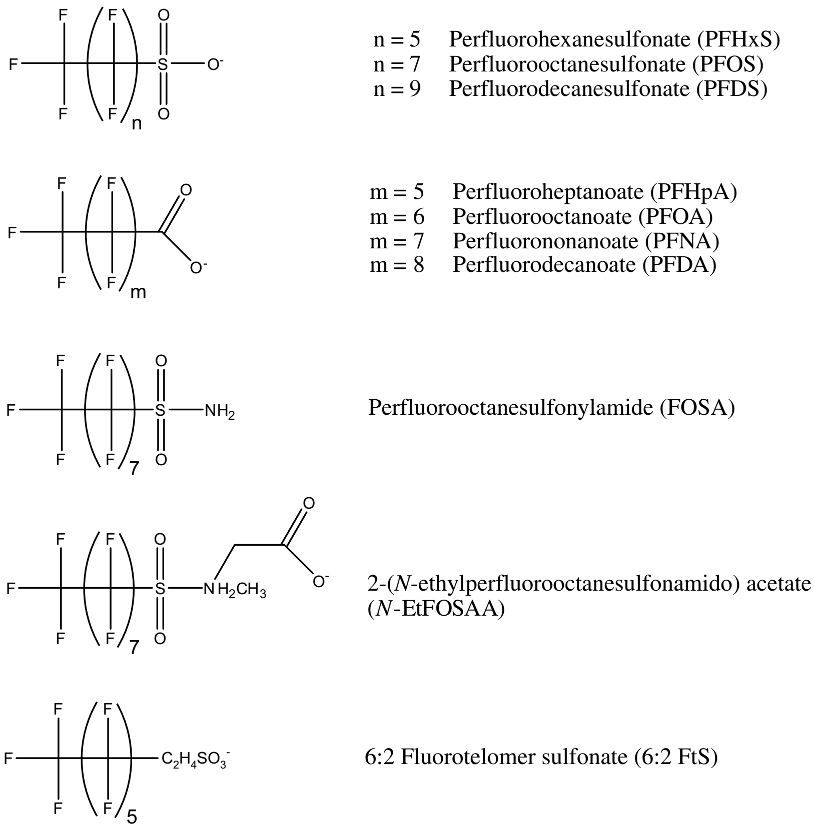

Fig. 1. Perfluorochemicals monitored in the present study.

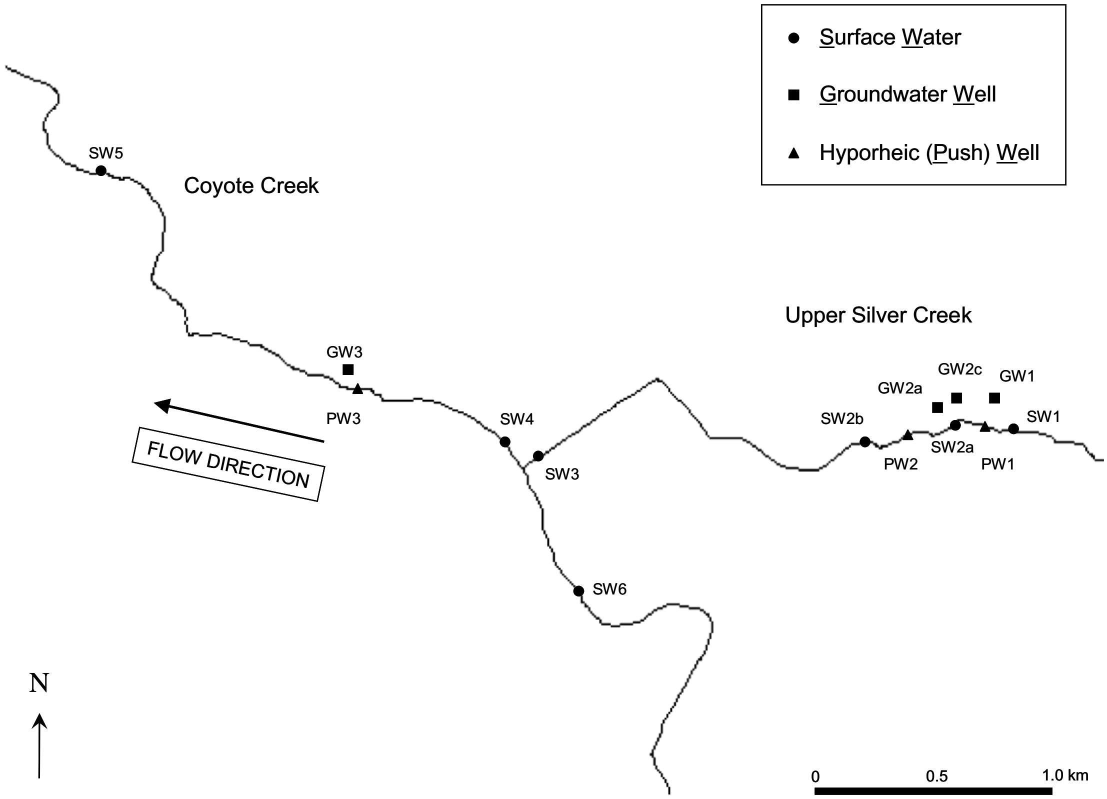

Fig. 2. Map of San Jose (CA) creek study reach, indicating surface water, groundwater, and hyporheic zone (push well) sampling sites. Creek flows northwest, eventually reaching the San Francisco Bay.

Table 2
Perfluorochemicals (ng/l) in reclaimed wastewater from four California treatment plants and in consecutive stages of a constructed wetland for wastewater treatment and wildlife habitat

Sample	PFHxS	PFOS	PFDS	PFHpA	PFOA	PFNA	PFDA	6:2 FtS	FOSA	*N*-EtFOSAA	Total PFCs
Reclaimed wastewater											
WWTP 1[a]	24	38	9.0	8.8	36	n.d. (<10)	11	11	2.8	11	150
WWTP 2[b]	17	190	n.d. (<2)	13	180	32	7.5	n.d. (<4)	3.2	23	470
WWTP 3[c]	6.5	20	n.d. (<2)	21	190	14	11	n.d. (<4)	4.8	5.5	270
WWTP 4[d]	8.0	42	3.3	5.6	12	n.d. (<10)	n.d.	n.d. (<4)	2.1	12	90
Constructed wetland using primary treated wastewater											
Oxidation pond influent	3.4	23	36	n.d. (<4)	14	9.1	3.4	n.d. (<4)	8.8	48	150
Oxidation pond effluent	3.2	21	23	n.d. (<4)	13	7.8	n.d. (<2)	n.d. (<4)	6.9	69	140
Treatment marsh effluent	3.0	25	29	n.d. (<4)	12	5.4	n.d. (<2)	n.d. (<4)	6.9	59	140
Enhancement marsh 1 influent	3.2	23	14	n.d. (<4)	11	3.3	n.d. (<2)	n.d. (<4)	5.3	40	100
Enhancement marsh 1 effluent	3.3	19	10	16	9.1	3.0	n.d. (<2)	n.d. (<4)	4.5	41	110
Enhancement marsh 3 effluent	3.2	29	36	n.d. (<4)	11	3.5	n.d. (<2)	n.d. (<4)	7.4	85	170

Values are the mean of duplicate samples (mean percent difference between duplicate samples was 21%).

[a] Tertiary treatment via dual media filtration and chlorination, followed by polymer treatment and repeated filtration for reclaimed wastewater.

[b] Tertiary treatment via dual media filtration and chloramination, followed by additional chloramination for reclaimed wastewater.

[c] Tertiary treatment via dual media filtration and chlorination.

[d] Tertiary treatment via fixed growth reactor (ammonia removal), flocculation, dual media filtration, and chlorination, followed by additional flocculation, dual media filtration, and chlorination for reclaimed wastewater.

(clarification and solids digestion) and discharges to the ocean. In addition to fulfilling treatment requirements for discharge, the wetland provides community recreation and wildlife habitat. Grab samples were taken in February 2006 from treatment stages including the oxidation ponds, treatment marshes, and enhancement marshes. Chlorination and dechlorination occur prior to the enhancement marshes. The hydraulic retention time of each stage varies from 1 to 2 months for the oxidation ponds, approximately 2 days for the treatment marshes, and nearly 10 days for the enhancement marshes.

In addition, grab samples of surface water were collected from several sites along Coyote Creek and a tributary, Upper Silver Creek, over a reach (Fig. 2) of approximately 5 km in San Jose, CA (USA) in May 2006 and June 2007. The Santa Clara Valley Water District (San Jose, CA, USA) was investigating the site for a potential flow augmentation with reclaimed wastewater; perfluorochemicals were evaluated in the creeks and reclaimed wastewater (from WWTP 2) to characterize baseline conditions. Nearby groundwater samples were obtained from four monitoring wells (GW1, 2a, 2c, and 3) installed to depths of 5–10 m. Depth-to-water ranged 2–5 m for the four wells. Very shallow “push” wells (PW1, 2, and 3) were also installed in or adjacent to the creek. The push wells were installed at a depth of just 0.6–0.9 m to capture young groundwater in the hyporheic zone, a region in which surface and groundwater exchange and flow velocity, relative to the surface, is reduced by orders of magnitude (Hoehn and Cirpka, 2006). In order to use temperature as a tracer for hydraulic residence time (Anderson, 2005), temperature monitors were installed at selected surface water sites and in push wells. The results from this survey represent background, pre-augmentation conditions for the site.

Samples and blanks were analyzed by direct, large-volume injection using liquid chromatography-tandem mass spectrometry (Higgins et al., 2005; Schultz et al., 2006). Analytical details may be found in the supplementary information.

3. Results

3.1. *Perfluorochemicals in four reclaimed wastewaters*

Perfluorochemicals were measured in reclaimed wastewater from four California treatment plants. Following primary and secondary treatment, the reclaimed wastewaters were treated using the tertiary treatments listed in Table 2. Nearly all of the perfluorochemicals monitored were detected in all wastewaters (Table 2). As evidenced by the detections, perfluorochemicals persisted beyond the tertiary treatment steps. Summing the ten perfluorochemicals, the total concentration ranged from 90 to 470 ng/l across the effluents. PFOS and PFOA made the largest contributions to the total, at 7.6–46% and 13–68%, respectively. The perfluorochemical concentrations are consistent with reports for other municipal wastewaters (Table 1), which vary between plants (Alzaga and Bayona, 2004; Boulanger et al., 2005; Schultz et al., 2006; Sinclair and Kannan, 2006).

3.2. *Perfluorochemicals in a constructed wetland receiving primary treated wastewater*

Perfluorochemicals were also measured at various treatment stages of a constructed wetland sustained using wastewater. All ten perfluorochemicals were detected (Table 2), with the exception of 6:2 FtS, which was not detected at any stage. No significant removal of the perfluorochemicals was observed across wetland treatment. Although PFOA and PFOS are often found in the highest concentrations compared to other perfluorochemicals in wastewaters, in this case PFDS and 2-(*N*-ethylperfluorooctanesulfonamido) acetic acid (*N*-EtFOSAA) were found at greater concentrations. According to a recent study by Rhoads et al. (2008), higher concentrations of *N*-EtFOSAA rather than PFOS in wastewater effluent are expected given the biodegradation kinetics of 2-(*N*-ethylperfluorooctanesulfonamido) ethanol (*N*-EtFOSE), a precursor to *N*-EtFOSAA that is used in protective paper coatings. *N*-EtFOSAA then biodegrades to PFOS, but more slowly. Few monitoring studies include PFOS-precursors like *N*-EtFOSAA; Boulanger et al. detected 3.6±0.2 ng/l *N*-EtFOSAA in WWTP effluent compared to 26±2.0 ng/l PFOS (2005). Because PFOS and PFOA are directly discharged to treatment plants (Prevedouros et al., 2006), their concentrations in most wastewaters may exceed precursors.

3.3. *Perfluorochemicals in an urban creek and groundwater*

Perfluorochemicals were detected in an urban stream evaluated for flow augmentation using reclaimed wastewater, as well as in the underlying groundwater (Table 3). Upper Silver Creek sites (2007) showed a range of 126–145 ng/l total perfluorochemicals. This would increase to approximately 300 ng/l during augmentation with reclaimed wastewater (WWTP 2) given a flow regime of equal parts wastewater and surface flow.

The concentrations found downstream of the confluence of Upper Silver and Coyote Creeks are a result of mixing of the upstream contributions: downstream PFOS and PFOA levels are within 10–30% of those predicted using flow measurements (data not shown). The source of perfluorochemicals to these two creeks is unknown, but is likely to be a combination of atmospheric deposition of volatile precursors (Ellis et al., 2004; Simcik and Dorweiler, 2005; Martin et al., 2006) and surface runoff. There is currently no known upstream wastewater discharge into either creek. Results are consistent with the urban surface water sites characterized by Simcik and Dorweiler (2005), which ranged from 2–47 ng/l PFOS to 0.5–20 ng/l PFOA (compared to remote sites with n.d.-1.2 ng/l PFOS and n.d.-0.7 ng/l PFOA).

The concentrations detected in the hyporheic zone were typically consistent with the nearby creek water (Table 3), indicating that the hyporheic zone was supplied by the overlying creek and that negligible perfluorochemical attenuation occurred in the hyporheic zone. Analysis of temperature data for select sites indicated a hyporheic residence time of 15–60 min (Hoehn et al., 2007). No significant attenuation was expected in the hyporheic zone, nor with distance downstream, as the perfluorochemicals monitored resist biodegradation and sorption is limited (Giesy and Kannan, 2002; Prevedouros et al., 2006).

Groundwater wells near the creeks showed perfluorochemical detections in all samples and generally on the order of the creek concentrations. PFOS ranged 19–192 ng/l and PFOA n.d.-22 ng/l in the four groundwater wells monitored in 2006 and 2007. The source of perfluorochemicals to the groundwater is not entirely clear. Although head measurements indicate that the stream is a losing stream, the groundwater sampled is not necessarily recharged from the creek alone. For instance, urban rain (Table 1) may be a source of perfluorochemicals to the aquifer, or potentially septic systems located upstream. Additionally, a nearby golf course

Table 3

Range of perfluorochemical (ng/l) concentrations measured in an urban creek and groundwater in San Jose, CA during the dry months of 2006 and 2007

	PFHxS		PFOS		PFDS		PFHpA		PFOA		PFDA		FOSA		*N*-EtFOSAA	
	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07
Detection limit	4	2	10	2	21	2	4	2	4	4	21	2	21	2	21	4
Upper silver creek surface water (sites 1, 2a, 2b, 3)[a]	n.d.	8.3–12	27–38	41–56	n.d.	3.1–36	n.d.	7.7–12	10–15	27–36	n.d.	11–19	n.d.	2.3–3.5	n.d.	n.d.-10
Coyote creek surface water (sites 4, 5, 6)	n.d.	2.3–3.8	9.3–20	4.8–25	n.d.-44	3.4–18	n.d.	n.d.-4.7	n.d.	8.0–13	n.d.	6.0–13	n.d.	n.d.-2.4	n.d.-31	n.d.-24
Hyporheic zone (3 wells)[b]	n.d.	3.8–10	44–58	25–48	n.d.	5.7–15	n.d.	7.3–8.1	10–23	22–28	n.d.	13–19	n.d.	2.9–4.3	n.d.	6.2–10
Groundwater (4 wells)	n.d.-11	4.0–17	31–192	19–87	n.d.	n.d.-3.3	n.d.	n.d.-4.8	n.d.-22	n.d.-18	n.d.	n.d.-10	n.d.	n.d.-3.7	n.d.-26	n.d.

PFNA and 6:2 FtS were also monitored but were not detected above detection limits of 4 and 10 ng/l in May 2006 and 10 and 4 ng/l in June 2007, respectively.

[a] Surface water site 2a was not monitored in May 2006.

[b] Hyporheic well 1 was not monitored in June 2007, hyporheic well 3 was not monitored in May 2006.

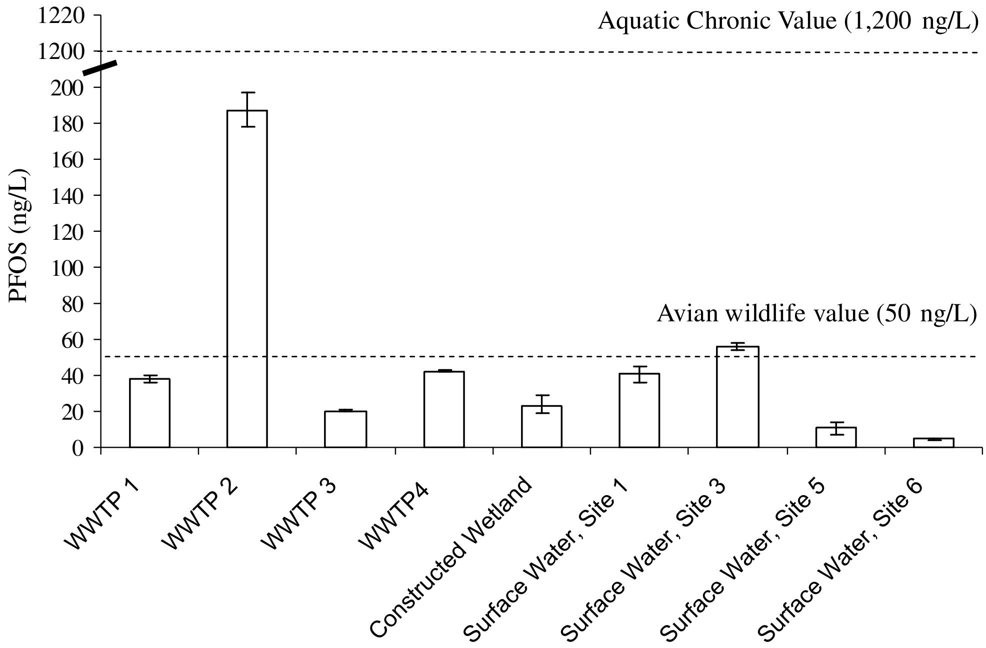

Fig. 3. Mean concentrations of PFOS in reclaimed wastewater (WWTP 1–4; June 2007, *n* = 2), a treatment and habitat wetland constructed using primary-treated wastewater (February 2006, mean of six treatment stages), and surface samples from an urban creek under consideration for stream flow augmentation with reclaimed wastewater (June 2007, *n* = 2). Error bars of mean values indicate the range. Threshold concentrations considered protective of aquatic and avian life are shown.

uses reclaimed wastewater for landscaping. Nevertheless, it is likely that the creek water is a significant source to the nearby groundwater given that the distribution and concentrations of the perfluorochemicals are consistent between surface and groundwater at the site. For example, perfluorohexanesulfonate (PFHxS), PFOS, PFDS, PFOA, and perfluorodecanoate (PFDA) were always or nearly always detected in the surface water, hyporheic zone, and groundwater (2007), whereas perfluoroheptanoate (PFHpA), perfluorooctane sulfonamide (FOSA), and *N*-EtFOSAA were detected only intermittently, and 6:2 FtS and PFNA were not present.

3.4. Implications of perfluorochemicals for water reuse

The potential contribution of water reuse projects to perfluorochemical exposure in humans will depend on the nature of the application and existing perfluorochemical background concentrations at the reuse site. No exposure to reclaimed wastewater is expected from drinking water given that in the US, recycled water is carried separately from potable water in clearly marked distribution systems.

Understanding the environmental risk requires analysis of perfluorochemical aquatic ecotoxicity at the ng/l-levels typically observed in reclaimed wastewater or at application sites. Perfluorochemical toxicity research is currently limited and must be extrapolated from laboratory organisms to complex ecosystems; however, suggested reference values provide some insight. Lowest observed effect concentrations (LOECs) for both acute and subchronic/chronic toxicity laboratory studies are greater than typical environmental concentrations (Lange et al., 2006), i.e. μg/l to mg/l-levels compared to ng/l-levels found in surface water, wastewater, and in water reuse sites characterized in the present study. A more conservative Tier II (potential risk) screening value of 1200 ng/l PFOS (aquatic chronic value) was determined by Beach et al. (2005) using EPA methodology by adjusting the lowest available LOEC, which is 70 times greater than the calculated aquatic chronic value. None of the reclaimed wastewaters or sites surveyed in this study exceed this screening value (Fig. 3).

For cases in which water recycling may expose organisms at upper trophic levels (i.e. wetland or stream flow enhancement), the fact that perfluorochemicals bioaccumulate in aquatic and terrestrial organisms (Giesy and Kannan, 2002; Schultz et al., 2003; Kannan et al., 2005) must be considered. The resulting tissue concentrations constitute an internal dose (Butenhoff et al., 2006), which may be more ecotoxicologically relevant than the aquatic perfluorochemical concentration. Taking into account bioaccumulation, Rostkowski et al. (2006) calculated a safe water concentration of 50 ng/l PFOS that is protective of trophic level IV avian species (avian wildlife value) that consume organisms in equilibrium with the water. Comparing this value to PFOS measured in the present study (Fig. 3), one of five reclaimed wastewaters (WWTP 2) and two of six urban creek sites (2b and 3) exceed this threshold. Assessment of the risk associated with recycled water projects is further complicated by the fact that perfluorochemicals are ubiquitous and thus are likely to be present at a site before application of reclaimed wastewater, as can be seen from the detections at the creek sites in the present study.

Compared to the global perfluorochemical burden from sources such as wastewater discharge and rain, water recycling plays only a limited role. Perfluorochemical occurrence is widespread and advanced wastewater treatment such as reverse osmosis or nanofiltration, while effective (Tang et al., 2006; Steinle-Darling and Reinhard, submitted for publication), may not be feasible for every situation. Furthermore, membrane technologies are nondestructive and typically produce brine that is released untreated. This brine is almost certain to contain perfluorochemicals at relatively high concentrations. Addressing the global perfluorochemical problem will require further research to predict the fate and toxicity of perfluorochemicals in the environment and an examination of source control.

Acknowledgements

Portions of this research were funded by the Santa Clara Valley Water District (SCVWD; California, USA), the California Department of Water Resources, the WateReuse Foundation, and the

National Science Foundation Graduate Research Fellowship program. We thank Alice Ringer and Sven Rosengreen (SCVWD), Eduard Hoehn (Eawag, Switzerland), Christopher P. Higgins, and Carlos Diaz. Any opinions, findings, conclusions, and recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the sponsoring agencies.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.04.057.

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Supplementary Information for

PERFLUOROCHEMICALS IN WATER REUSE

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Submitted to

Chemosphere

January 15, 2008

Analytical Method

For all sites, multiple samples of 6 to 30 mL were collected in polypropylene tubes (Cellstar, Greiner Bio-One; Monroe, NC) or bottles (Nalgene; Rochester, NY) and packed on ice in coolers until returned to Stanford University.

Perfluorochemical sources, purities, and calibration standard preparation are described in Higgins et al. (2005), from which the sediment perfluorochemical analysis method was adapted to water analysis for the present study. Methanol was added to 6 mL replicate water samples (60:40 aqueous/methanol) and a 2 mL aliquot was transferred to a polypropylene microcentrifuge tube (E & K Scientific; Santa Clara, CA) and centrifuged to remove particulates. Supernatant (800 μL) was transferred to a glass autosampler vial containing 200 μL of a 70:30 (v/v) mixture of methanol and 0.01% aqueous ammonium hydroxide (NH_4OH). 100 μL of an aqueous internal standard solution containing [1,2-$^{13}C_2$] perfluorooctanoic acid ([$^{13}C_2$]PFOA), and [1,2-$^{13}C_2$] perfluorodecanoic acid ([$^{13}C_2$]PFDA) was added.

Laboratory blanks were prepared by adding Milli-Q or HPLC-grade water to the same polypropylene storage containers used for sample collection and processed in the same manner as samples. Perfluorochemicals were not detected in the blanks above the detection limit, except for relatively low concentrations in the cases of PFHpA and PFDA (during the wetland analysis) and PFDS (during the June 2007 sampling event for reclaimed wastewater and the Coyote / Upper Silver Creeks stream and groundwater sampling). In those cases, the sample results were corrected for the blank contamination and detected values reported were two or more times greater than the blank contamination. Because plastic bailers were used to withdraw groundwater samples before transfer to polypropylene storage containers, additional blanks were prepared using Milli-Q water in the same bailers. No perfluorochemicals were detected in the bailer blanks.

Samples were directly injected and analyzed via liquid chromatography-tandem mass spectrometry (LC-MS/MS) with no sample preconcentration using the instrumentation, chromatography conditions, and multiple-reaction monitoring (MRM) operating parameters described in Higgins et al. (2005). To achieve low ng/L-detection limits, the method was modified to a large-volume injection (Schultz et al., 2006) of 490 μL with the following chromatography program: methanol increased from 35% to 100% over 0 to 7.5 min, held at 100% to 10 min, then returned to 35% until 15 min at a flow rate of 0.25 mL/min with aqueous 2mM ammonium acetate as the other mobile phase. Perfluorobutanesulfonate was dropped from the study due to poor chromatography at the large injection volume. Detection limit was defined as the lowest calibration standard having an accuracy of 70-130% and a signal-to-noise ratio of 3:1 or greater for the quantifier transition. Accuracy of the calibration standard is determined by the difference between the known concentration of the calibration standard and the concentration calculated using the integrated area of that standard’s peak and the linear regression of the calibration curve. Detection limits were typically 1-5 ng/L for the 10 perfluorochemicals and varied slightly (1-3 ng/L) with sample batch depending upon the sensitivity of the LC-MS/MS (though calibration curves were run with each sample batch, and thus variable sensitivity did not affect accuracy and precision). Precision was determined as the relative standard deviation (RSD) for multiple (n = 6) injections of an aqueous (Milli-Q) PFC solution processed in the same manner as samples. Precision for the ten perfluorochemicals monitored in the present study ranged from 6 to 31%.

Method Recovery

To test sample-specific method recovery, aliquots of all water samples or a representative water sample from each site were spiked with the ten monitored perfluorochemicals (100-200 ng/L) and compared to a reference standard spiked similarly. In addition, ion suppression or enhancement in the ion source of the LC-MS/MS caused by coeluting matrix compounds was measured (termed "matrix recovery") by performing a separate spike just before sample injection. Neither method nor matrix recovery were found to vary significantly with treatment stage (i.e., sample composition) for all stages of treatment of the constructed wetland. The same was found for the four reclaimed wastewaters tested and representative surface and groundwater selected for the San Jose creek study site.

Mean method (n = 2) and matrix (n = 4) recoveries of the ten perfluorochemicals for the San Jose creek and groundwater sites and the reclaimed wastewater samples were within one to two standard deviations of 100% and/or ranged between 70-130% except in the case of 6:2 FtS. For that compound, ion enhancement ranging from 157 ± 28% to 228 ± 26% (SD) (where "100%" represents full recovery of the spike with no ion suppression or enhancement) was observed in the wastewater samples. No corrections were made to sample results. In the constructed wetland samples, mean method recoveries (n = 2) for each perfluorochemical across the six treatment stages were typically 70-130%, except PFHxS (47±4%), and PFDS (<40%). Mean matrix recoveries (n = 4) were within one to two standard deviations of 100% and/or ranged between 70-130% except for PFDS, 6:2 FtS, and EtFOSAA showing ion enhancement. Mean ion enhancement across the six treatment stages for these perfluorochemicals was 174 ± 30%, 142 ± 17%, and 135 ± 14%, respectively. No corrections were made to sample results.

Perfluorochemicals in an Urban Creek and Groundwater

Table S1 below expands upon Table 3 of the manuscript to provide the site-specific perfluorochemical results for Coyote Creek, its tributary Upper Silver Creek, and the underlying groundwater.

Table S1. Mean (n = 2) perfluorochemicals (ng/L) measured in an urban creek and groundwater in San Jose, CA during the dry months of 2006 and 2007. PFNA and 6:2 FtS were also monitored but were not detected above detection limits of 4 and 10 ng/L in May 2006 and 10 and 4 ng/L in June 2007, respectively. Range of the n = 2 measurements are given with each value in parentheses.

	PFHxS		PFOS		PFDS		PFHpA		PFOA		PFDA		FOSA		EtFOSAA	
	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07	May-06	Jun-07
Detection Limit	4	2	10	2	21	2	4	2	4	4	21	2	21	2	21	4
Creek water																
Site 1	n.d.	8.5 (1.0)	32 (11)	41 (8.3)	n.d.	36 (61)	n.d.	8.7 (1.5)	15 (0.8)	27 (10)	n.d.	11 (2)	n.d.	3.5 (0.6)	n.d.	10 (2.6)
Site 2a	n.m.	12 (1.1)	n.m.	45 (1.8)	n.m.	3.1 (0.1)	n.m.	10 (5.7)	n.m.	36 (0.7)	n.m.	12 (0.7)	n.m.	2.9 (0.3)	n.m.	5.7 (0.8)
Site 2b	n.d.	8.3 (0.5)	27 (5.7)	56 (30)	n.d.	11 (16)	n.d.	7.7 (0.8)	10 (0.4)	29 (2.3)	n.d.	19 (10)	n.d.	3.1 (0.6)	n.d.	n.d.
Site 3	n.d.	12 (2.0)	38 (4.8)	56 (4.4)	n.d.	6.3 (1.8)	n.d.	12 (1.2)	11 (0.5)	31 (6.2)	n.d.	19 (2.9)	n.d.	2.3 (0.3)	n.d.	6.1 (0.07)
Site 4	n.d.	3.8 (1.6)	14 (2.0)	25 (9.5)	n.d.	18 (15)	n.d.	4.7 (1.3)	n.d.	13 (5.2)	n.d.	13 (9.0)	n.d.	n.d.	n.d.	23.5 (24)
Site 5	n.d.	3.0 (1.2)	20 (0.8)	11 (7.3)	44 (0.0)	9.1 (6.4)	n.d.	3.2 (1.9)	n.d.	10 (6.0)	n.d.	6.0 (7.3)	n.d.	2.4 (0.2)	31 (2.1)	5.0 (0.6)
Site 6	n.d.	2.3 (0.4)	9.3 (0.6)	4.8 (0.7)	n.d.	3.4 (1.2)	n.d.	n.d.	n.d.	8.0 (4.1)	n.d.	7.7 (2.1)	n.d.	n.d.	n.d.	n.d.
Hyporheic zone																
Push well 1	n.d.	n.m.	58 (3.7)	n.m.	n.d.	n.m.	n.d.	n.m.	23 (0.3)	n.m.	n.d.	n.m.	n.d.	n.m.	n.d.	n.m.
Push well 2	n.d.	10 (1.9)	44 (12)	48 (7.5)	n.d.	15 (0.7)	n.d.	8.1 (1.0)	10 (1.3)	28 (3.9)	n.d.	19 (2.4)	n.d.	4.3 (0.9)	n.d.	10 (0.6)
Push well 3	n.m.	3.8 (1.6)	n.m.	25 (9.5)	n.m.	5.7 (3.8)	n.m.	7.3 (0.9)	n.m.	22 (2.7)	n.m.	13 (1.2)	n.m.	2.9 (0.3)	n.m.	6.2 (0.3)
Groundwater																
Well 1	n.d.	8.9 (0.7)	85 (8.7)	40 (3.4)	n.d.	2.9 (1.3)	n.d.	n.d.	14 (5.9)	12 (1.6)	n.d.	7.3 (0.8)	n.d.	2.2 (0.2)	26 (18)	n.d.
Well 2a	n.d.	8.9 (4.2)	82 (1.1)	26 (4.8)	n.d.	n.d.	n.d.	4.8 (2.9)	22 (1.1)	18 (5.7)	n.d.	8.6 (2.6)	n.d.	n.d.	n.d.	n.d.
Well 2c	11 (3.8)	17 (3.5)	192 (33)	87 (5.3)	n.d.	3.3 (1.8)	n.d.	2.4 (0.6)	10 (0.6)	12 (1.6)	n.d.	10 (0.9)	n.d.	3.7 (0.7)	n.d.	n.d.
Well 3	9.2 (1.4)	4.0 (0.3)	31 (6.0)	19 (3.1)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

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Appendix F

Montgomery-Brown, J., Li, Y., Ding, W.-H., Mong, G.M., Campbell, J.A., Reinhard, M., 2008.
NP1EC Degradation Pathways Under Oxic and Microxic Conditions. Environ. Sci. Technol.
DOI: 10.1021/es702561t.

NP_1EC Degradation Pathways Under Oxic and Microxic Conditions

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Received October 11, 2007. Revised manuscript received February 7, 2008. Accepted February 7, 2008.

The degradation pathway of nonylphenol ethoxyacetic acid (NP_1EC) and the conditions favoring dicarboxylated alklyphenol ethoxyacetic acid (CA_nP_1EC; where n = the number of aliphatic carbon atoms) formation were studied in oxic microcosms constructed with organic carbon-poor soil from the Mesa soil aquifer treatment (SAT) facility (Arizona) and pristine organic carbon-rich sediments from Coyote Creek (California). Results suggest that the availability of dissolved oxygen determines the dominant biodegradation pathway; ether cleavage and the formation of NP is favored by oxic conditions, while alkyl chain oxidation and the formation of CAP_1ECs is favored under microxic conditions. In the Mesa microcosms, *para*-NP_1EC was transformed to *para*-nonylphenol (NP) before being rapidly transformed to nonyl alcohols via *ipso*-hydroxylation. In the Coyote Creek microcosms, large quantities of CAP_1ECs were observed. Initially, CA_8P_1ECs were the dominant metabolites, but as biodegradation continued, CA_6P_1ECs became the dominant metabolites. Compared to the CA_8P_1ECs, the number of CA_6P_1ECs peaks observed was small (<6) even though their concentrations were high. Several novel metabolites, tentatively identified as 3-alkylchroman-4-carboxylic acids (with alkyl groups ranging from C_2 to C_5), were formed in the Coyote Creek microcosms. These metabolites are presumably formed from *ortho*-CAP_1ECs by intramolecular ring closure.

Introduction

Alkylphenol polyethoxylates (APEOs) are nonionic surfactants synthesized by polyethoxylating an alkylphenol (~90% are *para* isomers, the remainder are *ortho* isomers). Commercially available APEOs are predominantly (>80%) branched nonylphenol polyethoxylates (*1*); the remaining ~20% are octyl- and decylphenol polyethoxylates. Approximately 60% of APEOs entering municipal and industrial wastewater treatment plants (WWTPs) are removed with the remainder released to the aquatic environment as APEO metabolites (APEMs) (*2*). Wastewater treatment produces mixtures of short-chained APEOs (with 1–3 ethoxy units), alkylphenol polyethoxycarboxylates (APECs), carboxyalkylphenol polyethoxycarboxylates (CAPECs), and alkylphenols (APs) (*2, 3*). These metabolites, collectively known as APEMs, are among the most frequently detected aquatic contaminants in the environment (*4*), and may be cause for concern as several of these compounds can persist in the environment (*5–7*), bind to and accumulate in soils and sediments (*8–10*), and be estrogenic to wildlife at low concentrations (*11–14*).

The study of APEO biodegradation is complicated by the highly branched alkyl chain (>22 isomers for nonylphenol ethoxylates), the presence of *ortho*- and *para*-isomers, the fact that both the alkyl and ethoxy side chains can be degraded simultaneously, and aerobic and anaerobic biodegradation pathways are different (*15*). It is generally accepted that the ethoxy side chain is degraded by sequential hydrolysis of the ether groups. Under aerobic conditions, the terminal alcohol tends to be oxidized prior to ether hydrolysis (*16*); the main products of these reactions are relatively stable APECs having one to three ethoxy units (AP_nECs, where n = 1–3). Under anaerobic conditions, ether hydrolysis continues until APs are formed; no further degradation of APs has been observed under anaerobic conditions. Aerobically, the alkyl side chain can be degraded via a combination of ω-, α-, and β-oxidation (*15*). However, alkyl chains containing ternary and quaternary carbon atoms are difficult to degrade and, consequently, these highly branched metabolites resist complete mineralization. APEO metabolites with oxidized alkyl and ethoxy side chains are known as CAPECs; these metabolites are frequently detected in wastewater treatment plant effluents (*3, 17, 18*).

The formation and mineralization of both APECs and CAPECs under aerobic conditions is not well understood. In 1997, an interesting metabolite, 2,4,4-trimethyl-2-pentanol, was detected in aerobic microcosms containing octylphenol ethoxycarboxylate (OP_1EC) (*19*). The same metabolite was observed in aerobic column studies a few years later (*20*). The mechanism by which these metabolites were formed was elucidated in recent work on the aerobic biodegradation of nonylphenol (NP) by *Sphingomonads* (*21, 22*). These studies demonstrated that cleavage of the benzylic carbon and the formation of tertiary alcohols (ROHs) occurs via *ipso*-hydroxylation (Figure 1).

Since *ipso*-hydroxylation requires the formation of a cyclohexa-2,5-dienone, it appears impossible that APECs can be degraded by this mechanism. Therefore, the observations of refs (*19*) and (*20*) suggest that the OP_1EC may have initially been transformed to octylphenol prior to the formation of 2,4,4-trimethyl-2-pentanol. However, the formation of alkylphenols, the key intermediate, from APECs under aerobic conditions has not yet been observed (*19, 20, 23, 24*).

In this paper, we examine the degradation of NP_1EC in oxic microcosms containing soils and sediments from two sites, the Mesa soil aquifer treatment (SAT) facility in Arizona and an uncontaminated creek (Coyote Creek) in California; under anaerobic conditions, no degradation was observed. The formation and degradation of NP_1EC metabolites in these microcosms was used to determine whether NP_1EC is degraded to NP prior to being further transformed and the role of dissolved oxygen in the formation of CAP_1ECs. The influence of structure (*ortho*- versus *para*-NP_1EC) on transformation pathways revealed novel metabolites that appear to be specific to *ortho*-isomers. Finally, results from the Mesa

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10.1021/es702561t CCC: $40.75

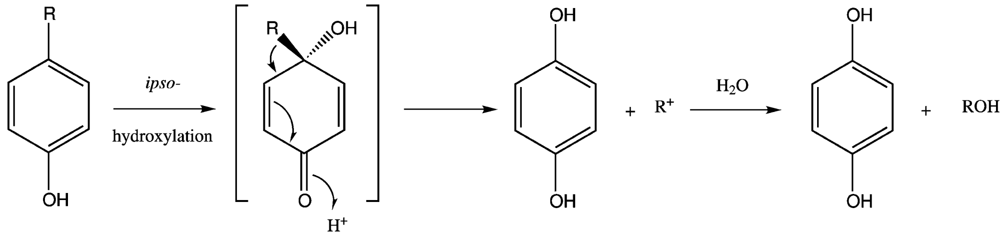

FIGURE 1. *ipso*-Hydroxylation of nonylphenol, where R = a tertiary nonyl isomer.

microcosms were used to confirm the rapid degradation of APECs previously observed in the field (*18*), and results from the Coyote Creek microcosms were used to evaluate the ability of a pristine river sediment to degrade APEMs.

Materials and Methods

Chemicals. Unless otherwise specified, all chemicals were obtained from either Fisher Scientific (Los Angeles, CA) or Sigma-Aldrich (St. Louis, MO). Hydrochloric acid was diluted to 2 N with MilliQ water (Synergy 185 system; Bedford, MA). Chrysene-d_{12} was purchased from Chem Service Inc. (West Chester, PA). The NP_1EC (Ciba IRGACOR NPA, Switzerland), was a gift from Dr. Marijan Ahel (Zagreb, Croatia) and contained small impurities of *ortho*- and *para*-NP.

Site Information. Soils were collected from the Mesa Soil Aquifer Treatment (SAT) facility. This facility has been in operation since 1990 and discharges tertiary treated wastewater effluent into rapid infiltration basins for groundwater recharge and subsequent nonpotable reuse; more information about this site can be found in Montgomery-Brown et al. (*18*). Sediments were collected from Coyote Creek (San Jose, CA), the proposed location of a stream augmentation project using tertiary treated wastewater effluent. Soil from the Mesa site was collected from depths between 15 and 30 cm below the ground surface and sediments from Coyote Creek were collected from the top 10 cm; the soils and sediments were stored at 4 °C until use. On average, the Mesa and Coyote Creek soils had organic carbon contents (f_{oc}) values of 0.09 and 2.88% (n = 3), respectively (as determined by Huffman Laboratories, Colorado).

Microcosm Construction. The oxic microcosms were constructed in 125 mL glass bottles and contained 75 mL of minimal media (1 g NaCl, 0.4 g $MgCl_2 \cdot 6H_2O$, 0.15 g $CaCl_2 \cdot 2H_2O$, 0.20 g KH_2PO_4, 0.50 g KCl, and 0.25 g NH_4Cl per L of MilliQ water). One milliliter of an SL10 trace element solution (8.5 mL of HCl (37% by weight), 1.5 g $FeCl_2 \cdot$4H2O, 6 mg H_2BO_3, 190 mg $CoCl_2$v$6H_2O$, 100 mg $MnCl_2 \cdot 4H_2O$, 70 mg $ZnCl_2$, 36 mg Na_2MoO4$\cdot 2H_2O$, 24 mg $NiCl_2 \cdot 6H_2O$, and 2 mg $CuCl_2 \cdot 2H_2O$ per L of MilliQ water) and 1 mL of a selenite-tungstate solution (0.4 g NaOH, 6 mg $Na_2SeO_3 \cdot 5H_2O$, and 8 mg Na_2WO_4v$2H_2O$ per L of MilliQ water) were added to each L of medium), and 15 g of soil. The microcosms were buffered using equimolar amounts of KH_2PO_4 and K_2HPO_4 (10 mM phosphate buffer) and then spiked with resazurin (final concentration 1 mg/L) and 10 μL (in methanol) of the contaminant of interest. The microcosms were then lightly capped, covered with aluminum foil, and placed on a rotary shaker (~100 RPM). The microcosms were respiked as necessary and fresh minimal media was added when necessary. Because of the high f_{oc} of the Coyote Creek sediments, the Coyote Creek microcosms were prepared as above, but were sealed with butyl rubber stoppers and their headspace was purged with oxygen on a weekly basis.

Anoxic microcosms were prepared in crimp top bottles as above, but were filled with deoxygenated media, spiked with resazurin (final concentration 1 mg/L), sealed with butyl rubber stoppers, and their headspace was purged with nitrogen for 15 min. Residual oxygen was quenched with 1 mL of 0.5 M sodium sulfide; excess sulfide was removed via the addition of 0.5 mL of 1 M ferric chloride. The microcosms were then spiked with nitrate (final concentration 1 mg/L) and the contaminant of interest (in 10 μL of methanol). No degradation was observed in any of the constructed anoxic microcosms.

Abiotic control microcosms were prepared by autoclaving the soil three times over a period of three days whereupon the microcosms were prepared as outlined above. The microcosms were autoclaved again and spiked with sodium azide to a final concentration of 0.1% (w/w).

Sorption controls were prepared by adding 3 g (dry weight) of soil and 15 mL of 0.01 M $CaCl_2$ to a 25 mL vial. The vials were autoclaved three times (over three days) and then spiked with 20 μL of stock NP_1EC solutions (final aqueous NP_1EC concentrations of 10, 50, 100, 500, and 1000 μg/L). Three replicates were performed at each concentration and the vials were sampled after 1 week. No significant sorption was observed.

Sample Preparation. For the analysis of NP_1EC and its metabolites, extensive modifications were made to the GC-MS method used previously (*18*). NP_1EC was extracted using a dichloromethane (DCM) liquid–liquid extraction. After acidifying the sample with 50 μL of 2 N HCl, 50 μL of DCM was added to a 1 mL sample and vigorously shaken for 30 s. The DCM was then removed from the vial with a syringe and placed in a 2 mL reactivial (Pierce Chemical Co., IL). The extracts were allowed to evaporate to approximately 50 μL and then the carboxylic acid functional groups were derivatized to propyl esters by adding 10 μL of *n*-propanol/acetyl choride (9:1, v/v) and heating the sample for 1 h at 85 °C. After cooling, 100 μL of a 2% (by weight) potassium bicarbonate solution was added to the reaction mixture and mixed vigorously. The two phases were allowed to separate and the organic phase was withdrawn and added to a 200 μL glass insert containing 10 μL of a 50 ng/μL chrysene-d_{12} solution (methanol). Another 50 μL of DCM was added to the final extract to rinse the walls of the glass insert. The neutral analytes were extracted in a similar manner, except the samples were not acidified prior to extraction and the extracts were placed a 200 μL glass insert containing 10 μL of a 50 ng/μL chrysene-d_{12} solution. Information about sample methylation can be found in the Supporting Information.

GC-MS Analysis. An Agilent 6890N Gas Chromatograph (GC) with an Agilent 7683 series autosampler coupled to an Agilent 5973N Mass Spectrometer (MS) was used for the analysis and quantification of NP_1EC and its metabolites. The column was a Zebron ZB-5 (Phenomenex; 30 m long; 0.25 mm i.d.; 0.25 μm film thickness), and helium was the carrier gas. The system was operated under constant flow conditions (1.6 mL/min) and the injector was operated in splitless mode at 275 °C. The temperature program was as follows: 40 °C for 2 min, followed by a temperature ramp of 20 °C/min to 240 °C and then a ramp of 10 °C/min up to 280 °C. The transfer line was held constant throughout the run at 280 °C, and the final oven temperature was held for 6 min. The MS source and quadrupole temperatures were 230 and 150 °C, respectively. Electron ionization (70 eV) was used to ionize the samples and the data were analyzed in full scan

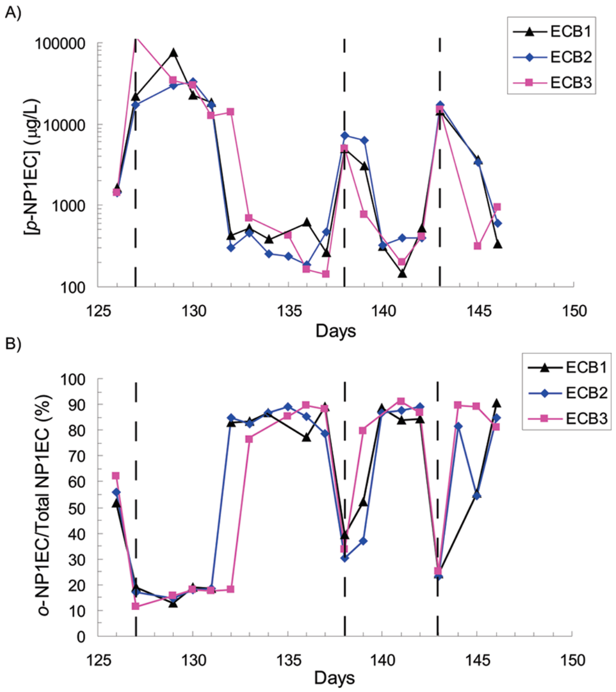

FIGURE 2. After acclimation (125 days), (A) aqueous *para*-NP_1EC concentrations in the Mesa microcosms (ECB1, ECB2, and ECB3) as a function of time and (B) percent *ortho*-NP_1EC as a function of time. Dashed lines indicate NP_1EC respike events.

mode (m/z −50 to 550). For each analysis, 1 μL of sample was injected. Under these conditions, *ortho*-NP_1EC isomers eluted between 12.0 and 12.8 min, while *para*-NP_1EC isomers eluted between 12.8 and 13.6 min.

Additional information on the operating conditions used for chemical ionization (CI)-MS, MS-MS, and high-resolution MS analyses can be found in the Supporting Information. Information on the identification and quantitation of NP_1EC and its metabolites is also presented in the Supporting Information.

Results and Discussion

SAT (Mesa) Microcosms. After acclimation (125 days), NP_1EC degradation was very rapid (3–5 days) in the fully aerobic Mesa microcosms (Figure 2). The sharp increase in the fraction of *ortho*-NP_1EC isomers during degradation (e.g., between days 131 and 132), indicates that the *para* isomers are being rapidly degraded while the *ortho* isomers persist; the relative recalcitrance of the *ortho* isomers is most likely a function of steric hindrance. Interestingly, a small fraction of the *para* isomers are more persistent, implying that alkyl chain structure plays a role in NP_1EC degradation (e.g., α-methyl isomers may be more recalcitrant than α,α-dimethyl isomers).

On analyzing the neutral fraction, we observed substantial quantities of nonyl alcohols (NOH), similar to results by Fujita and Reinhard (*19*) and Wild and Reinhard (*20*). At present, the only known mechanism by which nonyl alcohols (NOHs) are produced is via the *ipso*-hydroxylation of nonylphenol. Based on the degradation mechanisms proposed by Gabriel et al. (*21*) and Corvini et al. (*22*) (Figure 1), it is not possible to degrade APECs by a similar process because a ketone in *para* position to the alkyl chain can not be formed. This conclusion is supported by the fact that experiments with *S. xenophagum* Bayram found that it was incapable of degrading NP_1EC, both in the presence and absence of NP (data not shown). Therefore, the presence of the nonyl alcohols in our oxic microcosms implies that NP_1EC was first degraded to NP, which was subsequently degraded to NOHs. The formation of NP from NPECs under aerobic conditions however, has not previously been observed (*23, 24*).

A new set of Mesa microcosms was constructed and spiked with NP_1EC (and OP_1EC) to determine whether or not NP (and OP) is an intermediate in the formation of NOHs (and 2,4,4-trimethyl-2-pentanol) from AP_1ECs. Figure 3 shows a sequence of chromatograms illustrating the transformation of NP_1EC to NP and NP to NOHs in one microcosm. Between days 7 and 14, almost all NP_1EC is converted to NP and between days 14 and 16, the NP was rapidly converted to NOHs. OP_1EC showed very similar results (data not shown). These results were observed in two of the four microcosms prepared; the other microcosms showed no NP_1EC degradation during this period.

The transformation of NP_1EC to NP to NOH was also observed in the original microcosms (ECB microcosms) after starving them for approximately one month and then respiking the microcosms with NP_1EC (Figure 4). These results appear to indicate that in acclimatized systems, the degradation rate of NP to NOHs is faster than the degradation rate of of NP_1EC to NP and could explain why previous researchers (*23, 24*) did not observe the formation of NP under oxic conditions. Interestingly, very few CAP_1ECs were formed under these conditions and only at low concentrations, suggesting that highly oxygenated conditions favor ether cleavage and the formation of NP followed by its rapid degradation to NOHs.

Coyote Creek Microcosms. Similar to the Mesa microcosms, nonyl alcohols were observed in Coyote Creek microcosms spiked with NP (data not shown); their presence indicates that NP degradation is occurring via *ipso*-hydroxylation. In microcosms spiked with NP_1EC, degradation was also observed (Figure 5A), however, unlike the Mesa microcosms substantial amounts of CAP_1ECs were formed during the degradation (Figure 5B). CAP_1EC degradation is seen between days 109 and 139 for both CCGB1 and CCGB2 and after 156 days for CCGB1; CAP_1EC concentrations in CCGB2 decreased after 223 days (data not shown).

Initially, CA_8P_1ECs were the dominant metabolites (in both number and quantity), but as time progressed, CA_6P_1ECs became the dominant metabolites even though there were generally only two to three CA_6P_1ECs present in the chromatogram (Figure 6). This suggests that some CA_6P_1EC metabolites are significantly more recalcitrant than others, presumably the most branched ones. An analysis of a highly concentrated sample also revealed the presence of several *ortho*-CAP_1EC isomers (these peaks eluted approximately a minute earlier than their *para*-CAP_1EC counterparts). Since *ortho* APEMs are more recalcitrant than *para* APEMs, these highly branched CA_6P_1ECs are likely the most recalcitrant of all APEMs with the exception of halogenated APEMs and octylphenol ethoxylate metabolites (*25*).

One reason for the significant differences in NP_1EC degradation between the Mesa and Coyote Creek microcosms is dissolved oxygen concentrations. The Mesa soils are primarily silty sands with a low f_{oc} (0.09%). In contrast, the Coyote Creek sediments are primarily a sandy silt with a high f_{oc} (2.88%); the high f_{oc} of these sediments guarantees anaerobic conditions within the sediments, at least at some depth. As a result, the Mesa microcosms likely remained oxic throughout the experiments because there was very little demand for dissolved oxygen in the system (due to the low f_{oc}). In contrast, the high f_{oc} of the Coyote Creek sediments indicates that there is likely a high oxygen demand in these microcosms. This means that while the overlying aqueous phase may have remained oxic due to oxygen diffusion (from the oxygen-filled headspace), the porewater within the sediments may have been microxic. In this paper, microxic refers to the condition in which a microcosm contains a trace amount of oxygen, supplied at a diffusion limited rate;

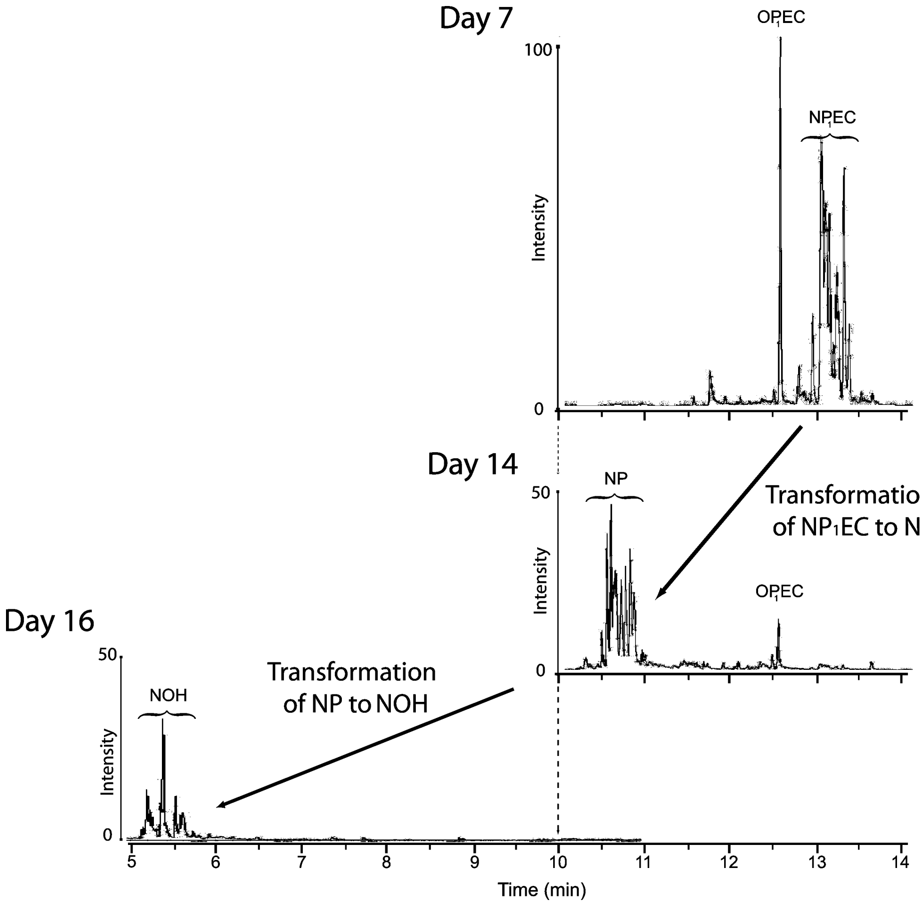

FIGURE 3. Total ion chromatograms for a Mesa microcosm on Day 7, Day 14, and Day 16. The transformation of NP_1EC to NP is observed between Days 7 and 14, and the conversion of NP to nonyl alcohols (NOH) is seen between Days 14 and 16.

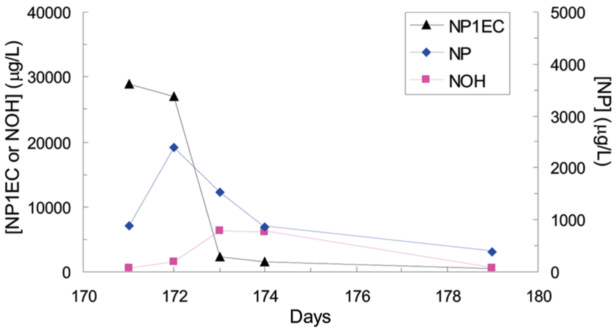

FIGURE 4. Aqueous NP_1EC, NP, and nonyl alcohol (NOH) concentrations as a function of time in one Mesa ECB microcosm. Transformation is rapid, with NP production occurring within one day. Two additional microcosm replicates showed very similar results.

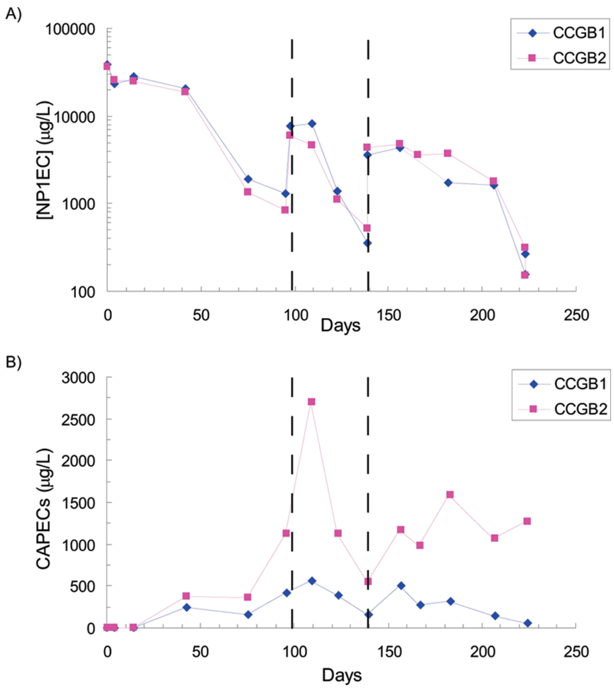

FIGURE 5. (A) NP_1EC (log scale) and (B) CAP_1EC concentrations as a function of time in the Coyote Creek microcosms (CCGB1 and CCGB2) The dashed lines indicate NP_1EC respike events.

the redox potential within this microcosm is typically below that indicated by resazurin (−110 mV; for additional information on the redox conditions please see the Supporting Information). Another possible reason for the differences between the Mesa and Coyote Creek microcosms is different microbial communities: Mesa soils were collected from recharge basins that are filled with tertiary treated wastewater effluents and allowed to drain and dry, whereas the Coyote Creek sediments were collected from a year-round stream that has never been exposed to wastewater effluents.

To test the hypothesis that limited dissolved oxygen may result in higher CAP_1EC concentrations, four microcosms were constructed with Mesa soil. The microcosms were spiked with resazurin (1 mg/L) and NP_1EC, placed on the rotary shaker, and left uncapped until the NP_1EC was degraded; no CAP_1ECs were observed. The microcosms were then respiked, and two microcosms were sealed with butyl rubber stoppers. The unsealed microcosms remained pink (oxic) and degraded

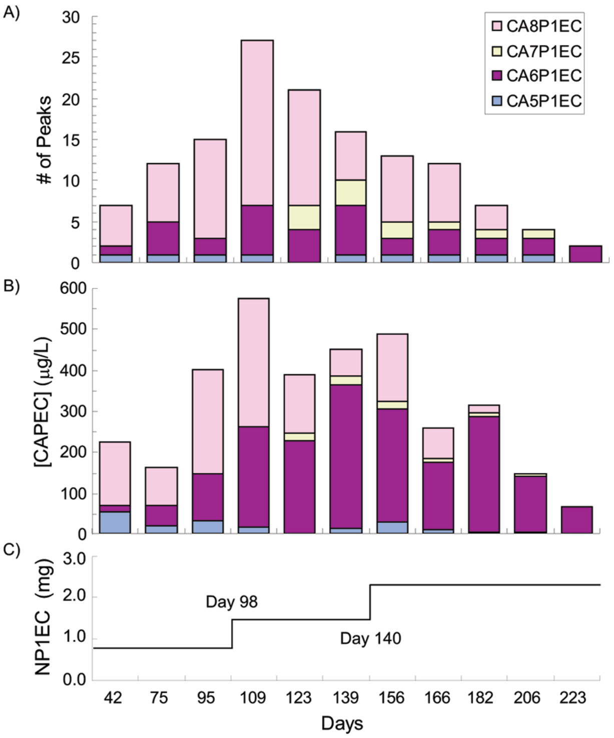

FIGURE 6. CA_nP_1EC formation and degradation as a function of time in a Coyote Creek microcosm. (A) Number of CA_nP_1ECs, (B) CA_nP_1EC concentrations, and (C) cumulative mass of NP_1EC added to the microcosm. The microcosm was respiked with NP_1EC on Days 98 and 140. A replicate microcosm showed very similar results.

NP_1EC without the formation of CAP_1ECs (Figure 7A). In contrast, the media close to the sediments in the sealed microcosms went colorless (indicating very low dissolved oxygen concentrations) and several CAP_1ECs were observed (Figure 7B). As a result of these experiments, we do not believe microbial speciation is more influential on CAPEC formation than dissolved oxygen concentrations. If microbial speciation were more influential than dissolved oxygen concentrations, we most likely would not have observed the abundant formation of CAPECs in the capped Mesa microcosms.

These findings suggest that in some cases microbial pathways may not be predictable based on conventional microcosms studies (e.g., under aerobic and anaerobic conditions) because the pathways observed under microxic conditions (i.e., conditions where oxygen is present only at trace levels) may be different from those observed under aerobic or strictly anaerobic conditions, as appears to be the case for NP_1EC. This issue merits further investigation.

Approximately halfway through the time series shown in Figures 5 and 6, several peaks were observed in chromatograms from the biotic samples but not in chromatograms from the abiotic samples. Over time, the concentrations of these peaks increased, and several new peaks were observed. Based on manual interpretation of EI and CI mass spectra, EI MS/MS analyses of select ions, selective derivatizations, high resolution MS, and a proposed fragmentation mechanism, these metabolites were tentatively identified as 3-alkylchroman-4-carboxylic acids (Figure 8; for additional information on the mass spectral analyses performed and model reactions, please see the Supporting Information). Microbial speciation likely plays a role in the formation of the alkylchroman carboxylic acids as these metabolites were not observed in the capped Mesa microcosms.

We believe that the alkylchroman carboxylic acids are a small fraction of the *ortho*-NP_1EC isomers (<10%), and hence, a small fraction overall. However, given their apparent persistence (concentrations increased over the course of multiple NP_1EC additions), these metabolites are likely significant when compared to other refractory APEMs.

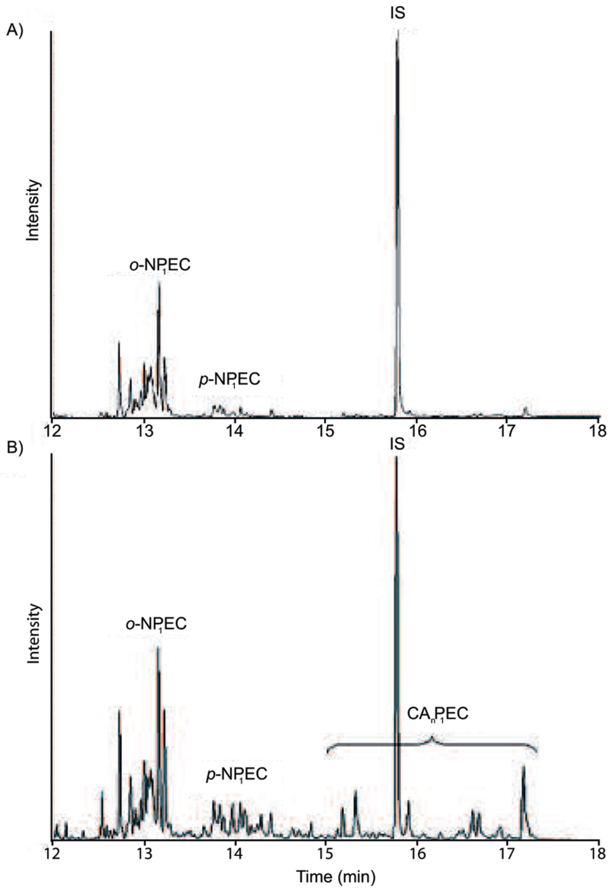

FIGURE 7. TIC chromatograms for the (A) uncapped and (B) capped Mesa microcosms spiked with NP_1EC.

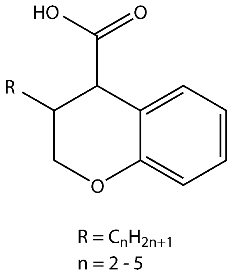

FIGURE 8. Proposed structure for new metabolites: 3-alkylchroman-4-carboxylic acids. In these experiments, the alkyl groups contained between two and five carbon atoms.

Acknowledgments

Funding was provided by the Environmental Protection Agency (EPA) and the American Water Works Association Research Foundation (AWWARF) through a grant to the National Center for Sustainable Water Supply at Arizona State University (Tempe, Arizona), Nanyang Technological University (Singapore), the Santa Clara Valley Water District, and the National Science Foundation of China (Grant 50578114). We thank Drs. Frédéric Gabriel and Hans-Peter Kohler (EAWAG, Dübendorf, Switzerland) for providing *S. xenophagum* Bayram. Opinions, findings, conclusions, and recommendations in this publication are those of the authors and do not necessarily reflect the views of the sponsoring agencies.

Supporting Information Available

Additional details (chromatograms, mass spectra, and fragmentation schemes) relating to the identification of the unknown metabolites. This information is available free of charge via the Internet at http://pubs.acs.org.

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ES702561T

NP_1EC Degradation Pathways Under Oxic and Microxic Conditions: Supplemental Information

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Number of Pages: 12

Number of Figures: 5

Number of Tables: 2

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0.1 GC-MS Analysis

A Varian 3800CP GC coupled to a Varian Saturn 2000 Ion Trap MS was used for the chemical ionization and MS-MS analyses. The column was a DB-XLB (30 ml 0.25 mm internal diameter; 0.1 μm film thickness, and helium was the carrier gas. The system was operated under constant flow conditions (1.6 mL/min) and the injector was operated in splitless mode. The injector was initially held at 80^{o}C for 2 min, and then ramped at 275^{o}C/min to 275^{o}C and maintained at this temperature for 20 minutes. The temperature program was as follows: 40^{o}C for 5 min, followed by a temperature ramp of 20^{o}C/min to 240^{o}C and then a ramp of 10^{o}C/min up to 280^{o}C. The transfer line temperature was held constant throughout the run at 280^{o}C and the final oven temperature was held for 10 minutes. The ion trap temperature was 160^{o}C and the emission current was 10 μA. The samples were scanned in full scan mode (m/z – 50 to 550) and for each analysis, 1 μL of sample was injected. For liquid CI-MS analyses, the reagent gas was methanol was used as the CI reagent gas and the ejection voltage was 15V. Nonresonant collision-induced dissociation (CID) MS/MS conditions for m/z 145 ions were as follows: Window 3 m/z, Amplitude 73V, CID-RF 63 m/z, CID time 20 ms. More information on liquid CI-MS and nonresonant CID MS/MS can be found in Ding and Tzing [1] and Ding and Wu [2].

GC coupled with high resolution mass spectrometry (HRMS) was performed at Pacific Northwest National Laboratory (PNNL; Richland, WA, USA). Accurate mass measurements were performed using a JEOL SX-102/SX-102 double-focusing, tandem mass spectrometer equipped with a JEOL UNIX data system (JEOL USA Inc., Peabody, MA, USA). The instrument was tuned to a resolution of 5000 (10% valley definition). Data were acquired by scanning over the mass range of 50 to 500 mass units at a rate of one scan per second. Instrument tuning and real-time mass measurements were performed by leaking a controlled amount of perfluorokerosene (PFK) into the electron ionization ion source from a septum inlet reservoir. Accurate mass measurements were made on data obtained by averaging consecutive scans over the GC elution profile of the analyte. The MS was equipped with a Hewlett Packard 5890 GC fitted with a DB-5 capillary column (30m x 0.25 mm id, 0.25 m film thickness). The GC oven was held at 40^{o}C for 2 minutes, then 20 C/min to 240^{o}C, a ramp of 10^{o}C/min to 280^{o}C, and then held at 280^{o}C for 6 minutes. The injection port temperature was 275^{o}C, the transfer line was 280^{o}C, and the source temperature was 200^{o}C. Helium was used as the carrier gas, and the injection volume was 1 μL performed in the splitless mode.

0.2 Sample Preparation: Methylation

Samples were methylated using two different techniques. The first derivatized carboxylic acid functional groups to their methyl esters using the procedure outlined above but substituting the 10 μL of *n*-propanol/acetyl choride (9:1, v/v) with 10 μL of methanol/acetyl choride (9:1, v/v). The second technique derivatizes carboxylic acids and alcohols to their methyl esters using (trimethylsilyl)diazomethane. Briefly, the extract was added to a 200 μL glass insert and allowed to evaporate to approximately 10 μL. 50 μL of methanol and 20 μL of 2M (trimethylsilyl)diazomethane in diethyl ether were added to the insert and the vial was capped and allowed to react for 30 minutes. After derivatization, 10 μL of a 50 ng/μL chrysene-d$_{12}$ solution was added and the samples analyzed without further preparation.

0.3 Quantitation

In this study, the concentrations of NP$_1$EC and its metabolites were determined semi-quantitatively using chrysene-d$_{12}$ as an internal standard. Table S1 presents the characteristic ions used to identify NP, the nonyl alcohols, the propylated NP$_1$ECs and CAP$_1$ECs. Additional information on APEO

Table S1: Characteristic ions and neutral losses for the identification of NP_1EC metabolites

Compound	MW[a]	Characteristic fragments (m/z)	
		I	II
Nonyl alcohols (NOH)	129	59, 73, 87, 101, 115	129
NP	220	121, 135, 149, 163, 177	220
NP_1EC	320	221, 235, 249, 263, 277	193, 320
CA_5P_1EC	350	221, 235, 249	193, 281, 350
CA_6P_1EC	364		193, 305, 364
CA_7P_1EC	378		193, 305, 321, 378
CA_8P_1EC	392		193, 281, 333, 363, 392

[a] The molecular weights presented for the acidic metabolites correspond to the propylated derivatives

metabolite fragmentation patterns can be found in [7, 3, 2, 4, 5, 6]. Signal-to-noise ratios of 5:1 and 10:1 were selected as the limits of detection (LOD) and quantification (LOQ), respectively, and correspond to concentrations of 5 μg/L and 20 μg/L for NP and NP_1EC.

1 Results and Discussion: Redox Conditions

The criteria used to delineate the concentration of oxygen in the microcosms was essentially based on the coloration of the redox indicator, resazurin, the presence of oxygen, and our anoxic microcosms. In this paper, microxic refers to the condition in which a microcosm contains a trace amount of oxygen, supplied at a diffusion limited rate; the redox potential in this microcosm is typically below that indicated by resazurin.

Microcosms in which resazurin remained pink throughout the water column were considered oxic (e.g., the uncapped Mesa microcosms). Microcosms in which resazurin changed color near the oxygen-containing air-liquid interface (i.e., microcosms in which oxygen was being rapidly consumed) were considered microoxic (e.g., the Coyote Creek microcosms). Microcosms that contained no oxygen and were colorless were considered anoxic (e.g., our nitrate-containing microcosms). While we did not measure oxygen concentrations with an electrochemical probe, it is unlikely we would have obtained meaningful results at oxygen concentrations below 0.1 mg/L.

2 Results and Discussion: Additional Mass Spectrometry Results

Approximately half way through the time series in Figures 5 and 6 (approximately 140 days), several unidentified peaks were observed in the Coyote Creek biotic microcosms (Figure S1). These metabolites were identified as alkylchroman carboxylic acids and additional mass spectral information related to their identification is presented below.

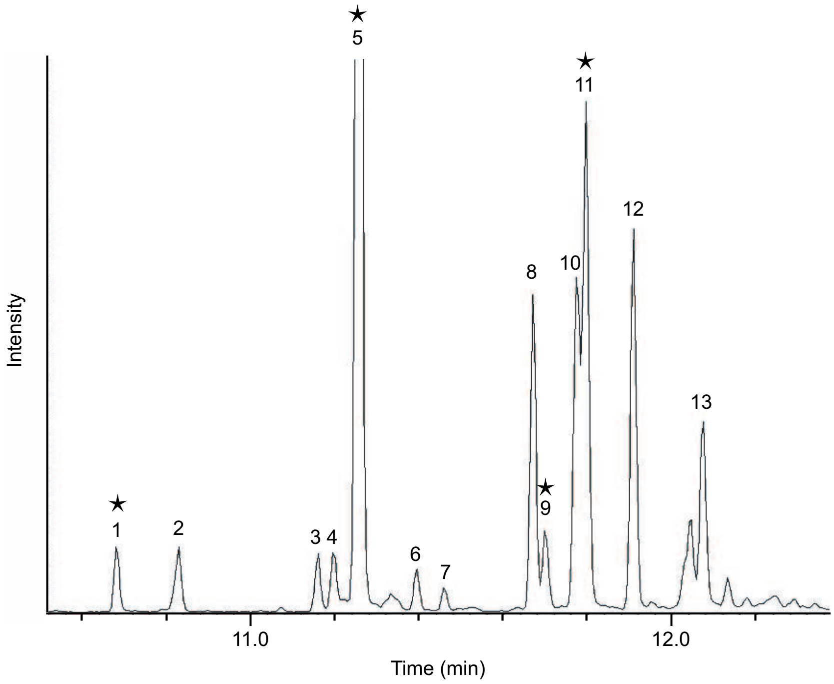

Figure S1: A chromatogram of the propylated unknown peaks observed in the biotic Coyote Creek microcosms. Stars indicate peaks for which the mass spectrum is illustrated in Figure S2.

The mass spectra of these peaks were very similar and could be divided into four groups (m/z 248, 262, 276, and 290; Figure S2) based on their molecular masses (confirmed by chemical ionization mass spectrometry). Table S2 summarizes the major ions and molecular weights of the unidentified peaks.

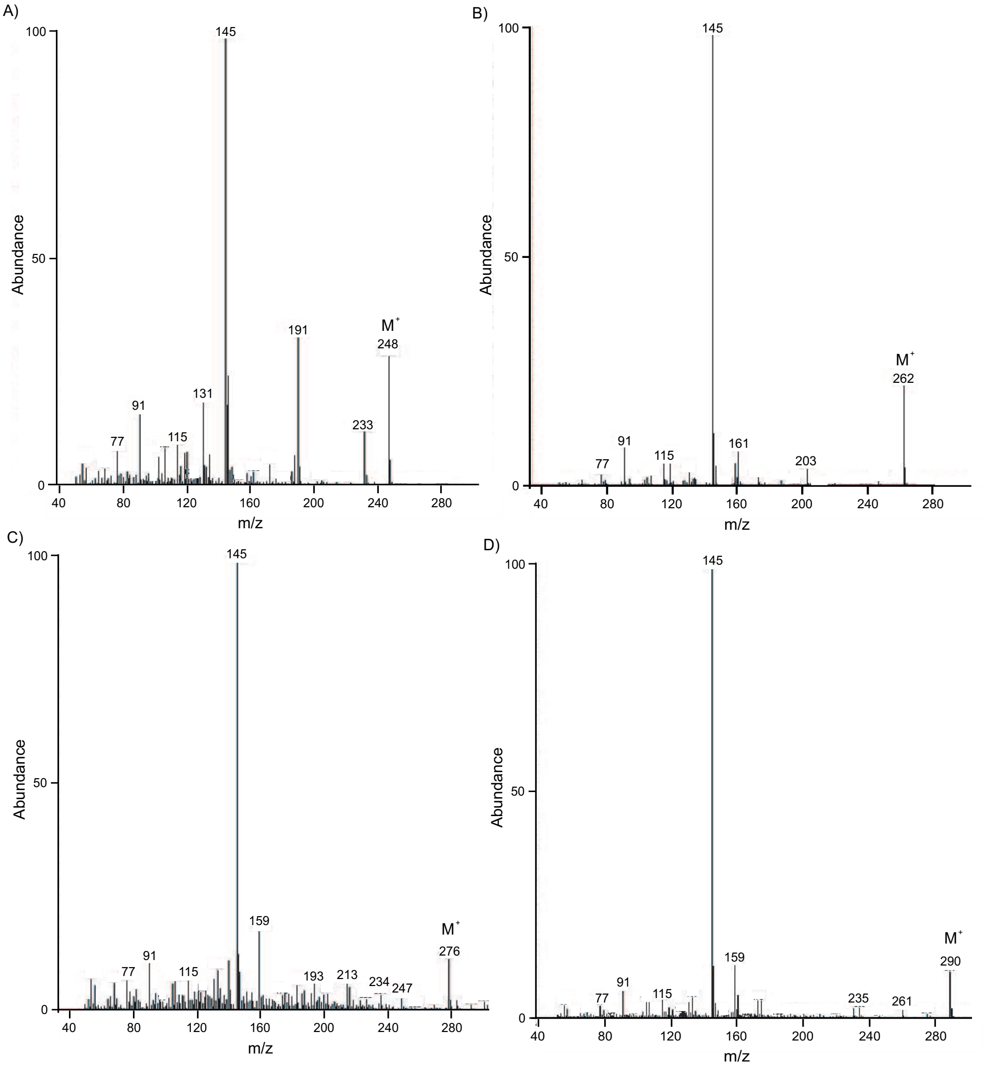

Figure S2: Typical EI mass spectra for the unknown propylated peaks having molecular masses of A) 248, B) 2262, C) 276, and D) 290.

Table S2: Major ions and molecular weights of unidentified peaks (Figure S1) in the Coyote Creek microcosms.

Peak Number	MW[a]	Major ions of unidentified peaks (intensity in parentheses)
1	248	248(29), 233(12), 191(33), 145(100), 131(18), 91(16)
2	248	248(49), 233(13), 191(15), 161(100), 145(85), 131(23), 119(41), 91(34)
3	262	262(17), 233(21), 191(35), 163(21), 145(100), 131(21), 91(16)
4	262	262(19), 233(16), 191(28), 159(18), 145(100), 131(23), 91(17)
5	262	262(22), 203(4), 161(7), 145(100), 131(3), 119(5), 115(5), 91(8)
6	276	276(32), 161(48), 145(100), 119(18), 91(20)
7	262	262(40), 203(12), 159(28), 147(100), 145(56), 131(29), 91(46)
8	290	290(11), 159(25), 145(100), 91(6)
9	276	276(11), 159(17), 145(100), 91(10)
10	290	290(9), 159(5), 149(25), 145(100), 91(6)
11	290	290(10), 159(11), 145(100), 115(4), 91(6)
12	290	290(11), 145(100), 115(8), 91(6)
13	290	290(10), 145(100), 91(10)

[a] Molecular weights were obtained from methane CI mass spectra

As seen in Figure S2 unidentified metabolites had strong base peaks at m/z 145; this mass to charge ratio was not present in the mass spectra of any CAP$_1$EC. The dominant products from a daughter ion scan on m/z 145, were ions with m/z values of 115(100) and 91(∼10) and 126(∼10) (Figure S3). The loss of 30 (giving rise to m/z 115) corresponds to a CH_2O group (a loss of C_2H_6 is unlikely as one would expect a significant peak at m/z 130). A loss of 54 is consistent with a loss of C_3H_2O and results in a peak at m/z 91 which typically corresponds to the tropylium cation and often indicates the presence of a -CH_2-C_6H_4- fragment.

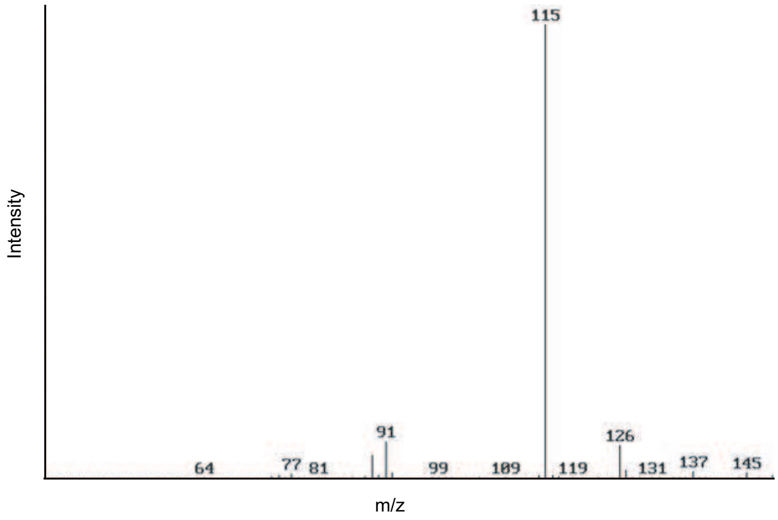

Figure S3: Daughter ion scan of m/z 145 ion (Figure S1; Peak 5).

The number of carboxy groups present in the molecule was determined by comparing the molecular masses after propylating and methylating the sample. The molecular ions in the methylated extracts were 28 mass units lower than those of the propylated extracts (Figure S4); this indicates the presence of only one carboxy group. Methylation using (trimethylsilyl)diazomethane resulted in spectra identical to those methylated using methanol/acetyl chloride and indicates the absence of hydroxyl groups in the unknown compounds (Data not shown).

To obtain the elemental composition of the unknown peaks, the Coyote Creek microcosms were respiked with NP$_1$EC several more times, to increase the abundance of the unknown compounds,

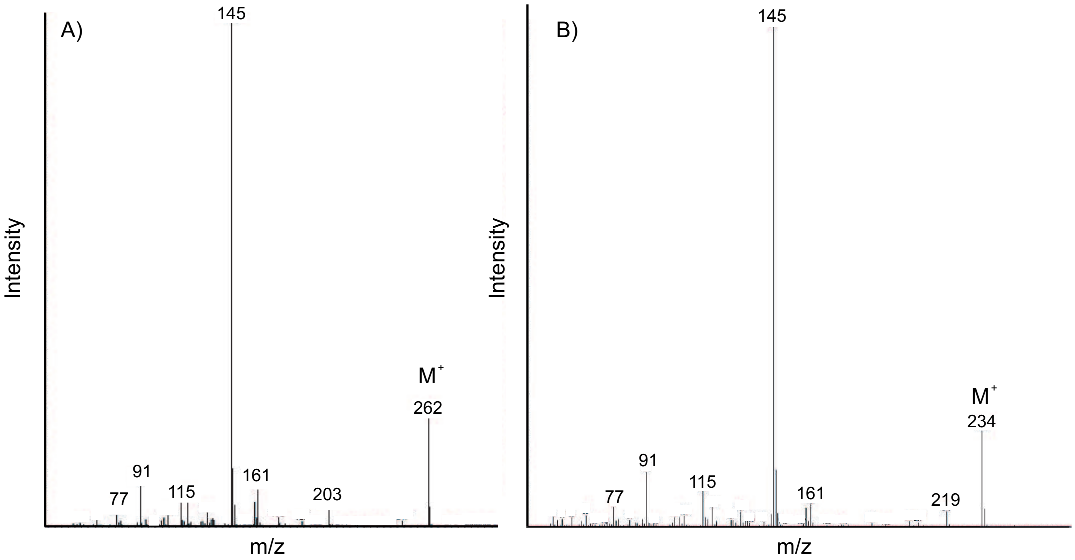

Figure S4: EI mass chromatograms of the A) propylated peak at 11.3 minutes (Figure S1; Peak 5) and B) the corresponding methylated peak.

and then sacrificed (around day 340), extracted and analyzed by high-resolution MS (at a resolving power of 5000). Examples of the elemental compositions of $C_{16}H_{22}O_3$ (1.5 millimass unit (mmu) error) and $C_{18}H_{26}O_3$ (0.7 mmu error) were obtained for the m/z 262 and m/z 292 peaks, respectively. In addition, the elemental composition for the m/z 145 ion was found to be $C_{10}H_9O$ (0.0 mmu error). Unfortunately, we were unable to find model compounds of sufficient similarity readily available for confirmation and reference spectra are not available. A model reaction for the proposed fragmentation scheme is illustrated in Figure S5.

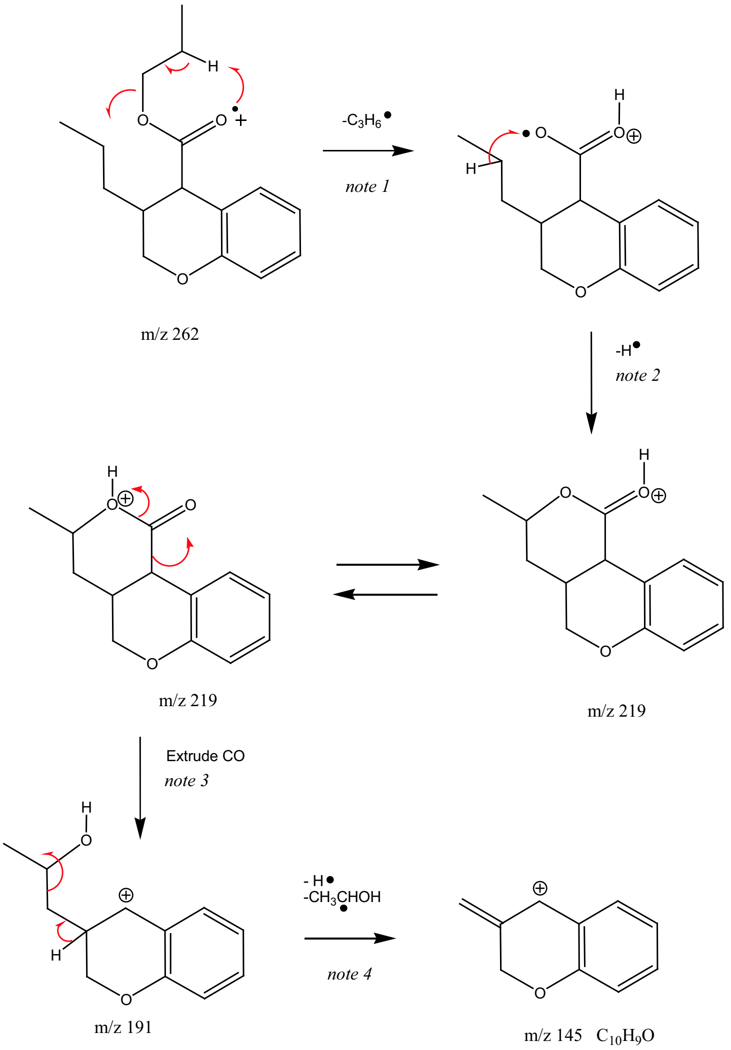

Figure S5: Proposed fragmentation scheme that gives rise to m/z 145. *Note 1*: This is the usual δ-Hydrogen migration and cleavage that higher alkyl esters normally do. *Note 2*: As long as there is a radical on O and a long alkyl chain nearby, the structure may cyclize, with the loss of an H. The relatively fast kinetics of 6-ring formation permit the re-establishment of an ester function. *Note 3*: The hydrogen on the ester oxygens can be in tautomeric equilibrium. Once the hydrogen is transferred to the ester, the extrustion of CO is facilitated. The stability of the benzylic cation (over that of the protonated ester) drives the reaction forward. There should be an m/z 191 ion in the EI spectrum, but it may be minor due to the next step. *Note 4*: No stability is gained by sequential loss of fragments associated with the alkanol. However, if the alkanol is lost *in toto*, a great deal of stabilization results in the allyl-benzyl cation that is formed (which can be drawn with a number of resonance structures). This cation, $C_{10}H_9O$, ought to be in enough of an energy-well to have a longer life in the EI mass spectrum, and it might even be a base ion.

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Appendix G

Plumlee, M.H., McNeill, K., Reinhard, M., 2008. Hydroxyl Radical-Mediated Indirect Photolysis of Perfluoroalkanesulfonamides, in progress.

Hydroxyl Radical-Mediated Indirect Photolysis of Perfluoroalkanesulfonamides

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Abstract

Selected perfluoroalkanesulfonamides were irradiated in aqueous hydrogen peroxide solutions using artificial sunlight to simulate aquatic environmental conditions. Indirect photolysis mediated by hydroxyl radical was observed for *N*-ethyl perfluorooctane sulfonamidoethanol (N-

EtFOSE), *N*-ethyl perfluorooctane sulfonamido acetate (*N*-EtFOSAA), *N*-ethyl perfluorooctane sulfonamide (*N*-EtFOSA), and perfluorooctane sulfonamide acetate (FOSAA). A proposed reaction pathway for degradation of the parent perfluorochemical, *N*-EtFOSE, to the other perfluoroalkanesulfonamides, perfluorooctane sulfonamide (FOSA), and perfluorooctanoate (PFOA) was developed and includes oxidation and *N*-dealkylation steps. As they did not undergo additional degradation, FOSA and PFOA were the final degradation products of hydroxyl radical-mediated indirect photolysis. UV-visible absorption spectra for the perfluorochemicals, showing absorbance in the UV region below the range of natural sunlight, are also reported. Given the slow rates expected for biodegradation and sorption, indirect photolysis of perfluorochemicals may be important in the determination of their environmental fate.

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Introduction

Perfluorochemicals are persistent environmental contaminants found in water, air, and sediment (Boulanger et al., 2004; Ellis et al., 2004; Boulanger et al., 2005; Schultz et al., 2006; Skutlarek et al., 2006) as well as in wildlife and humans (Hansen et al., 2001; Giesy and Kannan, 2002; Kannan et al., 2005). The persistence of this ubiquitous class of chemicals arises from the strength of the carbon-fluorine bond, and thus degradation of the fluorinated carbon chain is generally not observed. Instead, transformation of one perfluorochemical to another may occur by modification of the hydrophilic functional group, as has been observed in biological studies (Dinglasan et al., 2004; Rhoads et al., 2008) and in atmospheric reactions (Ellis et al., 2004; D'eon et al., 2006; Martin et al., 2006). With regard to their environmental fate, biodegradation is quite slow (Rhoads et al., 2008) and sorption is minor (Higgins and Luthy, 2006).

Volatilization may be important for those perfluorochemicals having significantly large Henry's constants, such as *N*-EtFOSE (Rhoads et al., 2008).

Aquatic photolysis of perfluorochemicals due to sunlight irradiation may occur but has received limited attention. While absorption of light resulting in direct photolysis of perfluorochemicals is not expected in the environment (PFOA, as a representative case, does not absorb within the spectrum of natural sunlight (Hori et al., 2004)), indirect photolysis may instead take place. Indirect photolysis occurs via reaction between the target compound and photochemically-produced reactive intermediates (PPRIs). One important PPRI is the hydroxyl radical, which is found in freshwaters at steady-state concentrations ranging from 1.5 x 10^{-18} to 8.4 x 10^{-16} M (Mabury and Crosby, 1994), in atmospheric water droplets (Chin and Wine, 1994) and in radical oxidation processes (advanced oxidation) for wastewater treatment (Haag and Yao, 1992; Bolton and Cater, 1994). Hydroxyl radicals typically react with the target substrate near the diffusion-controlled limit (10^{10} $M^{-1}s^{-1}$) (Haag and Yao, 1992) via hydrogen atom abstraction or addition to double bonds (Larson and Weber, 1994).

Perfluorochemical photolysis research to date has typically focused on UV irradiation and/or advanced oxidation for wastewater treatment. Hori et al. (2004) observed direct photolysis of PFOA by light absorption in the UV-region which was enhanced by a heteropolyacid photocatalyst; other studies have reported the degradation of perfluorochemicals using persulfate-induced indirect photolysis (Hori et al., 2005; Hori et al., 2007). More relevant to environmental conditions, Gauthier and Mabury (2005) reported the aqueous indirect photolysis of 8:2 FtOH in hydrogen peroxide solutions (used to generate hydroxyl radical), as well as in synthetic and natural field water. Hydroxyl radical was found to be the main degradation agent compared to nitrate and dissolved organic carbon. 3M has produced some internal studies on the direct and indirect photolysis of perfluorochemicals including PFOA, PFOS and *N*-EtFOSE: neither direct nor indirect (including H_2O_2-induced) photolysis of PFOA or PFOS was observed (Hatfield, 2001a; Hatfield, 2001b), while indirect photolysis (H_2O_2-induced) of *N*-EtFOSE was observed and produced *N*-EtFOSA, PFOA, and FOSA (direct photolysis of *N*-EtFOSE was not observed) (Hatfield, 2001c).

The objectives of the present study were to investigate the potential for aqueous indirect photolysis of perfluorooctanesulfonamides, such as *N*-EtFOSE and *N*-EtFOSAA, and to determine the reaction pathway and products. *N*-EtFOSAA has been detected in wastewater and wastewater-impacted surface waters (Boulanger et al., 2004; Boulanger et al., 2005; Plumlee et al., 2008), and *N*-EtFOSE is also expected to occur in wastewater (Rhoads et al., 2008). Although some perfluorochemical manufacturers have transitioned from the C8 to C4 chemistry due to the greater extent of bioaccumulation observed for the C8 compounds (Renner, 2006), the perfluorooctane-based chemicals that have been released are persistent and ubiquitous; additionally, findings for C8 compounds are expected to be analogous to that of the C4 parent and degradation products.

Experimental Section

Materials and Methods

Perfluorochemical sources and impurities are described in Rhoads et al. (2008). For perfluorochemical analysis, 800 μl of a 60/40 aqueous sample:methanol (Optima grade, Fisher Scientific; Pittsburgh, PA, USA) mixture were transferred to autosampler vials containing 200 μl aqueous 0.01% ammonium hydroxide (EMD; Madison, WI, USA). Using large-volume injection, samples were analyzed by liquid chromatography-tandem mass spectrometry, according to the method described by Plumlee et al. (2008) and Higgins et al. (2005). Prior to injection, 100 μl of an internal standard solution containing [D_9] *N*-EtFOSE (for analysis of *N*-EtFOSE), [D_5] *N*-EtFOSAA (for *N*-EtFOSAA and FOSA), [D_5] *N*-EtFOSA (for *N*-EtFOSA), [$^{13}C_2$] PFDA (for FOSAA), and [$^{13}C_2$] PFOA (for PFOA) was added (Rhoads et al., 2008).

UV-Visible (UV-Vis) absorption spectra of the perfluorochemicals were measured in methanol using a Cary 50 UV-Vis spectrophotometer (Varian, Inc.; Palo Alto, CA, USA).

Irradiations were performed using an Atlas Suntest CPS+ photosimulator (Chicago, IL, USA) equipped with a 1.1-kW xenon arc lamp. The lamp was fitted with special glass filters to block the transmission of wavelengths below 290 nm to simulate natural sunlight (passing wavelength, $290\ \text{nm} < \lambda < {\sim}800\ \text{nm}$). All irradiations were performed at an intensity of 765 W/m^2.

Irradiation Experiments

Perfluorochemicals (5 – 15 μg/l initial concentration of *N*-EtFOSE, *N*-EtFOSAA, *N*-MeFOSAA, *N*-EtFOSA, FOSAA, FOSA, or PFOA) were irradiated in individual solutions of 10 mM H_2O_2 (Fisher Scientific; Pittsburgh, PA, USA). Additional tubes containing the target perfluorochemical and H_2O_2 were covered with aluminum foil and irradiated to serve as dark controls. Because the critical micelle concentrations (CMCs) of several of these perfluorochemicals are unknown, the experimental concentrations were chosen to be well below the CMC of PFOA (1 – 4 g/l) (Mukerjee and Mysels, 1970). H_2O_2 was used to generate hydroxyl radicals according to the reaction:

$$H_2O_2 \xrightarrow{h\nu} 2\,{}^{\bullet}OH$$

Aqueous solutions were prepared by spiking a small volume of a methanol-based perfluorochemical stock and allowing the methanol to evaporate before addition of Milli-Q water

(Millipore, Billerica, MA). The solution was poured into identical capped 20 ml quartz test tubes (Quartz Scientific, Fairport, OH, USA), which were completely filled to avoid headspace and placed horizontally in a constant temperature (20 ± 2°C) water bath 25 cm directly below the photosimulator lamp. Because perfluorochemicals are surface-active and therefore may accumulate at the air-water interface or on surfaces in aqueous samples, special care must be taken in the experimental and sampling design. Observation of relatively constant perfluorochemical concentration in the controls confirmed that a consistent initial concentration was attained in each sample tube following transfer from the aqueous starting solution regardless of the surface-active properties of the perfluorochemical. Rather than sub-sampling, an entire quartz tube was sacrificed at various time points during irradiations ranging from one to six days. Samples were taken by transferring the contents of the quartz tube into a polypropylene microcentrifuge tube (E & K Scientific; Santa Clara, CA) containing methanol such that the final solution was 60/40 aqueous sample:methanol. Methanol serves to solvate the perfluorochemicals into the bulk solution, allowing sub-sampling, and also quenches hydroxyl radical. Duplicate aliquots of the sample mixture were taken for analysis.

Kinetics and Product Study

Where analytical standards were available, the products generated upon reaction of hydroxyl radical with the perfluorochemical of interest were monitored, and each product was irradiated individually to elucidate the reaction pathway. Due to the low starting concentration, total organic fluorine analysis could not be used to monitor fluorine mass balance. The observed decay rate of the starting compound was determined as the slope of $\ln(C_0/C)$ vs. time, with the standard error determined from linear regression analysis. The rates measured are useful for relative purposes only, as the concentration of hydroxyl radical generated was not representative of environmental conditions.

Results and Discussion

UV-Visible Absorbance

Because UV-vis absorbance data could only be found for PFOA (Hori et al., 2004), the absorbance of the perfluorochemicals tested in the present study was measured to confirm the lack of light absorption in the range of natural sunlight (Figure 1). Given that no light is absorbed in this region, direct photolysis in the natural environment is not expected. The perfluoroalkanesulfonamides and PFOA absorb UV light, with maximum absorption near ~204 nm. PFOA and other perfluorochemicals have been observed to decompose when irradiated with UV light in wastewater treatment studies (Hori et al., 2004; Hori et al., 2007).

Indirect Photolysis

Irradiation of the perfluorooctanesulfonamides *N*-EtFOSE, *N*-EtFOSAA, *N*-MeFOSAA, *N*-EtFOSA, and FOSAA in the presence of H_2O_2 resulted in significant degradation relative to controls, indicating that reaction with hydroxyl radical photochemically produced in the aquatic environment will result in the indirect photolysis of these compounds. The observed decay rate constants and products are reported in Table 1 and were determined from independent irradiations of each starting compound. In addition to the formation of PFOA and FOSA observed in all cases, irradiation of *N*-EtFOSE in the presence of H_2O_2 resulted in *N*-EtFOSAA, *N*-EtFOSA, and FOSAA formation (56% mass balance as fluorine); *N*-EtFOSAA irradiation produced *N*-EtFOSA and FOSAA (34% mass balance), and *N*-EtFOSA irradiation produced FOSAA (73% mass balance). Irradiation of FOSAA produced solely PFOA and FOSA (97%

mass balance). Analogous to *N*-EtFOSAA, the irradiation of *N*-MeFOSAA produced FOSAA, PFOA and FOSA (*N*-MeFOSA was likely produced but could not be monitored due to the lack of an analytical standard). PFOA and FOSA appeared to be the final degradation products, as neither further degraded nor resulted in product formation during independent irradiations. The resistance of PFOA to indirect photolysis via hydroxyl radical is consistent with the findings of an internal 3M laboratory report (Hatfield, 2001a). Gauthier and Mabury (2005) also observed PFOA as the major product of the indirect photolysis of 8:2 FtOH.

The formation of PFOS was not observed, which differs from the findings of D'eon et al. (2006) for the atmospheric reaction of *N*-MeFBSE with hydroxyl radical. *N*-MeFBSE is analogous to the starting compound used in the present study, *N*-EtFOSE, but with a shorter perfluorocarbon chain and methyl- rather than ethyl- substitution of the sulfonamide. D'eon et al. (2006) observed PFBA (analogous to PFOA; major pathway) as well as PFBS (analogous to PFOS; minor pathway). The lack of the minor pathway in the present study may be explained by the use of solvent (water). In agreement with these findings, Hatfield (2001c) did not observe PFOS formation following aqueous irradiation of *N*-EtFOSE and H_2O_2 as reported in an internal 3M laboratory study.

Product Pathway

The products observed during each independent irradiation along with expected radical chemistry were used to generate the proposed pathway given in Figure 2. Because complete mass balances were not observed in all cases (which is reasonable given the variety of potential radical reactions), the formation of "other products" is depicted in the pathway.

We propose the following reaction mechanisms, illustrated in Figure 3 through Figure 7, for the formation of PFOA and FOSA from the indirect photolysis of perfluorooctanesulfonamides. In several cases, loss of an R-group (ethanol, ethyl, or acetic acid) bonded to the nitrogen was observed upon reaction with hydroxyl radical. As noted by D'eon et al. (2006), *N*-dealkylation reactions are common in aqueous systems and may occur via the mechanism proposed by Tauber and von Sonntag (2000) for atrazine, involving peroxy radical formation and loss of the hydroperoxyl radical $HO_2^{\bullet}$. For example, *N*-EtFOSA may undergo *N*-deethylation via this mechanism (Figure 3). When the nitrogen is not bound to an available hydrogen, we propose that *N*-dealkylation may instead occur by formation and hydrolysis of an iminium ion (March, 1985) as shown for formation of FOSAA (Figure 4) and *N*-EtFOSA (Figure 5) from *N*-EtFOSAA. Alternatively, oxidation of the R-group may occur by hydroxyl radical attack via the mechanism shown for *N*-EtFOSE in Figure 6 (Larson and Weber, 1994; Bahnemann, 1999), in which *N*-EtFOSAA is produced. The oxidation of the aldehyde intermediate to the acid may occur spontaneously in oxygenated waters or be hydroxyl radical-mediated. The perfluorooctanesulfonamides may also proceed directly to the end-product PFOA via hydroxyl radical attack at the sulfur atom, as proposed by D'eon et al. (2006) and illustrated for FOSAA in Figure 7.

Extrapolation to Environmental Conditions

Given the slow rates expected for biodegradation and limited sorption, indirect photolysis of perfluorochemicals is likely to be important in the determination of their environmental fate. For instance, Rhoads et al. (2008) observed half-lives ranging 0.71 to 9.2 d for the same compounds assessed in the present study for biodegradation in activated sludge from a wastewater treatment plant, which is highly concentrated biologically compared to natural aquatic systems. Higgins and Luthy (2006) report log K_{oc} values of 3.11 ± 0.16 and 3.23 ± 0.18

for *N*-MeFOSAA and *N*-EtFOSAA, respectively, which indicate that the perfluorochemicals sorb minimally to sediments. In their study of the aqueous, indirect photolysis of 8:2 FtOH, Gauthier and Mabury (2005) measured a rate constant of 0.84 h^{-1} ($t_{½}$ = 0.83 ± 0.2 h) in 10 mM H_2O_2 and 0.007 h^{-1} ($t_{½}$ = 93 ± 10 h) in natural water from Lake Ontario. Their rate in 10 mM H_2O_2 is comparable to the rates measured in the present study (0.04-0.24 h^{-1}) for perfluorooctanesulfonamides. By comparison, we may expect half-lives in sunlit natural waters of approximately 75 d for *N*-EtFOSE and two to three weeks for *N*-MeFOSAA, *N*-EtFOSAA, *N*-EtFOSA and FOSAA.

Figures and Tables

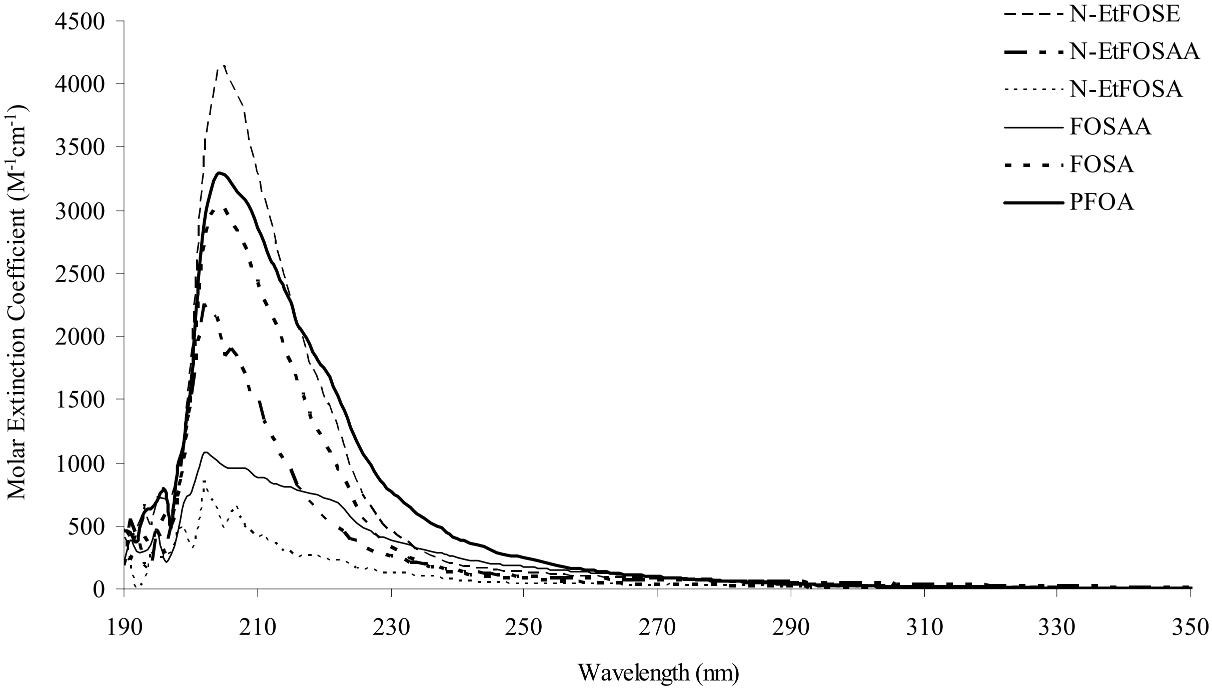

Figure 1. Absorbance spectra for selected perfluorochemicals in methanol.

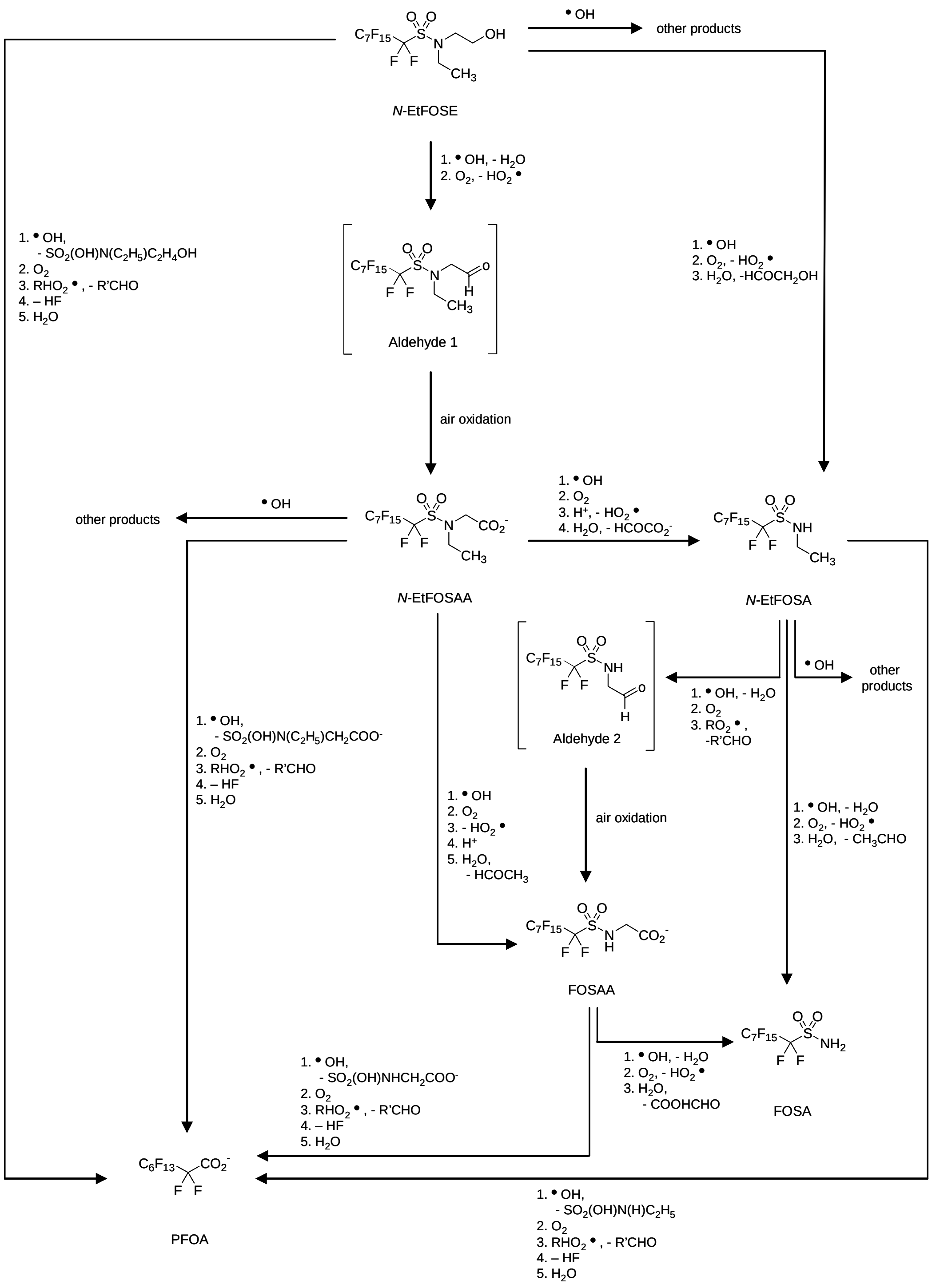

Figure 2. Proposed pathway for the aqueous indirect photolysis of perfluoroalkanesulfonamides via reaction with hydroxyl radical. All compounds shown were observed, with the exception of the aldehydes depicted in brackets. Formation of "other products" (unknown) indicates that an incomplete mass balance was measured for the starting compound.

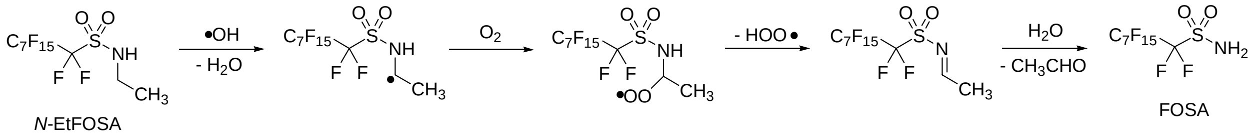

Figure 3. Reaction mechanism for *N*-dealkylation of a perfluoroalkanesulfonamide via reaction with hydroxyl radical.

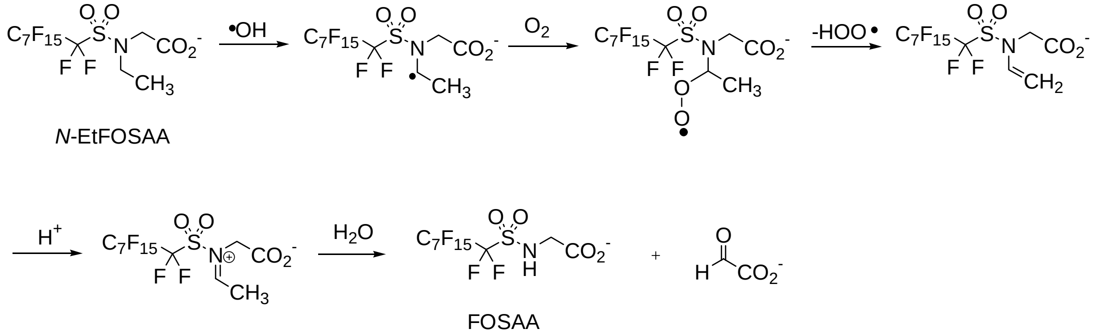

Figure 4. Reaction mechanism for oxidation of *N*-EtFOSAA to FOSAA via an iminium ion.

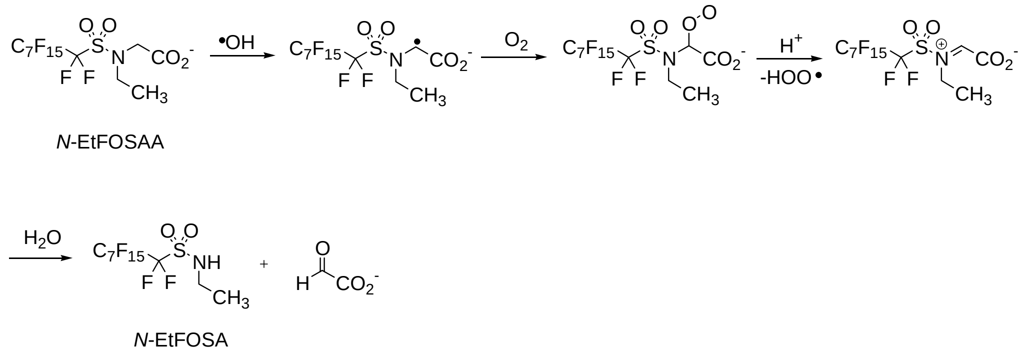

Figure 5. Reaction mechanism for oxidation of *N*-EtFOSAA to *N*-EtFOSA via an iminium ion.

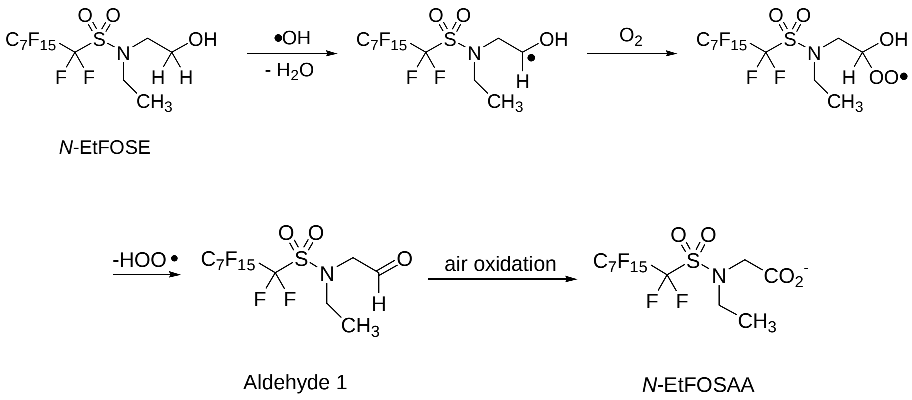

Figure 6. Reaction mechanism for oxidation of *N*-EtFOSE to *N*-EtFOSAA via reaction with hydroxyl radical.

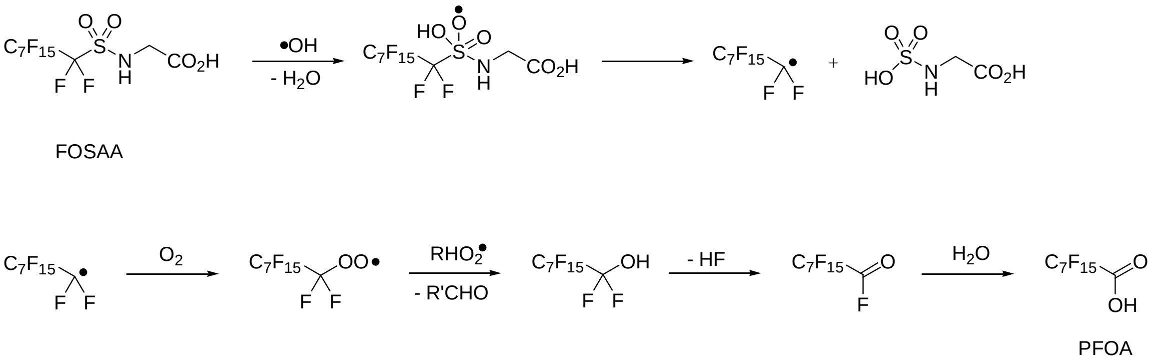

Figure 7. Reaction mechanism for transformation of FOSAA to PFOA via reaction with hydroxyl radical.

Table 1. Observed decay rate constants and products observed for 765 Wm^{-2} irradiation of selected perfluorochemicals in 10 mM aqueous hydrogen peroxide.

Perfluorochemical	**Observed Decay Rate Constant, k [h^{-1}]**	**Half-Life [h]**	**Products**	**Fluorine Mass Balance**
N-EtFOSE	0.04	16.12	*N*-EtFOSAA, *N*-EtFOSA, FOSAA, FOSA, PFOA	77%
N-EtFOSAA	0.24 ± 0.04	2.89	*N*-EtFOSA, FOSAA, FOSA, PFOA	34%
N-MeFOSAA	0.15	4.61	FOSAA, FOSA, PFOA	62%
N-EtFOSA	0.18	3.81	FOSAA, FOSA, PFOA	73%
FOSAA	0.13	5.16	FOSA, PFOA	97%
FOSA	no decay	--	none	--
PFOA	no decay	--	none	--

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Appendix H

Steinle-Darling, E., Reinhard, M., 2008. Nanofiltration for trace organic contaminant removal: structure, solution and membrane fouling effects on the rejection of perfluorochemicals. Environ. Sci. Technol. 42, 5292-5297.

Environ. Sci. Technol. **2008,** *42,* 5292–5297

Nanofiltration for Trace Organic Contaminant Removal: Structure, Solution, and Membrane Fouling Effects on the Rejection of Perfluorochemicals

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Received December 20, 2007. Revised manuscript received March 31, 2008. Accepted April 2, 2008.

The use of nanofiltration (NF) membranes for water recycling requires an improved understanding of the factors that govern rejection of potentially harmful organic trace contaminants. Rejections of 15 perfluorochemicals (PFCs)—5 perfluorinated sulfonates, 9 perfluorinated carboxylates, and perfluorooctane sulfonamide (FOSA)—by four nanofiltration membranes (NF270, NF200, DK, and DL) were measured. Rejections for anionic species were >95% for MW > 300 g/mol. FOSA (MW = 499 g/mol), which is uncharged at the pH of deionized water (5.6), was rejected as little as 42% (DL membrane). Decreasing the pH to less than 3 decreases rejection by up to 35%, effectively increasing the MWCO of NF270 by >200 g/mol, while a 2500 mg/L NaCl equivalent increase in ionic strength reduces rejections <1%. An alginate fouling layer increases transmission, where quantifiable, by factors of 4–8. Accumulation of PFCs on membranes was measured after the completion of rejection experiments. Based on rejection kinetics and the extent of sorption, we infer that two different sorption processes are significant: charged species adsorb quickly to the membrane surface, whereas the uncharged FOSA absorbs within the membrane matrix in a much slower process.

1. Introduction

Reverse osmosis (RO) and nanofiltration (NF) are increasingly used to treat recycled waters to the necessary standards due to their efficiency in removing a broad range of dissolved organic contaminants (*1*, *2*). However, recent results show that NF and RO membranes are permeable for certain, relatively small trace organic contaminants, including some disinfection byproducts, pharmaceuticals, and personal care products (*1–4*). The rejection process has been shown to depend on a large number of factors, which can be grouped into three main categories: charge repulsion, size exclusion, and factors governing "solute-membrane affinity", which include hydrophobicity, hydrogen bonding capacity, and dipole moment (*2*, *5*, *6*).

Variations in feed conditions (e.g., pH, ionic strength, presence of foulant material) can affect the rejection of trace contaminants. For example, the charges of solute and membrane surface can be affected by the solution pH, which can affect the net repulsive forces between the two (*7–9*); an increase in ionic strength may result in shielding of some of those charges from one another, leading to a decrease in rejection under otherwise similar conditions.

Previous studies showing the effects of membrane fouling on the rejection of trace organic contaminants have led to disparate results: Some show that fouling will primarily increase the rejection of trace contaminants (*10*), others have shown the opposite (*11*, *12*), and still others have shown that both are possible (*3*, *13*). The explanations for this divergent set of results are that increased rejection can be caused by increased charge repulsion or sorption of contaminants to loose foulant material which is then swept away (*10*, *13*). Decreased rejection is caused by an increase in concentration polarization that is due to a build-up of contaminant in the fouling layer. This increases the chemical gradient and thus the driving force for contaminant transport across the membrane, a phenomenon that has been named "foulant enhanced concentration polarization" (*14–16*).

Sorption of organic solutes onto membranes is often discussed in the context of fouling, where the sorption of a compound causes a flux decline (e.g., ref (*17*)). Fewer studies exist on the relationship between sorption and rejection. These have shown that a high affinity for the membrane material generally leads to a smaller rejection than expected based purely on the size of the compound (*18*). Additionally, several studies show that sorption causes a high initial rejection, followed by a steady decrease in rejection over time until the sorptive capacity of the membrane is exhausted. At this point, the rejection stabilizes at a constant value. Unless solute rejection is monitored over time, the effects of sorption on rejection are overlooked, which can lead to overestimation of the steady-state rejection (*4*, *11*, *19*).

The perfluorochemicals (PFCs) studied here lend themselves well to the study of the contribution of individual factors to rejection because they span a wide range of sizes as well as several different functional group and charge categories. In addition, they are an important class of contaminants in recycled water, known to be recalcitrant, bioaccumulative, and toxic to aquatic life. PFCs are ubiquitous in our every-day lives (e.g., Gore-Tex, Stainmaster, and Teflon brands) and have been found in San Francisco Bay sediment (*20*) and places as remote as the Canadian Arctic (*21*). Recently, they have been found in secondary-treated wastewater effluent (*20*, *22*) and tertiary-treated recycled water (*23*), indicating that these contaminants would be in the feed to NF and RO membrane installations used to produce recycled water. The only previous work on PFC rejection by membranes is two studies by Tang et al. (*24*, *25*), which show high rejections (>99%) of perfluorooctane sulfonate (PFOS) by RO membranes and 90–99% removal by NF membranes at concentrations relevant to semiconductor wastewater (mg/L). The flux decline reported in these previous studies indicates some amount of PFOS sorption by the membrane.

To ensure safe use of recycled water, it is imperative to know not only the specific rate of rejection for the particular contaminants studied here *at concentrations observed in practice* (*19*), but also to understand the factors that govern contaminant rejection in general. The objective of this paper is therefore to quantify the importance of membrane type, solute size, pH, ionic strength, sorption, and the existence of a fouling layer on the rejection of 15 PFCs by four NF membranes. Finally, rejection and sorption data are used to

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10.1021/es703207s CCC: $40.75

TABLE 1. PFCs Used in This Study with Abbreviations, Chemical Formulas, Molecular Weights, and pK_a Values

full name	abbreviation	formula	MW	pK_a[a]	log K_{oc}[c]
perfluoropentanoate	PFPnA	$CF_3-(CF_2)_3-COO^-$	263	−0.1	
perfluorobutane sulfonate	PFBS	$CF_3-(CF_2)_3-SO_3^-$	299	0.14	
perfluorohexanoate	PFHxA	$CF_3-(CF_2)_4-COO^-$	313	−0.16	
perfluoroheptanoate	PFHpA	$CF_3-(CF_2)_5-COO^-$	363	−0.19	
perfluorohexane sulfonate	PFHxS	$CF_3-(CF_2)_5-SO_3^-$	399	0.14	
perfluorooctanoate	PFOA	$CF_3-(CF_2)_6-COO^-$	413	−0.2	2.06
1H,1H,2H,2H-perfluorooctane sulfonate	6:2 FtS	$CF_3-(CF_2)_5-(CH_2)_2-SO_3^-$	426	0.36	
perfluorononanoate	PFNA	$CF_3-(CF_2)_7-COO^-$	463	−0.21	2.39 ± 0.09
perfluorooctane sulfonate	PFOS	$CF_3-(CF_2)_7-SO_3^-$	499	0.14	2.57 ± 0.13
perfluorooctane sulfonamide	FOSA	$CF_3-(CF_2)_7-SO_2-NH_2$	499	6.52[b]	
perfluorodecanoate	PFDA	$CF_3-(CF_2)_8-COO^-$	513	−0.21	2.76 ± 0.11
perfluoroundecanoate	PFUnA	$CF_3-(CF_2)_9-COO^-$	563	−0.21	3.30 ± 0.11
perfluorodecane sulfonate	PFDS	$CF_3-(CF_2)_9-SO_3^-$	599	0.14	3.53 ± 0.12
perfluorododecanoate	PFDoA	$CF_3-(CF_2)_{10}-COO^-$	613	−0.21	
perfluorotetradecanoate	PFTA	$CF-(CF_2)_{12}-COO^-$	713	−0.21	

[a] pK_a values were obtained using the SPARC calculator (*31*), a model whose results have been shown to agree well with experimental data for other fluorinated compounds (*32*). [b] pK_a given is for the transition between neutral and negative charge on the amide nitrogen. [c] logK_{oc} values were obtained from Higgins and Luthy (*30*).

hypothesize the locations of sorption sites for the different types of PFCs.

2. Experimental Section

2.1. Materials. *2.1.1. Membranes.* Four types of nanofiltration membranes were used in this study. Most experiments were performed with NF270 (Dow/FilmTec, Minneapolis, MN). For comparison, rejection experiments in deionized water were also performed with NF200 (Dow/FilmTec), DK, and DL (both GE Osmonics, Minnetonka, MN) NF membranes. All of these membranes are piperazine-based polyamide membranes. However, while the FilmTec membranes are composed only of polypiperazine, the GE Osmonics membranes have been modified from this chemistry (*26*). All the membranes have isoelectric points in the range of pH = 4−5, as measured via zeta potential (*7, 27*). Selected rejection parameters for these membranes are listed in Table 2.

2.1.2. Chemicals. All reagents used in this study were of HPLC grade unless otherwise specified. The PFCs used in this study are shown in Table 1. Their sources and purities are given by Higgins et al. (*20, 28*) and Stevenson et al. (*29*). They are all linear molecules consisting of perfluorinated backbones ranging from 4 to 14 carbons, and one of three different functional groups (carboxylate, sulfonate, and one sulfonamide). Two additional descriptors, pK_a and log K_{oc} are given for those compounds for which the parameters were available. Due to their surface active nature, the traditional measure of hydrophobicity, K_{ow}, has not been determined for these compounds. Instead, K_{oc}, the distribution coefficient for water/sediment systems (normalized for the fraction of organic content in the sediment) is used as a surrogate (*30*).

2.2. Membrane Test Setup. The membrane apparatus used in this study has been described previously (*3*). Briefly, the setup consists of three flat sheet membrane cells configured in parallel and operated in a cross-flow configuration. Each cell has an active membrane area of 103 cm^2 (8.1 cm wide × 12.7 cm long) and a channel height of 1 mm. No feed spacers were used. Retentate and permeate are recycled to the feed tank. Detailed descriptions of the experimental protocol as well as sample analysis can be found in the Supporting Information. The sample preparation and analysis method employing direct-injection liquid chromatography−tandem mass spectrometry (LC-MS/MS) are described in Plumlee et al. (*23*), which is based on a method by Higgins et al. (*20*). The extraction procedure for quantifying the sorbed PFCs is based on a method by Tang et al. (*25*).

2.3. Fouling Method. Some rejection experiments were conducted under simulated fouling conditions using a method similar to one described previously (*3, 33*). After the membranes were equilibrated in deionized water for at least 48 h, 60 mg/L alginate, 0.3 mM $CaCl_2$, and 10 mM NaCl were added to the feed as follows: Alginate (alginic acid sodium salt from brown algae; Sigma-Aldrich, St. Louis, MO) was predissolved in 2 L of 150 mM NaCl (Mallinckrodt-Baker, Phillipsburg, NJ) solution, which was then added to the feed tank. Calcium chloride (Mallinckrodt-Baker) was predissolved in ca. 200 mL of deionized water and added to the feed tank. After a flux decline of >30% was reached, the membrane coupons were temporarily removed from the membrane cells, the system was flushed with deionized water, and the fouled coupons were placed back into the cells. Then the feed tank was spiked with PFCs and the experiment proceeded as described in Section 2.2.

3. Results and Discussion

3.1. Steady-State PFC Rejections in Deionized Water. Figure 1 shows the steady-state rejections of PFCs in deionized water, defining steady-state as the drop in rejection over a 24 h period being less than 1%. The rejections are quite high in general. Nearly all the compounds are rejected to 95% or greater, with two notable exceptions: First, perfluoropentanoic acid (PFPnA), the smallest PFC studied here, is rejected 72% (by NF270; PFPnA was not chromatographically resolved for the experiments with the remaining membranes). This indicates that the size cutoff for compounds of this type is close to PFPnA's molecular weight of 263 g/mol for this membrane.

The second exception to the trend of high rejection is perfluorooctane sulfonamide (FOSA), a larger PFC at 499 g/mol, which is rejected as little as 42% (DL) and as much as 98.5% (NF200). FOSA was the only compound detected in the NF200 permeate. This compound differs from the rest of the set in that it is the only PFC expected to be at least partially uncharged at circumneutral pH levels. Thus, the lack of electrostatic repulsion of FOSA from the negatively charged NF membranes might explain the marked difference in steady-state rejections.

While difficult to ascertain from Figure 1, the relative transmissions of most PFCs among the four membranes are consistent with relative descriptors of membrane "tightness", as shown in Table 2. The charged PFCs are not detected in the permeate of NF200, which is the "tightest" according to salt rejection data. NF270 and DK are "looser" than NF200 and have similar $MgSO_4$ trans-

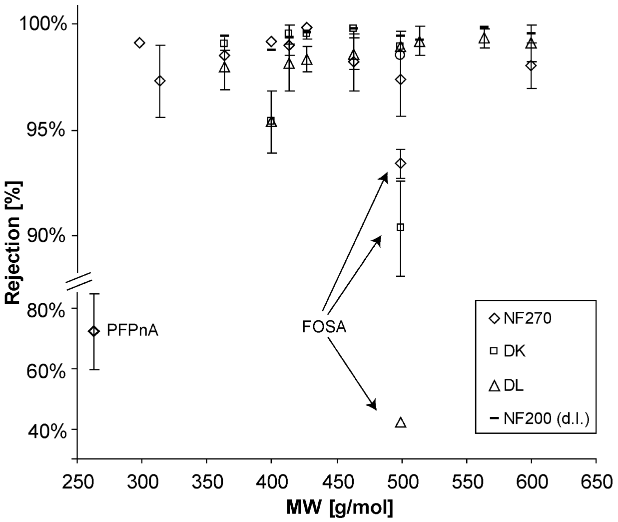

FIGURE 1. Steady-state rejection versus molecular weight of the PFCs listed in Table 1 for 4 membrane types in deionized water. Note that values given for NF200 are the detection limits (d.l.), since the permeate concentrations were not quantifiable, except in the case of FOSA. Error bars indicate one standard deviation from the mean of 6 samples (duplicates for each of three cells).

TABLE 2. Comparison of Transmissions for the Membranes (Ordered Tightest to Loosest): Salts versus PFCs

	NF200	NF270	DK	DL
MgSO$_4$ transmission[a]	<3%	<3%	2%	4%
NaCl transmission	40%[b]	43%[c]	44%[c]	50%[c]
average PFC transmission[d]	<d.l.	1.2%	1.3%	2.1%
FOSA transmission	1.5%	7%	10%	58%

[a] MgSO$_4$ transmissions as given by manufacturers, determined at 2000 mg/L feed concentration (*34, 35*). [b] From ref (*9*), determined at 80 psi (550 kPa). [c] From ref (*36*), determined at 10 mM NaCl feed concentration and 200 psi (1400 kPa). [d] Average PFC transmission calculated from the transmissions of anionic PFCs between 300 and 600 g/mol, (<d.l. = permeate below detection limits).

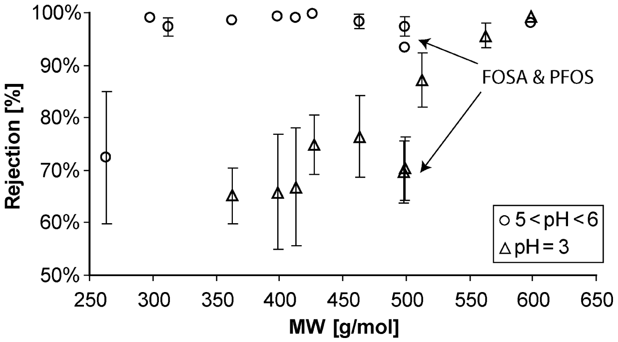

FIGURE 2. Rejection versus molecular weight for the PFCs shown in Table 1 by NF270 at pH = 2.8 and 5 < pH < 6. Note that with the decreased pH, the effective MWCO shifts upward from ca. 250 to ca. 500 g/mol. Error bars indicate one standard deviation from the mean of 6 samples.

missions, which is consistent with their similar transmissions of charged PFCs. Finally, DL is the "loosest" of the membranes according to both PFC and salt transmission data. The same trends are seen for the transmission of FOSA, although it is interesting to note that a relatively small increase in salt transmission between DK and DL results in a large increase in FOSA transmission.

An additional difference between the behavior of FOSA and that of the other PFCs is that the latter all reach their steady-state rejections within the first few minutes of operation, whereas the rejection of FOSA declines steadily over the course of several days (data not shown). This distinctive behavior is observed for all four NF membranes and is very similar to that observed by Ng and Elimelech (*11*) and Nghiem et al. (*4*), where the rejection of hormones by NF membranes declines over time to a steady value. These authors attribute the declining rejection to sorption of the hormones to the membrane and hypothesize that once the sorptive capacity of the membrane is exhausted, the rejection stabilizes.

With some experiments, the feed was replaced with deionized water at the end, in order to determine the extent of "redissolution" of PFCs from the membrane. While some amounts of PFCs were found in the feed (probably due to incomplete flushing of the membrane system), the PFCs were not detected in the permeate stream after the switch to clean feed water, suggesting that the sorption of PFCs to the membrane is not readily reversible under the clean-water flush usually used to clean NF membranes.

In general, one can therefore conclude that nanofiltration membranes are very effective (>95%) at removing ionic perfluorinated surfactants with a size of 300 g/mol or greater. For those PFCs which are not deprotonated (e.g., FOSA), rejection can be much lower and should be measured as a function of time until it stabilizes.

3.2. Effect of pH and Ionic Strength on Rejections. Figure 2 shows the rejection of PFCs by NF270 as a function of molecular weight at two pH levels. The data for 5 < pH < 6 (deionized water) are the same as shown in Figure 1 for NF270. Despite the larger errors on the data for pH = 2.8, it is clear that the change in pH has a large effect on the effective molecular weight cutoff (MWCO) of this membrane. Whereas at 5 < pH < 6, the 90% rejection cutoff point lay below 300 g/mol, at pH = 2.8, it lies somewhere between 500 and 550 g/mol.

Since the perfluorinated anionic surfactants studied here (except FOSA) have $\mathrm{p}K_a < 1$ (see Table 1), the effects of pH variation on the speciation of these compounds are expected to be negligible. However, the membrane charge at pH = 2.8 is neutral or even positive, since the iso-electric point of the membrane is at 4 < pH < 5 (*7*). Thus at pH = 2.8, the charge repulsion effect is removed from the overall balance of forces governing the rejection of the solutes. A comparison between the charged and uncharged PFCs of identical size, FOSA and perfluorooctane sulfonate (both 499 g/mol), supports this conclusion: At 5 < pH < 6, the transmission of the uncharged FOSA (7%) is several times that of the charged PFOS (2.5%), whereas at pH = 2.8, the transmission of FOSA and PFOS are nearly equal (both 30%).

The effect of pH on the rejection of FOSA is much more pronounced, as would be expected from a compound with a $\mathrm{p}K_a$ value (6.5) within the range that the pH was varied. Figure S1 in the Supporting Information shows that the rejection of FOSA increases monotonically with increasing pH, from a low of 70% at pH = 2.8 to a high of >99% at pH = 10. Thus one possible way to increase the rejection of a contaminant of concern such as FOSA would be to increase the feed pH, since a large gain in rejection can be made for only a small shift in pH.

The effect of ionic strength on the rejection of the PFCs is much less pronounced. As shown in Figure S2 in the Supporting Information, an increase in ionic strength (adjusted via the concentration of sodium chloride) has a minor influence, reducing the rejections 0.5−1% over the span of 2500 mg/L NaCl. This indicates that the role of increased ionic strength in reducing the charge repulsion is not significant in this range. Similar results showing a strong

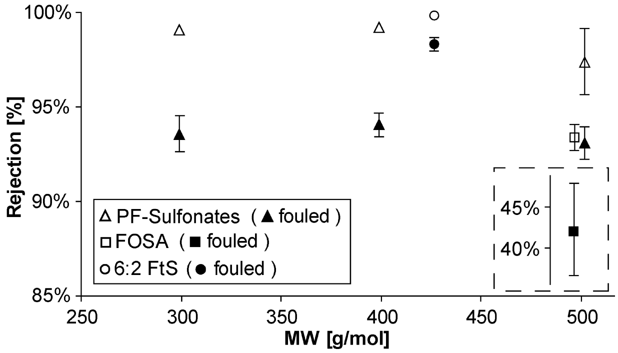

FIGURE 3. Rejection of selected PFCs as a function of fouling state and molecular weight for NF270 (open symbols = clean, filled symbols = fouled). Error bars indicate one standard deviation from the mean of 6 samples.

effect of pH and an insignificant effect of ionic strength have been shown before for other trace organic contaminants (*8, 37*).

3.3. Effects of Foulant Layer. For the experiments with fouled membranes, there was no foulant present in the feed solution when the PFCs were spiked into the membrane system. For this reason, a mechanism by which fouling could increase rejection (sorption onto free-floating foulant particles) would not be relevant. Therefore, the expectation was that the foulant layer would decrease the rejection of PFCs via "foulant-enhanced concentration polarization", as observed previously in some cases (*14–16*).

As shown in Figure 3, fouling indeed decreases rejection significantly for perfluorosulfonates and FOSA, increasing transmission by factors of 4−8. The data for the perfluorocarboxylates (not shown) is not as clear due to large errors on the data for the fouled case.

To confirm that increased concentration polarization is indeed the cause of reduced rejection, a calculation using a much-simplified version of the cake-enhanced concentration polarization model (*14–16*) was performed, as described in detail in the Supporting Information. Briefly, as a result of several simplifying assumptions, the concentration polarization layer thickness is assumed to be increased by the thickness of the foulant layer. From the intrinsic rejection of the membrane (determined in deionized water) and this information, the expected rejection for the membrane with a foulant gel layer can be calculated. This was done for the compounds shown in Figure 3, as these were the only data obtained with enough accuracy to make a calculation meaningful. The average rejections were 99.3% by clean membranes, 95.3% by fouled membranes, and the calculations predicted an average of 93.1% rejection for the fouled case. On average, the simple calculation thus overpredicted the effect on the rejection reduction by approximately 30%, but successfully captured the general trend.

3.4. PFC Sorption. Figure 4 shows the mass of PFCs sorbed to the membrane coupons (after rejection experiments) as a function of molecular weight on a log-linear plot. With the exception of FOSA, a linear correlation exists between the logarithm of sorbed mass and molecular weight ($R^2 = 0.95$). This result indicates that a positive interaction takes place between the membrane surface and the perfluorinated chains, increasingly overpowering the repulsion between the membrane surface and the negative charge on the carboxylate and sulfonate groups.

The logarithmic correlation between sorption and molecular weight within a homologous series is not surprising. These larger sorptive interactions for the larger PFCs are also evident from the larger K_{oc} values reported by Higgins and Luthy (*30*) shown in Table 1. The linear correlation between log K_{oc} and molecular weight has $R^2 = 0.98$ (data not shown), and thus the linear correlation between log K_{oc} and the logarithm of the amount sorbed shown in Figure S3 of the Supporting Information is equally good ($R^2 = 0.95$). A similar linear correlation has been shown between size, log K_{ow} and the logarithm of sorption in pervaporation processes (*38*). Since molecular weight and log K_{oc} are not independent variables, it is difficult to distinguish between effects related to hydrophobicity uncoupled from size.

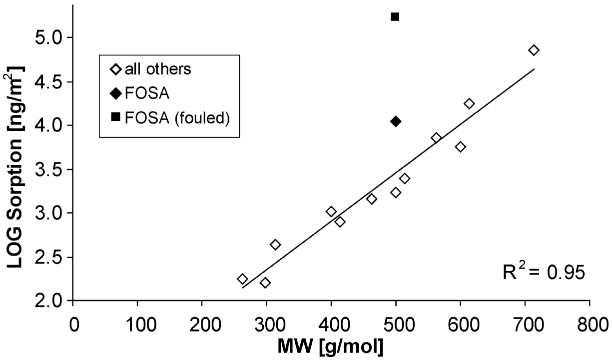

FIGURE 4. Logarithm of mass of PFCs sorbed on NF270 membrane coupons after rejection experiments (in deionized water unless otherwise specified). The linear correlation includes all PFCs except FOSA. Error bars were omitted for clarity, as most are smaller than the symbols and all are 1/2 log unit or less.

If the declining rejection over time described in Section 3.1 for FOSA (and none of the other PFCs) is to be attributed to sorption to the membrane, one should find significantly more FOSA than other PFCs sorbed on the membrane. Figure 4 shows that FOSA does indeed sorb nearly an order of magnitude more than would be expected for its size.

The effect of a foulant layer on the sorption of PFCs is minor for all PFCs (data not shown) except FOSA. The large increase in sorption of FOSA with a fouling layer (Figure 4) indicates a strong interaction with the foulant as well as the membrane surface. It is likely that the lack of charge that allows FOSA to approach the membrane surface unimpeded by electrostatic repulsion is also the cause for increased sorption within the fouling layer, which is also negatively charged.

3.5. Implications of Internal and Surface Sorption on Membrane Performance. According to the data shown in Figure 4, *all* PFCs sorb to a certain degree. The compounds that immediately reach steady-state rejection (i.e., all but FOSA), are all charged at the pH of deionized water (ca. 5.5). For these compounds, sorption must be on a time scale shorter than that required to take the first permeate samples (ca. 5 min). These same compounds are those for which a strong correlation is found with molecular weight, which implies that the perfluorinated chain length controls the extent of sorption. A plausible explanation for these observations is that the charged PFCs are *ad*sorbing to the surface of the membrane with their uncharged perfluorinated ends via van der Waals interactions, a process which is fast due to the lack of significant mass transport limitations. FOSA, on the other hand, sorbs much more relative to its size and takes nearly a week to reach its steady-state rejection (data not shown). With FOSA, a very different sorption process is thus hypothesized to be at work: Internal *ab*sorption within the membrane would require a longer time scale to allow FOSA to partition into the membrane phase and diffuse to its eventual sorption site. The slow sorption of FOSA is observed to affect neither the water flux nor the rejections of the remaining PFCs, implying that its internal sorption sites are not in their transport path.

Though the PFCs studied here all share the same somewhat unusual perfluorinated chemistry, the general observations made in this study are consistent with the results from previous rejection studies with other trace organic contaminants (*2, 5–9* and others): Charged species are repelled from the membrane surface, resulting in high, time-invariant rejections relative to the size of the solute and comparatively little association with the membrane as measured by sorption. The uncharged, moderately hydrophobic compound associates more strongly with the membrane, leading to a greater extent of sorption and a rejection that declines over time until it reaches a steady-state value that is much lower than that of charged compounds of similar size. While size continues to be a dominating factor in the rejection of trace organic contaminants, the influence of charge and solute-membrane interactions on rejection can be equally important when the solute is near the MWCO of the membrane.

Acknowledgments

Funding for this work was provided by the Santa Clara Valley Water District, the California Department of Water Resources, the Singapore Economic Development Board, and a joint National Water Research Institute/American Membrane Technology Association Graduate Fellowship awarded to E.S.-D. We thank Dow/FilmTec and GE Osmonics for providing membrane samples and Megan H. Plumlee for help with analytical measurements.

Supporting Information Available

Part A, Detailed Experimental Protocols; Part B, Additional Figures; Part C, Simplified Gel-Enhanced Concentration Polarization Equations; and Part D, Calculations of Expected Rejection Decline due to Gel-Enhanced Concentration Polarization. This information is available free of charge via the Internet at http://pubs.acs.org.

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Appendix I

Stanford University, Dr. Martin Reinhard Research Group, 2004. Technical Memorandum: Review of Available Historical Water Quality Data, Coyote Creek Streamflow Augmentation Project.

Technical Memo

Date: 09/02/04

To: Ray Wong, Project Manager, Santa Clara Valley Water District

From: Stanford University, Dr. Martin Reinhard Research Group

RE: Review of Available Historical Water Quality Data, Coyote Creek Streamflow Augmentation Project

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This technical memorandum presents the results of a review of historical water quality data for both Coyote Creek and the recycled water proposed to be added to Coyote Creek during summer of 2006, as part of the Coyote Creek Streamflow Augmentation Project.

What are the Sources of Water Quality Data?

- Williamson, Rhea, 2002. "The Impact of Recycled Water on Water Quality in Coyote Creek in San Jose, California in 2001." Prepared by Prof. Williamson of San José State University to investigate whether recycled water would cause Coyote Creek to become eutrophic.
- Tetra Tech, Inc. 2001. "Final Water Quality Monitoring Report For May – November 2000." Conducted for the City of San Jose Environmental Enhancement Program, Coyote Creek Streamflow Augmentation Pilot Project. July, 2001.
- South Bay Water Recycling water quality website: http://www.ci.san-jose.ca.us/sbwr/WaterQualReport.htm
- Analyses of recycled water conducted by Dr. Birgit Gross at Stanford University and the Sedlak Research Group at UC Berkeley

What are the Applicable Regulatory Criteria for Recycled Water and Coyote Creek?

Coyote Creek

The San Francisco Bay Regional Water Quality Control Board (RWQCB) has primary authority for implementing the State's policy and ensuring water quality and designated beneficial uses of water resources. Narrative and numerical water quality objectives are established in RWQCB's *Basin Plan* to protect established beneficial uses of surface water and groundwater in the San Francisco Bay region. RWQCB implements the *Basin Plan* by imposing waste-discharge requirements for releases such as those proposed under an NPDES permit. A comparison of water quality of recycled water and coyote creek water quality versus *Basin Plan* criteria is presented in Table 1 below.

The *Basin Plan* does not contain regulations for hormones, endocrine disrupting compounds, or other pharmaceutically active compounds. Nevertheless, the Water District has initiated monitoring of some of these compounds. Data collected by the District is presented in tables 2 and 3 below.

NOTE: The City of San José negotiated an NPDES amendment specifically for the streamflow augmentation. The NPDES permit states that the water quality of Coyote Creek shall not violate the objectives of the *Basin Plan*. Furthermore, the NPDES permit specified actual temperature limits for the discharge. The CSJ permit has since expired, thus we will need to get a new one. According to the District's Environmental Planner, the RWQCB will not want to re-negotiate a new NPDES permit, but rather will retain all of the stipulations present in San José's permit, including the temperature rules.

Table 1: Comparison of Coyote Creek and Recycled Water Quality.

Parameter	***Min or Max in Coyote Creek [source]***	***Min/Max 2003 Recycled Water***	***Basin Plan Rules [or other rules]***	***Conclusions***
pH	Range between 7.0 and 8.2	7.0 ± 0.1	Must be between 6.5 and 8.5	*No issue*
Dissolved Oxygen	Average around 7 mg/L, but varies over the summer (sometimes less than 5.0 mg/L)	Sept/Oct average 6.2 mg/L year min: 5.2 mg/L	"Warm water habitat": 5.0 mg/L "Cold water Habitat" 7.0 mg/L	*No issue*
Un-ionized Ammonia	Highest conc. of total ammonia (ammonium + ammonia) was 0.7 ppm as N measured at "Muni Golf" [Williamson]	Avg. <0.4 ppm as N total ammonia. $[NH_3] = \alpha_1 N_T$ α_1 depends on pH	0.796 mg/L NH_3-N is still not exceeded.	"Even when the highest pH (8.4) and highest temperature (22.0 C) measured during the study period are applied to the highest ammonia value measured, the criterion of 0.796 mg/L NH_3-N is still *not exceeded*." [Williamson]
Temperature	Yr. 2001 range from (F) 63 to 65 yr. 2000 range from (F) 65 to 67 [Williamson; Tetra Tech]	Averages for summer bimonthly (F) 71.8, 75.2, 73.6	NPDES amendment instates the following: "At no time shall the discharge exceed the ambient creek temperature for a period exceeding 12 hours . . . " [NPDES Amendment]	*Recycled water will need to be chilled to meet NPDES requirements.*
Pathogens	"Pathogen concentrations along the creek were exceedingly high, with concentrations of total coliform being as high as several orders of magnitude greater than the lowest applicable criterion" [Tetra Tech 2001]	<1 CFU/100ml	US EPA objective = 33 CFU/100ml [EPA]	Release of recycled water will be *beneficial* since the recycled water meets pathogen objectives, thus it will flush out the Creek's existing pathogen concentration.
Metals	"Measured concentrations of metals at all stations were below the lowest applicable criteria for each metal" [Tetra Tech 2001]	Concentrations are less than those in Coyote Creek	No guidance.	Release of recycled water will be *beneficial* since it will reduce metals concentrations in the Creek
Biostimulatory nutrients (N and P)	--	--	"Waters shall not contain biostimulatory substances in concentrations that promote aquatic growths to the extent that such growths cause nuisance or adversely affect beneficial uses" [Basin Plan]	"Nutrient concentrations in the creek were generally much lower than those in the recycled water. There was no apparent evidence of nuisance algal blooms occurring in the creek even though nutrient concentrations were elevated enough to saturate the requirements of *Cladophora*, the predominant algae living in the creek [Dr. Rhea Williamson, 2001]. This indicates that *nutrients are not the factors that are responsible for limiting algal and plant growth in Coyote Creek* and that releasing recycled water into the creek is not expected to result in nuisance algal blooms." [Tetra Tech 2001]

Table 2: Trace Organics Concentrations in the Recycled Water; Analyses conducted by Reinhard Research Group at Stanford University for SCVWD.

Analysis Date	12/1/01	3/2/02	6/2/02	7/2/02
Neutrals (μg/L)				
NP/OP	-	n.d.	n.d	n.d
AP1EO	-	n.d.	n.d	n.d
AP2EO	-	n.d.	n.d	n.d
AP3EO	-	n.d.	n.d	n.d
Total APEO	-	n.d.	n.d	n.d
Halog. AP/APEO	-	0.026 [d]	n.d	n.d
Alkylphenol Ethoxy Carboxylates (APECs) (μg/L)				
m/z 235	-	n.d.	n.d.	n.d.
m/z 249	-	n.d.	n.d.	n.d.
m/z 279	-	n.d.	n.d.	n.d.
Total APEC	-	n.d.	n.d.	n.d.
Halog. APEC	-	12.9 [b]	1.7	14.8
EDTA by HPLC	6	305	n.l.f.	n.l.f.
Pharmaceuticals (μg/L)				
Ibuprofen	n.d.	n.d.	n.d.	n.d.
Carba-mazepine	n.d.	n.d.	n.d.	n.d.
Gemfibrozil	n.d.	n.d.	n.d.	n.d.
Ketoprofen	n.d.	n.d.	n.d.	n.d.
Naproxen	n.d.	n.d.	n.d.	n.d.
Others (μg/L)				
BPA	n.l.f.	n.d.	n.l.f.	n.l.f.
Tris(3) phosphate	n.l.f.	0.011	0.003	0.022
Tris(2,3) phosphate	n.l.f.	0.01	0.01	0.32
NBBS	n.l.f.	0.015	0.017	0.27
Caffeine	n.l.f.	n.d.	n.d.	n.d.

All data semi-quantitative except EDTA
EDTA-Analysis: HPLC-UV, ion-pair reversed-phase method with external calibration
All others: GC/MS or GC/MS/MS, Mode: EI, semi-quantitative with d_{12}-chrysene as internal standard
Trace: above detection limit, below reporting limit
BPA: Bisphenol A, Tris(3)phosphate: Tris(3-chloropropyl)phosphate, Tris(2,3)phosphate: Tris(2.3-dichloropropyl)phosphate, NBBS: N-butyl benzenesulfonamide
Halogenated APEOs and APECs: Byproducts during chlorine disinfection.
Halog. APECs: halogenated (chlorinated or brominated) APECs; [a] 1.91 □g/L chlorinated and 0.15 □g/L brominated
[b] 11.43 □g/L chlorinated and 1.45 □g/L brominated;
Halog.AP/APEO: chlorinated AP and APEOs, [c] 0.006 □g/L AP,[d] 0.009 □g/L AP and 0.017 □g/L APEO
n.l.f.: not looked for
n.d.: not detected

Table 3: Hormone Concentrations in the Recycled Water; Analyses conducted by Sedlak Research Group, UC Berkeley, for SCVWD.

Hormones (ng/L)	6/20/02	8/27/02	11/4/02
Testosterone	n.d. (<0.5)	n.d. (<0.5)	n.d. (<0.5)
17β-Estradiol	n.d. (<0.5)	n.d. (<0.5)	n.d. (<0.5)
Estrone	n.d. (<1.0)	n.d. (<1.0)	n.d. (<1.0)
Medroxyprogesterone	n.d. (<1.0)	n.d. (<1.0)	n.d. (<1.0)

Appendix J

Streamflow Augmentation Project Upper Silver Creek and Coyote Creek Initial Study / Mitigated Negative Declaration (Draft), June 2006. Santa Clara Valley Water District.

Stream Flow Augmentation Project Upper Silver Creek and Coyote Creek Initial Study / Mitigated Negative Declaration

DRAFT

June 2006

Santa Clara Valley Water District
5750 Almaden Expressway
San Jose, CA 95118

SANTA CLARA VALLEY WATER DISTRICT

STREAM FLOW AUGMENTATION PROJECT

INITIAL STUDY/ MITIGATED NEGATIVE DECLARATION

DRAFT

Prepared for:
Santa Clara Valley Water District

Prepared by:
Thomas Reid Associates

Under the Direction of:
Alice Ringer, Program Administrator, SCVWD
Elise Latedjou-Durand, Environmental Planner, SCVWD

Hossein Ashktorab
Unit Manager

Keith Whitman
Deputy Operating Officer

Walter L. Wadlow
Chief Operating Officer

Stanley M. Williams
Chief Executive Officer

JUNE 2006

NOTICE OF INTENT
TO ADOPT A MITIGATED NEGATIVE DECLARATION

Santa Clara Valley Water District
Stream Flow Augmentation Project

The Santa Clara Valley Water District (SCVWD) is the Lead Agency and preparer of the Stream Flow Augmentation Initial Study/Mitigated Negative Declaration. The SCVWD, as Lead Agency, has found as a result of this Initial Study process that while the proposed project could have a significant effect on the environment, there will not be a significant effect in this case because mitigating measures will be incorporated into the project.

Pursuant to CEQA Guidelines Section 15072, the SCVWD will mail the Draft IS/MND to the name and address of all organizations and individuals who have requested such notice in writing, and will also give notice of intent to allow the public the 30-day review period provided under Section 15105 of the CEQA Guidelines.

***Project Location*:**
The project is located within Upper Silver Creek, approximately two miles upstream from the confluence with Coyote Creek, in San Jose.

***Project Description*:**
The Santa Clara Valley Water District (SCVWD) proposes the temporary release of tertiary treated recycled water into Upper Silver Creek for research purposes. The release would occur roughly 2 miles upstream of the confluence with Coyote Creek. The release point would be the inlet to an existing storm drain at the South Bay Water Recycling (SBWR) Yerba Buena Pump Station, which itself flows to Upper Silver Creek. Approximately 1 cubic feet per second (450 gallons per minute) of recycled water would be released continually during a trial period from August to November 2006. Surface and ground water quality monitoring will occur during this time at monitoring well stations on Upper Silver Creek and on Coyote Creek. New pipelines and equipment would be installed at the Pump Station to extract the recycled water from the existing storage tank, remove residual chlorine disinfectant (dechlorinate), and route it to the existing storm drain line for release to Upper Silver Creek.

***Project Applicant*:**

Santa Clara Valley Water District
5750 Almaden Expressway
San Jose, CA 95118
Attn: Ms. Alice Ringer, Program Administrator

Document Availability:
Copies of the Initial Study/Mitigated Negative Declaration will be available at the Dr. Martin Luther King, Jr. Public Library at 150 E. San Fernando St. in San Jose, California on June 22, 2006, and at the District office and website, www.valleywater.org. The 30-day public review period is from June 23, 2006 to July 22, 2006. If you would like to comment in writing on this project, please send your response to Ms. Alice Ringer, Program Administrator, Santa Clara Valley Water District, at the address shown above. Your comments must be received before the 30-day public review period ends.

Hazardous Waste and Substances:
Pursuant to Public Resources Code Section 15072(f)(5) and California Government Code Section 65962.5, no presence of hazardous waste or substances as contained on the lists compiled pursuant to Section 65962.5of the Government Code is known to exist within the subject work area.

Stanley M. Williams

6/22/2006
Date

Santa Clara Valley Water District
5750 Almaden Expressway
San Jose, CA 95118
Tel: 408/264-2600

Proposed Mitigated Negative Declaration

District Contact: Alice Ringer, Program Administrator
408/ 265-2607, Ext. 2330

Project Title: Streamflow Augmentation Project

Lead Agency: Santa Clara Valley Water District
5750 Almaden Expressway
San Jose, CA 95118
408/265-2607

Project Location: The project is located within Upper Silver Creek, approximately two miles upstream from the confluence with Coyote Creek, in San Jose.

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FINDINGS

An initial study has been prepared for the proposed project to determine whether the project might have a significant effect on the environment. The public can review documents used in preparation of the Initial Study at the SCVWD office, 5750 Almaden Expressway, San Jose, California 95118.

The initial study identified potentially significant impacts on the environment; however, all the potential impacts of the proposed project can be avoided or reduced to a less-than-significant level with implementation of mitigation measures identified in the initial study.

Therefore, the project has been mitigated to a point where no significant impacts would occur, and there is no substantial evidence that the project may have a significant effect on the environment. The specific mitigation measures that avoid or reduce impacts are included below.

BASIS OF FINDINGS

Based on the environmental evaluation presented in the Initial Study, the Project will not cause significant adverse effects upon the environment. In addition, substantial adverse effects on humans, either direct or indirect, will not occur. The Project will not affect any important examples of the major periods of California prehistory or history. Nor will the Project cause a fish or wildlife population to drop below self-sustaining levels, threaten to eliminate a plant or animal community, reduce the number or restrict the range of a rare or endangered plant or animal.

Based on the Initial Study, mitigation measures have been incorporated into the project to avoid, minimize, and reduce potential impacts to biological resources and water quality to less-than-significant levels.

District staff independently reviewed the initial study, and this mitigated negative declaration reflects the independent judgment of the District.

Mitigations Measures

The principal mitigation incorporated in the project is the regulation or termination of the pilot program based on ongoing monitoring of water quality parameters.

Measure WQ-1 Groundwater Protection

A groundwater monitoring program is proposed to detect whether groundwater recharge occurs in Upper Silver Creek. Although there is reason to believe that the release into Upper Silver Creek will not enter groundwater used for water supplies, if monitored parameters in Table 2 are found above their respective drinking water standards, this will be construed as possible evidence that there is recharge and will lead to immediate suspension of the recycled water release. (See Appendix B. Groundwater Management Unit Memorandum, Santa Clara Valley Water District, SCVWD, Work Plan Section 1, Dec 2004).

Measure WQ-2 Surface Water Chemistry Protection

The surface water monitoring program is based on parameters tested in Table 2. Remedial measures will be taken if the monitoring program indicates adverse water quality impacts, including immediate suspension of the recycled water release and investigation of appropriate treatment methods. These treatment methods may include reverse osmosis treatment, soil treatment, or blending with higher quality water.

Measure WQ-3 Surface Water Temperature Protection

Temperature monitoring will show the magnitude of release effects on Upper Silver Creek and on Coyote Creek, to which it is a tributary. The temperature data will be used to regulate the volume of release to keep temperature increases below permitted levels.

The proposed project does not propose to cool the treated water prior to release. Part of the purpose of the current study is to measure the thermal capacity of the streambed, the effects of solar warming and evaporative cooling, and to determine the effectiveness of pre-cooling the release.

The District proposes to regulate the release into Upper Silver Creek based on the biotic standard of a warm-water fishery. Release volume will be adjusted so as to prevent water temperature downstream of the release from rising above 75 °F. The measurement will be made at a point approximately 100 feet downstream of the storm drain outfall to allow adequate mixing.

Water temperature modeling indicates that this 75 °F limit will allow a treated water release of 0.5 to 1.0 cfs depending on temperature of the receiving water and incoming recycled water.

STREAM FLOW AUGMENTATION PROJECT
SILVER CREEK/COYOTE CREEK
INITIAL STUDY

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APPENDICES

1.0 INTRODUCTION

The Stream Flow Augmentation Project entails a one season release of tertiary treated recycled water (which is produced from treated wastewater) into Upper Silver Creek at the South Bay Water Recycling Yerba Buena Pump Station located off Yerba Buena Road. The Santa Clara Valley Water District (SCVWD) is the Lead Agency for environmental review under CEQA and would also carry out the project work itself. The proposed action is a pilot study for a possible future stream enhancement program.

This Initial Study/Mitigated Negative Declaration addresses the potential environmental impacts associated with augmenting the stream flows of Upper Silver Creek by discharging up to 1 cubic foot per second (cfs) of dechlorinated tertiary treated recycled water for a trial period from August to November. The project includes water quality monitoring at several stations along Upper Silver Creek and downstream Coyote Creek. Mitigation incorporated in the project is available for all potentially significant impacts. Based on the environmental analysis contained in the Initial Study, a Mitigated Negative Declaration has been prepared.

This Initial Study/Mitigated Negative Declaration has been prepared in compliance with the California Environmental Quality Act (CEQA)(Public Resources Code 21000 et seq.) and the State CEQA Guidelines (California Administrative Code 15000 et seq.), as amended. According to Section 15070 of the CEQA Guidelines:

> *"A public agency shall prepare or have prepared a proposed Negative Declaration or Mitigated Negative Declaration for a project subject to CEQA when:*
> *a) The Initial Study shows that there is no substantial evidence, in light of the whole record before the agency, that the project may have a significant effect on the environment, or*
> *b) The Initial Study identifies potentially significant effects but:*
>   *1. Revisions in the project plans or proposals made by or agreed to by the applicant before a proposed mitigated negative declaration and Initial Study are released for public review would avoid the effects or mitigate the effects to a point where clearly no significant effects would occur, and*
>   *2. There is no substantial evidence, in light of the whole record before the agency that the project as revised may have a significant effect on the environment."*

This document has been prepared as an objective, full-disclosure report to inform agency decision makers and the general public of the direct and indirect physical environmental effects of the proposed action and any measures which will be undertaken to reduce or eliminate potential adverse impacts. This document has five sections:

1. ***Introduction***. This section briefly describes the purpose and organization of the Initial Study.
2. ***Project Description***. This section provides a vicinity description of the project site and a description of the proposed stream flow augmentation, new and water quality monitoring program.
3. ***Initial Study Checklist and Responses***. The Initial Study Checklist is a standard form

used to examine the full range of potential environmental effects and is the basis used to determine the elements of the Negative Declaration. The form is based upon the California Environmental Quality Act (CEQA) Guidelines. The Response section provides detailed answers to the questions on the Checklist and identifies potentially significant impacts, mitigation measures to reduce those impacts, and a conclusion of impact after mitigation. CEQA Guidelines state that a brief explanation is required for all answers except "No Impact" answers that are adequately supported by the information sources a lead agency cites in the parentheses following each question. A "No Impact" answer is adequately supported if the referenced information sources show that the impact simply does not apply to projects like the one involved (e.g., the project falls outside a fault rupture zone). A "No Impact" answer should be explained where it is based on project-specific factors as well as general standards (e.g., the project will not expose sensitive receptors to pollutants, based on a project-specific screening analysis).

4. ***References***. The reference section identifies all sources used in responding to the Checklist Questions, persons consulted, and all consultants and subconsultants who prepared this project.
5. ***Maps and Figures***. This section contains on the Figures referenced throughout the Initial Study text.

2.0 PROJECT DESCRIPTION

2.1 Project Location and Site Description

The Santa Clara Valley Water District (SCVWD) is proposing to augment stream flows on the Upper Silver Creek with tertiary treated recycled water during a 6 month research period. The release would occur at the Yerba Buena Pump Station operated by South Bay Water Recycling (SBWR). Dechlorinated recycled water would be released into an existing storm drain which flows into Upper Silver Creek roughly 2 miles upstream of its confluence with Coyote Creek. Coyote Creek flows into San Francisco Bay.

The SBWR Yerba Buena Pump Station (Pump Station) is located off of Yerba Buena Road across from Baronet Court in southeast San Jose, approximately one mile east of US Highway 101 (Figure 1, Project Location). The Pump Station is connected to the South Bay Water Recycling Plant and is part of a larger system of water reuse. The proposed project is separate from the water recycling program and would use about 5% of the recycled water total.

The Pump Station compound also includes a large storage tank, an access road, and is surrounded by a chain link fence (Figure 7, Photo 1a). The Pump Station is adjacent to Upper Silver Creek and a recreational trail that follows the creek corridor (Figure 7, Photo 1b). The area immediately north and west of the project site is urbanized (Figure 2, Vicinity Aerial Photograph, and Figure 6, Upper Silver Creek Characteristics). Lower density residential development, the Ranch Golf Course, and Silver Creek Valley Country Club, are located to the south and east of the project site. Upper Silver Creek flows through Silver Creek Linear Park and the Pump Station in a heavily vegetated channel. Near Greenyard Street, the creek channel is lined with concrete for its remaining course until its confluence with Coyote Creek roughly one mile west. The Upper Silver Creek corridor and its confluence with Coyote Creek are shown in Figure 2 and Figure 6. Photos of the creek channel are shown in Figure 7.

2.2 Project Objectives

The Santa Clara Valley Water District manages wholesale drinking water resources and provides environmental stewardship for the county’s vast watersheds, including a series of reservoirs, more than 800 miles of streams and groundwater basins. District policies encourage the expansion of water recycling in Santa Clara County, as well as the enhancement or restoration of the County’s streams, when appropriate. This research project will potentially act to further both of these policies. Depending on the outcome of the study, recycled water could be used to enhance streams in many areas of the County.

The results from this study will permit future plans for augmenting streams with recycled water to be based on up-to-date and geographically specific scientific research.

The objectives of the project are to determine whether augmenting stream flow with tertiary-treated recycled water in the Coyote Creek watershed is feasible within economic, environmental, and county-wide policy objectives for water supply management.

In this grant-funded phase, the objectives are:

1. To evaluate the water quality impacts to surface water and groundwater (the upper aquifer) from the release of tertiary-treated recycled water to augment stream flows;
2. To determine whether the chemical constituents in tertiary-treated recycled water are adequately filtered or degraded by natural processes, or further treatment of the recycled water is needed before it can be used for streamflow augmentation;
3. To evaluate the major issues that are hurdles to implementing streamflow augmentation projects; and
4. To identify the potential solutions to these issues within existing policy and regulatory frameworks.

2.3 Project Background

2.3.1 City of San Jose Pilot Project

The City of San Jose previously proposed to augment stream flow in Coyote Creek by up to 400 percent with recycled water. Several relevant supporting studies were conducted for the City. Chief amongst these studies was the Revised Initial Study (Jones & Stokes, 2000) which evaluated the ecological and groundwater impacts of the augmentation. A primary objective of the San Jose scheme was to improve cold water habitat in Coyote Creek, thus recycled water was to be de-chlorinated and chilled significantly prior to release into the creek.

For groundwater, the study noted that the Santa Clara groundwater basin, which contains the reach of Coyote Creek to be studied, is divided into three zones: a shallow unconfined aquifer, a regional aquitard, and beneath the aquitard a potable deep confined aquifer.[*] Considering the location of the City's proposed outfall at Singleton Landfill, recycled water in Coyote Creek would only flow over the regional aquitard and infiltration to the potable deep aquifer would be unlikely. The report noted that there is low probability of infiltration to the shallow aquifer due to the clayey composition of the creek bottom; nevertheless, monitoring of the shallow aquifer water quality was recommended to confirm that no recharge with recycled water was taking place.

Another concern that arose during the City of San Jose project was the degradation of water quality due to trace organic compounds in treated wastewater, including a group of compounds considered as possible endocrine disruptors. The appearance of these compounds in the aquatic environment is a recent environmental concern. Some are biologically active and viewed as potentially harmful to wildlife and human health.

In late October 2000, the City of San Jose obtained a permit from the California Regional Water Quality Control Board to implement a demonstration stream flow augmentation project in

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[*] An aquifer is an underground layer of water-bearing permeable rock, or unconsolidated materials (gravel, sand, silt, or clay) through which groundwater flows and from which groundwater can be usefully extracted using a water well. An aquitard is an impermeable zone within the earth that restricts the flow of groundwater from one aquifer to another.

Coyote Creek. The City decided not to proceed with the project and the RWQCB permit expired in June 2003. (Source: SVWD, Work Plan, December 2004).

2.3.2 MWD Research Grant Study

In 2003, the SCVWD developed an agreement with the Metropolitan Water District of Southern California (MWD) to subcontract a research grant for the MWD by the California State Department of Water Resources. The research project investigates if large scale releases of tertiary treated recycled water into a streambed will be adequately filtered by streambed action and natural percolation or if it impacts the groundwater quality. Stanford University is assisting SCVWD in this research as the selected laboratory. Stanford's hypothesis is that stream flow can improve water quality by natural attenuation of trace organics.

This hypothesis is based in part on previous research conducted by Dr. Reinhard on the Santa Ana River which found that natural stream flow attenuates compounds. The Santa Ana River carries nearly 100 percent tertiary treated water during the summer months. Stanford University researchers found that trace organic contaminants such as pharmaceuticals and alkyphenol thoxylate metabolites (biological degradation products of nonionic detergents) are significantly attenuated during river transport suggesting that the river itself acts as an efficient treatment system. The subsequent infiltration of river water into the ground led to significant additional water quality improvement in terms of total organic carbon (dissolved and particulate) and trace organics. (Reinhard and J. 2001) (Reinhard et. al. 1999). Source: SCVWD work plan.

The District is partnering with Stanford to determine the presence, fate, and action of trace organic contaminants (e.g. endocrine disrupting compounds) which may be found in the recycled water. Stanford will conduct a literature review and experimental fate studies of relevant contaminants. Bench-top studies will simulate both percolation and river conditions, and control for important variables. Results will permit project personnel to discern the existence and magnitude of different fate mechanisms, including photochemical degradation, adsorption, and biotransformation.

2.4 Project Design

The proposed pilot research project will release up to 1 cubic foot per second (cfs)[*] of tertiary treated recycled water into a natural streambed to evaluate potential water quality impacts or benefits. The project entails using recycled water already available at the Yerba Buena Pump Station, removing residual chlorine (dechlorinating), and discharging the water to Upper Silver Creek through an existing storm drain. The release of recycled water would occur during the low flow months from August to November. Water quality would be monitored throughout the study.

2.4.1 Facility Construction

Facility construction for the proposed pilot project would be minimal. The water tank, pump station receiving treated water, and the storm drain outfall into Upper Silver Creek already

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[*] 1 cfs is approximately 450 gallons per minute, 646,000 gallons per day or 2 acre-feet per day.

exist. New construction entails a graded, graveled pad for the dechlorinator unit and temporary pipelines connecting the storage tank, the dechlorination unit, and the inlet to the storm drain. A site plan showing the location of the proposed equipment is shown in Figure 4 (Project Facilities Schematic).

The dechlorinator available for District use has two redundant process trains, each of which can handle flows greater than 20 cfs of influent reclaimed water. All the components of the dechlorination system are housed in a trailer-mounted steel marine cargo container, with dimensions in feet of 45 x 8 x 9.5. An area measuring approximately 60 feet by 15 feet along side of the water tank access road will be graded and graveled to park the dechlorinator unit. Power will be supplied from an existing PG&E pole located next to the facility fence. There will be no permanent foundations constructed.

Approximately 175 feet of pipelines will be installed on the site, above ground. A 6-inch diameter plastic pipe will convey recycled water from an existing Yerba Buena pipeline to the dechlorination trailer. The point of connection would be either near the pump station or near the base of the reservoir. A pressure-reducing valve will be installed to reduce the pressure of the water entering the dechlorination system. The pipeline would be from 50 to150 feet long, depending on the point of connection chosen. The pipe would cross the access road through a trench covered with a steel plate.

Another 6-inch diameter plastic pipe will convey dechlorinated recycled water via gravity to an existing storm drain inlet. This pipeline would be approximately 150 feet long and would cross the access road with covered by a steel plate. The release into the storm drain will be below the storm drain cover so that the recycled water is not exposed. The existing storm drain flows approximately 50 feet to its outfall location on Upper Silver Creek. All of the pipeline system will be within the City of San Jose's Yerba Buena Pump Station property.

After the pilot project, the equipment may remain on site for up to one year during which time the District and the City of San Jose will decide whether to dismantle the equipment or to keep it for another similar project.

2.4.2 Operation

Project operation is simple: tertiary treated recycled water is taken from the City of San Jose pipeline, treated to remove residual chlorine disinfectant, and metered for release into the creek. Equipment is automated and will not require on-site supervision.

The dechlorination system was designed and constructed for the City of San Jose's earlier streamflow augmentation project. Since the City's project never reached fruition, the dechlorination system was put into storage. The District will have the unit inspected for operability and make any necessary repairs. The system is sized to treat flows higher than those considered for the proposed project and is designed for an inflow chlorine residual of up to 5 ppm, which is much higher than the chlorine residual of 0.1 ppm measured at the Yerba Buena Pump Station in 2004 and 2005. The recycled water will receive no further on-site treatment.

The dechlorination system measures the chlorine residual in the inlet recycled water stream and injects a small amount of 25% sodium bisulfite solution suitable to react with the free chlorine and convert it to the non-toxic chloride form. The aqueous sodium bisulfite solution is a low hazard. The Material Safety Data Sheet for Sodium Bisulfite Solution states: "Emergency Overview: A pale yellow aqueous solution with a pungent sulfur-like odor. Non-combustible but excessive heat may liberate sulfur dioxide gas that is toxic and corrosive. The solution itself is relatively non-toxic and poses little immediate hazard to fire fighting personnel in an emergency situation. Solution is mildly acidic and can pose a threat to water courses in an emergency situation." (Source 33)

The proposed project would release up to 1 cfs on a continual basis. The volume of flow is chosen to provide enough treated waste water in the receiving waters to allow Stanford University to detect contaminants of interest while limiting the potential for temperature effects on the receiving water.

2.4.3 Water Source

The San Jose/Santa Clara Water Pollution Control Plant has the capacity to treat 167 million gallons of wastewater per day and serves a population of more than 1,500,000 people in San Jose, Santa Clara, Milpitas, Campbell, Cupertino, Los Gatos, Saratoga, and Monte Sereno. About ten percent of the treated wastewater is sold for irrigation or other recycled water uses through the South Bay Water Recycling program. The recycled water receives secondary and tertiary water treatment. In secondary treatment, the organic content of the sewage such as from human waste, food waste, soaps and detergent is substantially eliminated by biological oxidation. Tertiary treatment provides additional filtration, chemical treatment such as nitrification to reduce ammonia levels, and disinfection. For the South Bay Water Recycling program, effluent must meet requirements of California Code of Regulations (CCR) Title 22 - Division 4, Environmental Health.

Recycled water made from tertiary treated and disinfected wastewater is suitable for a wide range of use, including irrigation, industrial, construction, and impoundments. The recycled water may be used where the pubic has access, such as landscaping and golf course irrigation, and for irrigation of food crops. Recycled water is disinfected by chlorination, much the same as raw water is treated for municipal water supply. The chlorine is partly consumed in the disinfection reaction; residual chlorine levels measured at the Yerba Buena Pump Station ranged from 0 to 0.5 mg/L total chlorine.

Although recycled water has had the majority of organic material removed, some chemical compounds pass through treatment or are actually formed during treatment. These compounds are present at low levels, but are of concern due to their potential for biological activity. Understanding the fate and effect of trace contaminants is important to long range use of recycled water and is the main purpose of the proposed project.

The project evaluates several classes of trace contaminants, some of which are found in treated wastewater or watercourses elsewhere. Because these compounds are usually not subject to current regulation, but are of present concern and subject to possible future regulation, these are sometimes called "emerging contaminants".

- Pharmaceuticals. Compounds such as ibuprofen and caffeine enter wastewater through excretion or direct disposal.
- Hormones. Both synthetic and natural sources.
- Endocrine Disruptors. Compounds that mimic or interfere with endocrine (hormonal) regulation. Includes compounds from other classes (e.g. BPA is considered an endocrine disruptor).
- Alkylphenol polyethoxylates and metabolites (APEOs). APEOs are derived from nonionic surfactants used in various industrial and agricultural applications.
- Organophosphates. The compounds of interest are so-called "tris" flame retardants.
- Plasticizers. N-butyl benzenesulfonamide (NBBS) and Bisphenol-A (BPA) are persistent contaminants.
- Herbicides. Oxadiazon and others.
- Perfluorochemicals (PFCs). A large family of compounds derived from non-stick and stain-resistant coatings.
- Disinfection Byproducts. N-Nitrosodimethylamine (NDMA) is a disinfection byproduct formed during chloramination of waters containing dimethylamines and is considered a "probable carcinogen." Haloacetic Acids (e.g. Trichloroacetic Acid) and Haloforms (i.e. Trihalomethane) are formed by chlorination of organic material. Most Haloforms are considered carcinogenic.

Previous study in 2001 and 2002 showed presence of APEOs, NBBS, and the "tris" flame retardants, but an absence of hormones and pharmaceuticals in the SBWR effluent water (See Appendix B). Testing in 2005 found the pharmaceuticals carisoprodol and iminiostilbene. Recycled water was also found to have APEOs, the "tris" flame retardants, NBBS, PFCs, Chlorination byproducts, NDMA, Haloacetic Acids, and Haloforms (See Appendix A).

Recycled water was found to have Boron, Manganese, and Nickel present. Other metals of concern (e.g. Arsenic, Barium, Cadmium, Lead, Selenium, Silver, Chromium, Mercury) were not detected in three sample events.

The tertiary treated recycled water arriving at the proposed release point is usually in the temperature range 80^{o} to 82^{o} F during the summer months proposed for operation. The water quality characteristics of the recycled water proposed for release to Upper Silver Creek is further presented in the Hydrology section.

2.4.4 Water Quality Monitoring Program

A water quality monitoring program is an integral part of the project. Sampling would be done at the recycled water, seven surface water (SW) and three groundwater (GW) locations. The monitoring station locations are described in Table 1 below and mapped in Figure 5 (Groundwater and Surface Water Sampling Locations).

In order to monitor potential groundwater quality and migration occurring as a result of recharge in Upper Silver Creek, monthly water samples will be taken at three groundwater sampling locations before and after the project begins. The first well (GW1) is located close to the release point (within 100 feet in a northerly direction and screened in the first encountered permeable zone. The second well (GW2) is located 0.4 miles downstream of the release. The second well was planned to be screened in the second or third encountered permeable zone. However, bedrock was found below the first permeable zone, so the second well was screened at the first permeable zone. In order to confirm no recharge is occurring further downstream after the Upper Silver Creek's confluence with Coyote Creek, a third well (GW3) will be used to intercept groundwater in the first water bearing zone north of Coyote Creek in what is known as a confined zone of the SCV subbasin.

Table 1. Groundwater and Surface Water Sampling Locations
(See Figure 5.Water Quality Sampling Sites for locations)

Site ID	River distance from release point (miles)	Description
RW1	0.0	Recycled water from SJ/SC WPCP at Yerba Buena Pump Station
SW0	Upstream	Upper Silver Creek Control, upstream of release point
SW1	0.0	Upper Silver Creek, release point at Yerba Buena Pump Station
SW2	0.7	Upper Silver Creek, upstream of concrete channel
SW3	1.4	Upper Silver Creek in concrete channel
SW4	1.7	Coyote Creek at confluence with Upper Silver Creek (Singleton)
SW5	3.2	Coyote Creek downstream at Stonegate Park
SW6	Upstream	Coyote Creek Control at Yerba Buena Bridge, upstream of confluence with Upper Silver Creek
GW1	0.1	Shallow groundwater well just downstream of release point at Yerba Buena Road and Homepark Court
GW2	0.4	Shallow groundwater well next to Upper Silver Creek between SW1 and SW2, at Silver Creek Linear Park
GW3	~2	Shallow groundwater well next to Coyote Creek, between SW4 and SW5

Sampling will be done monthly. Water samples will be tested for water quality parameters based on California drinking water standards and water quality objectives in the San Francisco Bay RWQCB's Water Quality Control Plan. A list of these parameters is presented in Table 2.

Groundwater quality data will be reported to the SCVWD Groundwater Management Unit on a monthly basis to coincide with the surface water collection events. Should any of the parameters listed in Table 2 be detected in the shallow monitoring wells above their respective drinking water standard, stream augmentation will be suspended pending identification of the cause and possible remedies.

Table 2. Water Quality Parameters to be Screened at Monitoring Sites

General Water Quality
Temperature
Total dissolved solids (TDS)
Conductivity
PH

Total Alkalinity
SAR (calculated parameter)
Cations and Anions
Sodium
Potassium
Calcium
Magnesium
Sulfate
Chloride
Bicarbonate
Nitrate as NO_3
Metals
Aluminum
Arsenic
Barium
Boron
Cadmium
Total Chromium
Copper
Iron
Lead
Mercury
Manganese
Nickel
Selenium
Silver
Zinc
Trace Organic Compounds
NDMA (N-nitrosodimethylamine)
Organic Chemicals (Volatile Organic Compounds, etc)
Pharmaceuticals, EDC's (Endocrine Disrupting Compounds) and other Emerging Contaminants, including the following:
Acetaminophen
Caffeine
Carbamazepine
Carisoprodol
Gemfibrozil
Ibuprofen
Iminostilbene
Ketoprofen
Naproxen
Primidone
Propanolol
Estradiol
Estriol
Estrone
Ethynylestradiol
Bisphenol A
Oxadiazon
Alkyl phenols (nonyl, octyl)*
Alkylphenol polyethoxylates (AP1EO, AP2EO, AP3EO)*
Alkylphenol ethoxycarboxylates*
Carboxylated alkylphenol ethoxycarboxylates*
Tris(3-chloropropyl) phosphate
Tri(2,3-dichloropropyl) phosphate

N-butyl benzenesulfonamide
Perfluorochemicals (PFCs)

* Including halogenated by-products

Source: Appendix B, Groundwater Management Unit Memorandum,
Santa Clara Valley Water District (includes Final Workplan to DWR For The Project "Groundwater Impact Evaluation Partnership For Using Tertiary Treated Recycled Water In A Large-Scale Streamflow Augmentation Project", Santa Clara Valley Water District)

Water temperature will be logged continuously by in-stream data recorders placed at each of the surface water (SW) monitoring sites. Three units will be used to evaluate the effects of release on water temperature in Upper Silver Creek and three units will be used to show the effect of Upper Silver Creek release into Coyote Creek. Data from the units would be retrieved at the same time samples are taken for chemical analysis.

2.4.5 Schedule

The District anticipates that site preparation and equipment installation will be completed in one month. Inspection and repair of the dechlorinator will occur prior to the construction phase. The proposed release of dechlorinated recycled water to Upper Silver Creek would begin in August 2006 and end in November2006. Monitoring would be discontinued one month after release ceased.

2.5 Mitigation Incorporated into the Project

The principal mitigation incorporated in the project is the regulation or termination of the pilot program based on ongoing monitoring of water quality parameters.

WQ-1 Groundwater Protection

A groundwater monitoring program is proposed to detect whether groundwater recharge occurs in Upper Silver Creek. Although there is reason to believe that the release into Upper Silver Creek will not enter groundwater used for water supplies, if monitored parameters in Table 2 are found above their respective drinking water standards, this will be construed as possible evidence that there is recharge and will lead to immediate suspension of the recycled water release. (See Appendix B. Groundwater Management Unit Memorandum, Santa Clara Valley Water District, SCVWD, Work Plan Section 1, Dec 2004).

WQ-2 Surface Water Chemistry Protection

The surface water monitoring program is based on parameters tested in Table 2. Remedial measures will be taken if the monitoring program indicates adverse water quality impacts, including immediate suspension of the recycled water release and investigation of appropriate treatment methods. These treatment methods may include reverse osmosis treatment, soil treatment, or blending with higher quality water.

WQ-3 Surface Water Temperature Protection

Temperature monitoring will show the magnitude of release effects on Upper Silver Creek and on Coyote Creek, to which it is a tributary. The temperature data will be used to regulate the volume of release to keep temperature increases below permitted levels.

The proposed project does not propose to cool the treated water prior to release. Part of the purpose of the current study is to measure the thermal capacity of the streambed, the effects of solar warming and evaporative cooling, and to determine the effectiveness of pre-cooling the release.

The District proposes to regulate the release into Upper Silver Creek based on the biotic standard of a warm-water fishery. Release volume will be adjusted so as to prevent water temperature downstream of the release from rising above 75 ^{o}F. The measurement will be made at a point approximately 100 feet downstream of the storm drain outfall to allow adequate mixing.

Water temperature modeling indicates that this 75 ^{o}F limit will allow a treated water release of 0.5 to 1.0 cfs depending on temperature of the receiving water and incoming recycled water.

3.0 ENVIRONMENTAL CHECKLIST AND RESPONSES

1. **Project title:** Stream Flow Augmentation Project

2. **Lead agency name and address:** Santa Clara Valley Water District
5750 Almaden Expressway
San Jose, CA 95118

3. **Contact person and phone number:** Alice Ringer, Program Administrator
(408) 265-2607 ext. 2330 Fax (408) 979-5639

4. **Project location:** Upper Silver Creek in the City of San Jose, California

5. **Project sponsor's name and address:** Santa Clara Valley Water District
5750 Almaden Expressway
San Jose, CA 95118

6. **General Plan designation:** N/A

7. **Zoning:** N/A

8. **Description of project:**

Santa Clara Valley Water District (SCVWD) proposes the temporary release of tertiary treated recycled water into Upper Silver Creek for research purposes. The release would occur roughly 2 miles upstream of the confluence with Coyote Creek. The release point would be the inlet to an existing storm drain at the South Bay Water Recycling (SBWR) Yerba Buena Pump Station, which itself flows to Upper Silver Creek. Approximately 1 cubic feet per second (cfs) of recycled water would be released continually during a trial period from August to November 2006. Surface and ground water quality monitoring will occur during this time at monitoring well stations on Upper Silver Creek and on Coyote Creek. New pipelines and equipment would be installed at the Pump Station to extract the recycled water from the existing storage tank, remove residual chlorine disinfectant (dechlorinate), and route it to the existing storm drain line for release to Upper Silver Creek. The project is described in Section 2, Project Description.

9. **Surrounding land uses and setting: Briefly describe the project's surroundings:**

The SBWR Yerba Buena Pump Station is located off of Yerba Buena Road in San Jose and is included in the land encompassing Silver Creek Linear Park. The SBWR facility is adjacent to Upper Silver Creek and a recreational trail that follows the creek corridor. Urban uses are located immediately north and west of the project site. Further west lies the Coyote Creek corridor. Lower density residential development, the Ranch Golf Course, and Silver Creek Valley Country Club occur to the south and east of the project site. See Section 5, Maps.

10. **Other public agencies whose approval is required (e.g., permits, financing approval, or participation agreement.)**

The Santa Clara Valley Water District is the Lead Agency for approving the project.

The Regional Water Quality Control Board may need to issue an NPDES permit.

The California Department of Fish and Game may need to issue a Streambed Alteration Agreement under Section 1602.

ENVIRONMENTAL FACTORS POTENTIALLY AFFECTED:

The environmental factors checked below could be potentially affected by this project. Mitigation has been incorporated into the project to reduce all potentially significant impacts to a less than significant level, as indicated by the checklist on the following pages.

9 **Aesthetics**
± **Biological Resources**
9 **Hazards & Hazardous Materials**
9 **Mineral Resources**
9 **Public Services**
9 **Utilities / Service Systems**
9 **Agriculture Resources**
9 **Cultural Resources**
± **Hydrology / Water Quality**
9 **Noise**
9 **Recreation**
± **Mandatory Findings of Significance**
9 **Air Quality**
9 **Geology /Soils**
9 **Land Use / Planning**
9 **Population / Housing**
9 **Transportation/Traffic**

DETERMINATION: (To be completed by the Lead Agency)

On the basis of this initial evaluation:

☐ I find that the proposed project COULD NOT have a significant effect on the environment, and a NEGATIVE DECLARATION will be prepared.

☒ I find that although the proposed project could have a significant effect on the environment, there will not be a significant effect in this case because revisions in the project have been made by or agreed to by the project proponent. A MITIGATED NEGATIVE DECLARATION will be prepared.

☐ I find that the proposed project MAY have a significant effect on the environment, and an ENVIRONMENTAL IMPACT REPORT is required.

☐ I find that the proposed project MAY have a "potentially significant impact" or "potentially significant unless mitigated" impact on the environment, but at least one effect 1) has been adequately analyzed in an earlier document pursuant to applicable legal standards, and 2) has been addressed by mitigation measures based on the earlier analysis as described on attached sheets. An ENVIRONMENTAL IMPACT REPORT is required, but it must analyze only the effects that remain to be addressed.

☐ I find that although the proposed project could have a significant effect on the environment, because all potentially significant effects (a) have been analyzed adequately in an earlier EIR or NEGATIVE DECLARATION pursuant to applicable standards, and (b) have been avoided or mitigated pursuant to that earlier EIR or NEGATIVE DECLARATION, including revisions or mitigation measures that are imposed upon the proposed project, nothing further is required.

Signature ____________________ Date ____________

Signature ____________________ Date ____________

EVALUATION OF ENVIRONMENTAL IMPACTS:

1) A brief explanation is required for all answers except "No Impact" answers that are adequately supported by the information sources a lead agency cites in the parentheses following each question. A "No Impact" answer is adequately supported if the referenced information sources show that the impact simply does not apply to projects like the one involved (e.g., the project falls outside a fault rupture zone). A "No Impact" answer should be explained where it is based on project-specific factors as well as general standards (e.g., the project will not expose sensitive receptors to pollutants, based on a project-specific screening analysis).

2) All answers must take account of the whole action involved, including off-site as well as on-site, cumulative as well as project-level, indirect as well as direct, and construction as well as operational impacts.

3) Once the lead agency has determined that a particular physical impact may occur, then the checklist answers must indicate whether the impact is potentially significant, less than significant with mitigation, or less than significant. "Potentially Significant Impact" is appropriate if there is substantial evidence that an effect may be significant. If there are one or more "Potentially Significant Impact" entries when the determination is made, an EIR is required.

4) "Negative Declaration: Less Than Significant With Mitigation Incorporated" applies where the incorporation of mitigation measures has reduced an effect from "Potentially Significant Impact" to a "Less Than Significant Impact". The lead agency must describe the mitigation measures, and briefly explain how they reduce the effect to a less than significant level (mitigation measures from Earlier Analyses, may be cross-referenced).

5) Earlier analyses may be used where, pursuant to the tiering, program EIR, or other CEQA process, an effect has been adequately analyzed in an earlier EIR or negative declaration. Section 15063(c)(3)(D). In this case, a brief discussion should identify the following:
   a) Earlier Analysis Used. Identify and state where they are available for review.
   b) Impacts Adequately Addressed. Identify which effects from the above checklist were within the scope of and adequately analyzed in an earlier document pursuant to applicable legal standards, and state whether such effects were addressed by mitigation measures based on the earlier analysis.
   c) Mitigation Measures. For effects that are "Less than Significant with Mitigation Measures Incorporated", describe the mitigation measures which were incorporated or refined from the earlier document and the extent to which they address site-specific conditions for the project.

6) Lead agencies are encouraged to incorporate into the checklist references to information sources for potential impacts (e.g., general plans, zoning ordinances). Reference to a previously prepared or outside document should, where appropriate, include a reference to the page or pages where the statement is substantiated.

7) Supporting Information Sources: A source list should be attached, and other sources used or individuals contacted should be cited in the discussion.

8) This is only a suggested form, and lead agencies are free to use different formats; however, lead agencies should normally address the questions from this checklist that are relevant to a project's environmental effects in whatever format is selected.

9) The explanation of each issue should identify:
   a) the significance criteria or threshold, if any, used to evaluate each question; and
   b) the mitigation measure identified, if any, to reduce the impact to less than significance.

	Potentially Significant Impact	**Less Than Significant with Mitigation Incorporation**	**Less Than Significant Impact**	**No Impact**
3.1. AESTHETICS -- Would the project:				
a) Have a substantial adverse effect on a scenic vista?	9	9	9	±
b) Substantially damage scenic resources, including, but not limited to, trees, rock outcroppings, and historic buildings within a state scenic highway?	9	9	9	±
c) Substantially degrade the existing visual character or quality of the site and its surroundings?	9	9	±	9
d) Create a new source of substantial light or glare which would adversely affect day or nighttime views in the area?	9	9	9	±

ENVIRONMENTAL SETTING:

The Yerba Buena Pump Station (Pump Station) is located in southeast end of Santa Clara Valley in the City of San Jose one mile east of US Highway 101. The Pump Station itself is on a parcel zoned Planned Development adjacent to Silver Creek Linear Park. The surrounding area is generally low density residential, but no residences directly abut the Pump Station site. Land use development patterns in the project vicinity are shown on the aerial photograph (Figure 6, Upper Silver Creek Characteristics). Off-site views of the Pump Station facility are limited to the recreational footpath following the south side of Upper Silver Creek that passes in front of the Pump Station entrance driveway. The Pump Station compound perimeter is marked with a chain linked fence and partially screened by trees. Tall vegetation along the recreational foot trail and streambed corridor shields the Pump Station from adjacent views.

DISCUSSION:

Will the proposed project:

a. **Have a substantial adverse effect on a scenic vista?** *(Source #: 9, 12, 13, 19)*

No impact. There are no scenic vistas of the project site from surrounding areas. Views of the Pump Station are isolated to the recreation trail adjacent to Upper Silver Creek due to intervening topography and trees shown in the above photos. There are no views of the project area from offsite locations. The dechlorination equipment would be visible to trail users passing the facility entrance. The equipment is housed in a trailer mounted container and would be seen in context with the existing recycled water tank and pump equipment; this would not appreciably detract from surrounding adjacent views of the creek corridor.

b. Substantially damage scenic resources, including, but not limited to, trees, rock outcroppings, and historic buildings within a state scenic highway? *(Source #: 7, 12, 13, 19)*

No impact. The Pump Station project site does not contain scenic resources such as trees, rock outcroppings, or historic buildings within view of a state scenic highway. There are no state scenic highways near the project site. The nearest highway is U.S. Highway 101, which is not designated as scenic and does not have views of the project site.

c. Substantially degrade the existing visual character or quality of the site and its surroundings? *(Source #: 13, 19)*

Less than Significant. Grading associated with installing the dechlorination equipment and new pipelines would be minimal and not alter topography. The new equipment would be viewed in context with existing Pump Station infrastructure. The new equipment would not cause visual impacts. A recycled water pipeline would be constructed beneath the entrance driveway to connect to the existing storm drain. This would not result in visual impacts. The visual character of the site will not be altered or adversely impacted. The Pump Station is an existing facility and the new dechlorination unit will be viewed as an extension of that facility consistent with the existing visual character. Views of the Pump Station facility are isolated and limited to the immediate creek corridor. Visibility of the project site is limited to the foot trail immediately in front of the Pump Station. The Pump Station property line is set back from the foot trail by several feet. Trees screen views of the compound except directly in front of the facility at the entrance driveway.

d. Create a new source of substantial light or glare which would adversely affect day or nighttime views in the area? *(Source #: 13, 19)*

No impact. There will be no new sources of substantial light or glare as a result of this project. The construction of the project pipelines and dechlorination unit at the Pump Station improvements will only occur during the daylight hours.

	Potentially Significant Impact	**Less Than Significant with Mitigation Incorporation**	**Less Than Significant Impact**	**No Impact**
3.2. AGRICULTURE RESOURCES -- In determining whether impacts to agricultural resources are significant environmental effects, lead agencies may refer to the California Agricultural Land Evaluation and Site Assessment Model (1997) prepared by the California Dept. of Conservation as an optional model to use in assessing impacts on agriculture and farmland. Would the project:				
a) Convert Prime Farmland, Unique Farmland, or Farmland of Statewide Importance (Farmland), as shown on the maps prepared pursuant to the Farmland Mapping and Monitoring Program of the California Resources Agency, to non-agricultural use?	9	9	9	±
b) Conflict with existing zoning for agricultural use, or a Williamson Act contract?	9	9	9	±
c) Involve other changes in the existing environment which, due to their location or nature, could result in conversion of Farmland, to non-agricultural use?	9	9	9	±

ENVIRONMENTAL SETTING:

The Yerba Buena Pump Station is located in Silver Creek Linear Park and is surrounded by urban development.

DISCUSSION:

Will the proposed project:

a. **Convert Prime Farmland, Unique Farmland, or Farmland of Statewide Importance (Farmland), as shown on the maps prepared pursuant to the Farmland Mapping and Monitoring Program of the California Resources Agency, to non-agricultural use?** (*Source #s: 11, 12, 13, 19)*

No Impact. The tertiary recycled water will be dechlorinated at the SBWR Pump Station facility at Yerba Buena Road. The compound is surrounded by Silver Creek Linear Park. There is no farmland on or adjacent to the Pump Station site or along the Upper Silver Creek corridor. The proposed project would not directly or indirectly remove any acreage from agricultural production. The project would have no impact on prime farmland or other agricultural resources in the project vicinity.

b. Conflict with existing zoning for agricultural use, or a Williamson Act contract? *(Source #: 11, 12, 13, 19)*

No Impact. The project site is located within an existing recycled water Pump Station facility. The project does not affect any land that has been zoned for agricultural use or is currently in Williamson Act contracts. The proposed release of dechlorinated recycled water into Upper Silver Creek would not affect agriculture or Williamson Act contracts.

c. Involve other changes in the existing environment which, due to their location or nature, could result in conversion of Farmland, to non-agricultural use? *(Source #: 11, 12, 13, 19)*

No Impact. The project will not involve other changes in the existing environment that could result in the conversion of farmland to non-agricultural use.

	Potentially Significant Impact	Less Than Significant with Mitigation Incorporation	Less Than Significant Impact	No Impact
3.3. AIR QUALITY -- Where available, the significance criteria established by the applicable air quality management or air pollution control district may be relied upon to make the following determinations. Would the project:				
a) Conflict with or obstruct implementation of the applicable air quality plan?	9	9	9	±
b) Violate any air quality standard or contribute substantially to an existing or projected air quality violation?	9	9	9	±
c) Result in a cumulatively considerable net increase of any criteria pollutant for which the project region is non-attainment under an applicable federal or state ambient air quality standard (including releasing emissions which exceed quantitative thresholds for ozone precursors)?	9	9	±	9
d) Expose sensitive receptors to substantial pollutant concentrations?	9	9	9	±
e) Create objectionable odors affecting a substantial number of people?	9	9	9	±

ENVIRONMENTAL SETTING:

Regulatory Setting. The California Air Resources Board (CARB) is responsible for air pollution control and setting State ambient air quality standards and allowable emission levels for motor vehicles. The State is divided into air basins governed by districts. The project site is located in the Bay Area Air Quality Management District (BAAQMD). BAAQMD monitors and enforces District, State of California, and Federal air quality standards. The air pollution monitoring station nearest to the project site is located in east San Jose.

Existing Ambient Air Quality. The San Francisco Bay Air Basin is in attainment for all national pollutant standards set forth in the federal Clean Air Act with exception of ozone. In June 2004, the Bay Area was designated as a marginal non-attainment area for the national 8-hour ozone standard. The region also exceeds State ambient air quality standards for ozone and fine particulate matter (PM_{10} and $PM_{2.5}$). The state standards for these pollutants are more stringent than the national standards. All other pollutants are designated as “attainment” or “unclassified” for federal standards and state standard.

The air pollution potential of the Santa Clara Valley is high. The valley has a large population and the largest complex of mobile sources in the Bay Area making it a major source of carbon monoxide, particulate and photochemical air pollution. In addition, photochemical precursors from San Francisco, San Mateo and Alameda counties can be carried along by the prevailing winds to the Santa Clara Valley making it also a major ozone receptor. Geographically, the valley tends to channel pollutants to the southeast with its northwest/southeast orientation, and concentrate pollutants by its narrowing to the southeast. Meteorologically, on high-ozone low-inversion summer days, the pollutants can be recirculated by the prevailing northwesterlies in the afternoon and the light drainage flow in the late evening and early morning, increasing the impact of emissions significantly. On high particulate and carbon monoxide days during late fall and winter, clear, calm and cold conditions associated with a strong surface based temperature inversion prevail (BAAQMD, 2005).

Sensitive Receptors. The Yerba Buena Pump Station is located in a county park along Upper Silver Creek. The nearest sensitive air quality receptors are the residential areas located along Yerba Buena Road across from the Pump Station to the north. There are no hospitals in the immediate project vicinity. Silver Creek High School and Montgomery School are located ¾ mile from the site.

DISCUSSION:

Will the proposed project:

a. **Conflict with or obstruct implementation of the applicable air quality plan?** *(Source #: 1, 2, 13, 19)*

No Impact. The proposed stream flow augmentation project would not contribute to urban growth or introduce new sources of air pollutants into the air basin. Therefore, the project does not conflict with or obstruct the implementation of the Bay Area air quality management plan.

b. **Violate any air quality standard or contribute substantially to an existing or projected air quality violation?** *(Source #: 1, 2, 13, 19)*

No Impact. Emissions are minimal, see response c. below.

c. **Result in a cumulatively considerable net increase of any criteria pollutant for which the project region is non-attainment under an applicable federal or state ambient air quality standard (including releasing emissions which exceed quantitative thresholds for ozone precursors)?** *(Source #: 1, 2, 13, 19)*

Less than Significant. There will be some emissions of diesel exhaust, dust and fine particulate matter associated with the project, but the cumulative increase in the region is less than significant due to the short duration and small size of the project.

Construction entails only minor grading of an area of approximately 100 square yards along side of an existing gravel road. No earth will be excavated or removed from the site. One or two truckloads of gravel will be imported. Active construction will occur on portions of a few days. All of the constructed pipelines will be above-ground (Figure 4). The temporary emissions of diesel exhaust, dust and fine particulate matter are minimal. As a result, the air pollutants associated with this construction activity is negligible and would not violate any air quality standard or contribute substantially to an existing or projected air quality violation.

Operations are powered by electricity. The dechlorination reaction is water-based, enclosed and has no appreciable emissions.

d. Expose sensitive receptors to substantial pollutant concentrations? *(Source #: 1, 2, 12, 13, 19)*

No Impact. There are no long-term pollutant emissions associated with the stream flow augmentation project.

e. Create objectionable odors affecting a substantial number of people? *(Source #: 12, 13, 19)*

No Impact. The activities associated with the construction and operation of the stream flow augmentation project will not result in the creation of objectionable odors. The tertiary treated recycled water has no appreciable odor.

	Potentially Significant Impact	**Less Than Significant with Mitigation Incorporation**	**Less Than Significant Impact**	**No Impact**
3.4. BIOLOGICAL RESOURCES -- Would the project:				
a) Have a substantial adverse effect, either directly or through habitat modifications, on any species identified as a candidate, sensitive, or special status species in local or regional plans, policies, or regulations, or by the California Department of Fish and Game or U.S. Fish and Wildlife Service?	9	±	9	9
b) Have a substantial adverse effect on any riparian habitat or other sensitive natural community identified in local or regional plans, policies, regulations or by the California Department of Fish and Game or US Fish and Wildlife Service?	9	9	±	9
c) Have a substantial adverse effect on federally protected wetlands as defined by Section 404 of the Clean Water Act (including, but not limited to, marsh, vernal pool, coastal, etc.) through direct removal, filling, hydrological interruption, or other means?	9	9	9	±
d) Interfere substantially with the movement of any native resident or migratory fish or wildlife species or with established native resident or migratory wildlife corridors, or impede the use of native wildlife nursery sites?	9	9	9	±
e) Conflict with any local policies or ordinances protecting biological resources, such as a tree preservation policy or ordinance?	9	9	9	±
f) Conflict with the provisions of an adopted Habitat Conservation Plan, Natural Community Conservation Plan, or other approved local, regional, or state habitat conservation plan?	9	9	9	±

ENVIRONMENTAL SETTING:

Thomas Reid Associates assessed the biological resources of the Upper Silver Creek and Coyote Creek during site visits in November 2005 and February 2006. The aerial view of Upper

Silver Creek in Figure 6 clearly shows where the creek has riparian vegetation and the lower reach which is a concrete channel. Photographs of Upper Silver Creek from the point of release to its confluence with Coyote Creek are presented in Figure 7.

Upper Silver Creek Aquatic Habitat. The riparian habitat within Upper Silver Creek, immediately downstream of the release point is characterized by dense coast live oak woodland for approximately ¼ mile (Figure 7, Photos 2a, 2b, and 3). The next ¼ mile opens into a more open channel dominated by cattails (*Typha spp.*) (Figure 7, Photo 4). The creek enters into a concrete channel at the Greenyard Street Bridge (Figure 7, Photo5a). The creek flows through a concrete channel for another 1.5 miles before entering Coyote Creek (Figure 7, Photo 6).

Table 3 shows the water temperature in Upper Silver Creek near the proposed point of release as measured from May through November, 2005 (Appendix A, Results of the 2005 Baseline Study for Coyote Creek Stream Augmentation Project). Upper Silver Creek provides habitat for a warm-water fish species assemblage (personal observations and communications with Jae Abel, SCVWD). The normal temperature range for a warm water fishery is 20 - 25 ^{o}C or 68 - 77 ^{o} F during the warm season.

Table 3. Stream Conditions at Proposed Release Point

Sample Day (2005)	Temperature (^{o}F)	pH (pH units)	Dissolved Oxygen (mg/L)	Conductivity (uS/cm)
May 18	58.6	8.69	9.2	1109
July 20	66.5	8.59	9.9	1193
August 29	62.2	8.51	10.7	1164
October 3	60.4	8.72	10.8	1294
November 8	58.0	NM	NM	NM

NM = Not Measured

Source: Appendix A, Results of the 2005 Baseline Study for Coyote Creek Stream Augmentation Project).

Native fish species likely in the creek include California roach (*Hesperoleucus symmetricus*), three-spine stickleback (*Gasterosteus aculeatus*), Sacramento sucker (*Catostomus occidentalis*), prickly sculpin (*Cottus asper*); and nonnative species likely include mosquitofish (*Gambusia affinis*), carp (*Cyprinus carpio*), and various *centrarchidae* (bass/sunfish) species.

Upper Silver Creek is not listed in the San Francisco Bay Regional Water Quality Control Board's Basin Plan as having beneficial uses (SFBRWQCB, 2005). Due to its urbanized watershed, channelized sections, and relatively poor water quality, the creek is considered an impacted water body. Because Upper Silver Creek is a tributary to Coyote Creek, and because Coyote Creek has beneficial uses in the San Francisco Basin Plan (Plan), the Plan's "tributary rule" may apply and in this case, the beneficial uses for Coyote Creek should serve as baseline in determining the beneficial uses that are applicable for the Upper Silver Creek.

Beneficial uses for Coyote Creek specified in the Plan include: Cold Freshwater Habitat (COLD); Fish Migration (MIGR); Preservation of Rare and Endangered Species (RARE); Non Contact Water Recreation (REC2); Fish Spawning (SPWN); Warm Freshwater Habitat

(WARM);

and Wildlife Habitat (WILD). Coyote Creek beneficial uses that apply to Upper Sliver Creek include: SPWN; WARM and WILD.

The Basin Plan defines Warm Freshwater Habitat beneficial use as:

> "Uses of water that support warm water ecosystems including, but not limited to, preservation or enhancement of aquatic habitats, vegetation, fish, or wildlife, including invertebrates.
>
> "The warm freshwater habitats supporting bass, bluegill, perch, and other panfish are generally lakes and reservoirs, although some minor streams will serve this purpose where stream flow is sufficient to sustain the fishery. The habitat is also important to a variety of non-fish species, such as frogs, crayfish, and insects, which provide food for fish and small mammals. This habitat is less sensitive to environmental changes, but more diverse than the cold freshwater habitat, and natural fluctuations in temperature, dissolved oxygen, pH, and turbidity are usually greater."

Coyote Creek Aquatic Habitat. Coyote Creek has the largest watershed of any creek in Santa Clara County, and contains habitat for sensitive species such as California red-legged frog, western pond turtle, and steelhead. Native and non-native fish species are more diverse than those found in Upper Silver Creek, and the creek has a riparian tree corridor that provides important ecosystem function (Buchan, 2001). Coyote Creek has been described as providing both cold water habitat in its upper watershed, and warm water habitat in its lower watershed. Oxygen levels and algal growth in the lower reaches of Coyote Creek are more consistent with a warm water habitat (Hopkins, et. al. 2002), and habitat conditions in Coyote Creek become more degraded and less suitable for sensitive species downstream of the confluence with Upper Silver Creek (personal communications Jae Abel and Lucy Buchan).

Special Status Species. A special status species search was conducted for the stream flow augmentation project using the California Natural Diversity Database (CNDDB) and SCVWD special status amphibian and reptile survey data. Several special status species were identified within five miles of the project release point. Since the project will not impact upland areas, all upland species that are listed in the database can be disregarded from further consideration in the impact analysis. This includes all the plant species and most of the animal species.

The special status species that could potentially be present within Upper Silver Creek and/or Coyote Creek, and therefore potentially impacted by this project are: 1) California Tiger Salamander, 2) California Red-legged Frog, 3) Western Pond Turtle, and
4) Steelhead Trout.

1) California Tiger Salamander (*Ambystoma californiense*), Federally Threatened

California tiger salamander (CTS) typically require ephemeral ponds for breeding habitat, and only utilize creek habitats in very rare circumstances. This species has been recorded within cattle stockponds less than one mile of the project release point (CNDDB; SCVWD CTS Status and Distribution 1999). A field visit to the site confirmed that most of these ponds have been destroyed through increased development of the area, particularly during the last ten years. A residential and golf course development on the south side of the creek (the "Cerro Plata" project AKA "The Ranch on Silver Creek") may have removed the last area where this species occurred. It is not clear at this time if any of the mitigation installed as part of this development project was successful, however it appears the mitigation ponds that were created are too shallow to provide appropriate CTS breeding habitat (personal observations, personal communications Jae Abel, SCVWD). Because CTS does not typically use creeks (especially perennial creeks) for breeding, and because the site lacks suitable breeding pond habitat to support CTS, it is highly unlikely that the proposed stream flow augmentation project would impact this species.

2) California Red-legged Frog (*Rana aurora draytonii*), Federally Threatened

California red-legged frog has been recorded at a reservoir at the south end of Caldwallader Road approximately 0.6 miles east of the project release point, and in Upper Silver Creek approximately 2.5 miles southeast of the release point. There are also records of CRLF within Coyote Creek approximately 5 miles south of the project site (CNDDB; SCVWD CRLF Status and Distribution 1997). Aquatic habitat downstream of the release point has been heavily impacted by urbanization and there is a lack of riparian vegetation for cover; however, it is possible that CRLF could be present within the project reach.

CRLF use a variety of aquatic habitats including ponds, creeks, and marshes and occasionally shallow puddles (personal observations) with a variety of temperature regimes. The thermal maximum for this species as reported in the literature is 29 °C (84.2 °F) for adults (Jennings and Hayes 1990). It is likely that the thermal maximum temperatures for eggs and tadpoles are below this, and northern red-legged frog tadpoles have been shown to die in 77 °F water (Calef *in* EcoSystems West Consulting Group 2001).

3) Western Pond Turtle (*Emys marmorata*), California Species of Special Concern

Western pond turtle (WPT) has been observed in Upper Silver Creek, within approximately two miles of the release point (SCVWD, WPT Status and Distribution, 1999), and in Coyote Creek (several records). Based on the urbanization of the watershed, and the reliance of this species on adjacent floodplains for nesting, it is highly unlikely this species is breeding in the project reach. In general, WPT avoid prolonged exposure to water above 95 °F, but have been observed to be active in water temperatures as high as 100° F (Holland 1991c, Holland 1994 in Hays, et. al. 1999).

4) Steelhead Trout (*Oncorhynchus mykiss*), Federally Threatened

Steelhead trout have not been recorded in Upper Silver Creek in recent history, and are thought to be no longer present in this creek (personal communications Jae Abel, SCVWD). This is due to the low flow conditions, degraded water quality, including warm temperatures, and potential structural and velocity barriers downstream of the project reach. A concrete apron occurs in the Upper Silver Creek channel approximately 1.5 miles upstream of the Coyote Creek confluence and approximately ½ mile downstream of the proposed release point for the project at the Greenyard Street Bridge (Figure 7, Photo 5b). Such structures usually impose a significant barrier to upstream fish migration. The discharge structure at the confluence of Upper Silver Creek and Coyote Creek (Figure 7, Photo 7) also prevents passage of fish from Coyote Creek upstream into Upper Silver Creek.

DISCUSSION:

Will the proposed project:

a. **Have a substantial adverse effect, either directly or through habitat modifications, on any species identified as a candidate, sensitive, or special status species in local or regional plans, policies, or regulations, or by the California Department of Fish and Game or U.S. Fish and Wildlife Service?** *(Source #s: 3, 4, 5, 10, 13, 14, 15, 16, 18, 19, 22, 23, 24)*

Less than Significant Impact with Mitigation Incorporation. The new equipment and pipelines needed for the stream flow augmentation project would be installed at an existing facility. Minor ground disturbance would occur on a portion of the Pump Station site that has no vegetative cover. The unit would be located in an existing graded area next to a water reservoir and pumps. No endangered, threatened, or rare species or their habitats are present at the Pump Station site where ground disturbance will occur for equipment installation (Figure 4). The Pump Station does not support special status plants and would have no impact on terrestrial candidate, sensitive, or special-status species or their habitats.

The augmentation project has the potential to modify the aquatic environment of special status species in the Upper Silver Creek/Coyote Creek corridor. The recycled water will modify the receiving water temperature, water quality, and flow volume. Water quality impacts of the augmentation are described in Hydrology/Water Quality.

Water Temperature.

Uncontrolled release of recycled water with elevated temperatures could result in the temperature elevation of Upper Silver Creek and the receiving water downstream, causing adverse impacts to fisheries. Both the immediate receiving waters in Upper Silver Creek and the reach of Coyote Creek below the confluence with Upper Silver Creek are warm freshwater habitat and Salmonids will not be present during the season of project release. The project has been designed to include weekly monitoring of stream flow temperature to ensure that receiving waters temperature does not exceed a safe threshold for warm water ecosystems during the summer.

Although no specific beneficial uses are identified for Upper Silver Creek, it is presumed to function as a minor warm water fishery. Thus, project release should be regulated to keep the final temperature well within the normal summer temperature range of 68 - 77 ^{o}F for this habitat. The project proposes to limit temperature in the immediate receiving waters at the point of release to 75 ^{o}F, which is the basis for the biotic standard for warm water fisheries. With recycled water temperature of 80 °F to 82 °F and receiving water temperature of 62 °F to 67 °F, a project flow of 0.5 to 1.0 cfs would result in a temperature below 75 °F.

Increased flow in Upper Silver Creek may increase temperature in Coyote Creek. For low flows – on the order of a few cfs – water temperature of Upper Silver Creek at the confluence is independent of the release temperature 1.7 miles upstream. The potential impact comes from the tendency for flow in one mile of open concrete channel to be heated by sun and warm ambient air. The effect is pronounced on summer afternoons and Upper Silver Creek exceeds 80 °F just before it enters Coyote Creek. The conditions warming Upper Silver Creek also warm Coyote Creek so that the temperature difference is usually less than 10 degrees; when the warm water mixes with the flow in Coyote Creek, the temperature in Coyote Creek rises by one or two degrees. For this project, increased flow in Upper Silver Creek will increase temperature in Coyote Creek by approximately 1 °F above ambient. The temperature change would occur during summer low flow months when water temperature in Coyote Creek is seasonally elevated. Salmonids are unlikely to be present in the affected reach of Coyote Creek at this time and therefore would not be affected by the project.

Water Quality. Coyote Creek has impaired water quality (Hopkins, 2001) and is listed in the 2002 Clean Water Act, section 303 (d) list for diazinon from pesticide uses. The recycled water will have lower concentrations of some constituents such as heavy metals (e.g. Chromium and Arsenic) and usually also herbicides/pesticides. (See Table 4, Water Quality Monitoring Results 2005 in the Section on Hydrology and Water Quality). The addition of tertiary treated water to the existing stream flow will dilute the existing concentrations of heavy metals and other inorganic compounds in Coyote Creek, thus improving water quality in that regard.

The recycled water contains slightly higher concentrations of organic compounds and nitrate which promote algal growth. Seasonally, algal growth contributes to reduced oxygen levels and increased un-ionized ammonia levels which would adversely impact fisheries. The recycled water has been treated to eliminate ammonia. The pH is closer to neutral than surface waters (7.3 compared to 8.4) and is slightly less hard. Nutrient effects may diminish rapidly as the water flows through Upper Silver Creek so that impact on Coyote Creek will be minimal. It is not proposed to de-nitrify the water at present. Potential water quality impacts are addressed in Hydrology/Water Quality Section 8.a below.

It is theorized that the increased creek flow and natural processes in the creek will result in the natural attenuation of trace levels of organic compounds and will improve water quality (Gurr and Reinhard, 2006). This hypothesis is based on research findings as described in the Project Background Section 2.3. Thus the proposed stream flow augmentation project could have a beneficial effect on water quality in Coyote Creek.

Water Volume. Increased flow volume reduces fish density, which can improve the quality of fish habitat. The proposed flow volume increase by 1 cfs is small compared to winter storm flows, but during low flow months it could result in habitat improvement. Augmenting the stream flow volume will also increase flow velocity. Increased flow velocity could have an impact on spawning gravels habitat in Coyote Creek by favoring the native warm water fish that are present (Jones and Stokes, 2000). The increased flow velocity resulting from up to a 1 cfs flow augmentation would be well below the levels at which stream bed changes would occur. The increase in flow volume would not adversely impact special status aquatic species.

Mitigation Incorporated in Project: Measure WQ-3 Surface Water Temperature Protection described in Section 2.5 will provide effective response to observed potential for impact.

b. Have a substantial adverse effect on any riparian habitat or other sensitive natural community identified in local or regional plans, policies, regulations or by the California Department of Fish and Game or US Fish and Wildlife Service? *(Source #s: 13, 14, 15, 16, 18, 19, 20)*

Less than Significant Impact. Equipment installation would occur at the Pump Station in a previously disturbed area. An existing storm drain outlet would be used to release the recycled water to Upper Silver Creek so there would be no ground disturbance in the streambed of Upper Silver Creek. Changes in water quality are minor as described above in Section 4.a and would not adversely affect riparian habitat downstream of the release location.

c. Have a substantial adverse effect on federally protected wetlands as defined by Section 404 of the Clean Water Act (including, but not limited to, marsh, vernal pool, coastal, etc.) through direct removal, filling, hydrological interruption, or other means? *(Source #s: 14, 20, 26)*

No Impact. Implementation of the project would not result in the removal, filling, hydrological interruption, or other disturbances to federally protected wetlands. There are no wetlands within the Pump Station where ground disturbance for equipment installation will occur. The potential for water quality impacts downstream of the release location is described in Section 4.a above and in Hydrology in Section 8.a below.

d. Interfere substantially with the movement of any native resident or migratory fish or wildlife species or with established native resident or migratory wildlife corridors, or impede the use of native wildlife nursery sites? *(Source #s: 14, 20, 26)*

No impact. The project will not adversely interfere with the movement, corridors, or nursery sites of any native resident or migratory fish or wildlife species. Increased flow volume could enhance the movement of fish within Coyote Creek corridor providing a beneficial effect. See also Response 8.a above.

e. Conflict with any local policies or ordinances protecting biological resources, such as a tree preservation policy or ordinance? *(Source #s: 12, 13, 16, 18, 20)*

No impact. Minor grading at the Pump Station will not affect the existing riparian corridor. No trees will be removed or disturbed as part of the stream flow augmentation project.

Biological resources within the creek corridor are potentially affected by the change in water quality, water temperature, and water volume of the creek flow caused by the project release of recycled water into Upper Silver Creek. The project has been designed to minimize the potential impacts to biological resources by minimizing the release flow volume and monitoring the temperature change of the creek. The water quality impacts are described in Response 8.a above. The project does not conflict with local policies protecting biological resources. See also Response 9.a for a discussion of San Jose General Plan policies regarding riparian corridors.

f. Conflict with the provisions of an adopted Habitat Conservation Plan, Natural Community Conservation Plan, or other approved local, regional, or state habitat conservation plan? *(Source #: 12, 13, 16, 18, 20)*

No impact. There are no habitat conservation plans in effect which govern the project site or affected creek corridor.

	Potentially Significant Impact	Less Than Significant with Mitigation Incorporation	Less Than Significant Impact	No Impact
3.5. CULTURAL RESOURCES -- Would the project:				
a) Cause a substantial adverse change in the significance of a historical resource as defined in §15064.5?	9	9	9	±
b) Cause a substantial adverse change in the significance of an archaeological resource pursuant to §15064.5?	9	9	9	±
c) Directly or indirectly destroy a unique paleontological resource or site or unique geologic feature?	9	9	9	±
d) Disturb any human remains, including those interred outside of formal cemeteries?	9	9	9	±

ENVIRONMENTAL SETTING:

There are no known cultural or historical resources located on the project site at the Pump Station.

DISCUSSION:

Will the proposed project:

a. **Cause a substantial adverse change in the significance of a historical resource as defined in §15064.5?** *(Source #: 13, 14, 18, 20)*

No Impact. There are no known historical sites within the Pump Station project site. No impacts to known historical resources would occur as a result of this project.

b. **Cause a substantial adverse change in the significance of an archaeological resource pursuant to §15064.5?** *(Source #: 13, 14, 18, 20)*

No Impact. There are no known archaeological sites within the Pump Station. No impacts to known archaeological resources in the project vicinity would occur as a result of the stream flow augmentation project.

c. **Directly or indirectly destroy a unique paleontological resource or site or unique geologic feature?** *(*Source #*: 13, 14, 18, 20)*

No Impact. The proposed project is the augmentation of stream flow in the Coyote Creek watershed. Ground disturbance is limited to the Pump Station facility. This activity would not significantly modify existing topography or impact paleontological resources or geologic features. There are no significant paleontological resources, geological or physical features in or near the project site.

d. Disturb any human remains, including those interred outside of formal cemeteries? *(Source #: 13, 14, 18, 20)*

No Impact. The Pump Station does not contain human remains nor is it located in a sensitive area for cultural resources.

	Potentially Significant Impact	Less Than Significant with Mitigation Incorporation	Less Than Significant Impact	No Impact
3.6. GEOLOGY AND SOILS – Would the project:				
a) Expose people or structures to potential substantial adverse effects, including the risk of loss, injury, or death involving:				
i) Rupture of a known earthquake fault, as delineated on the most recent Alquist-Priolo Earthquake Fault Zoning Map issued by the State Geologist for the area or based on other substantial evidence of a known fault? Refer to Division of Mines and Geology Special Publication 42.	9	9	9	±
ii) Strong seismic ground shaking?	9	9	±	9
iii) Seismic-related ground failure, including liquefaction?	9	9	±	9
iv) Landslides?	9	9	9	±
b) Result in substantial soil erosion or the loss of topsoil?	9	9	±	9
c) Be located on a geologic unit or soil that is unstable, or that would become unstable as a result of the project, and potentially result in on- or off-site landslide, lateral spreading, subsidence, liquefaction or collapse?	9	9	9	±
d) Be located on expansive soil, as defined in Table 18-1-B of the Uniform Building Code (1994), creating substantial risks to life or property?	9	9	±	9
e) Have soils incapable of adequately supporting the use of septic tanks or alternative waste water disposal systems where sewers are not available for the disposal of waste water?	9	9	9	±

ENVIRONMENTAL SETTING:

Regional Geology. The proposed project site is located at the eastern edge of Santa

Clara Valley at the Silver Creek Linear Park off Yerba Buena Road. The site sets at the foot of the Yerba Buena hills approximately at elevation 240 feet (mean sea level).

Seismicity. The proposed project is located in the San Francisco Bay Region, which is one of the most seismically active regions in the United States. The project site is subject to strong ground shaking from a number of local and regional earthquake faults that are active or potentially active. The Silver Creek Fault (potentially active) is the closest fault to the site, located 00.5 miles north. The Evergreen Fault (active) lies approximately 1.75 miles north of the site and has been classified as potentially active. Other major faults in the vicinity include San Andreas, located approximately 16 miles southwest; Hayward, located approximately 2.5 miles northeast; and Calaveras, located about 4.5 miles northeast. Ground response during a seismic event is projected at a maximum ground-surface acceleration of 0.25 to 0.35 gravity (g). (Jones & Stokes, 2000)

Soil liquefaction is a natural phenomenon that occurs during seismic events. Liquefaction is the loss of shear strength resulting from excess pressure created in fine-grained, saturated soils during seismic events. As the excess pressure rises rapidly, the fine-grained sediment quickly shifts to a fluid-like state.

DISCUSSION:

Will the proposed project:

a. Expose people or structures to potential substantial adverse effects, including the risk of loss, injury, or death involving:

i. Rupture of a known earthquake fault, as delineated on the most recent Alquist-Priolo Earthquake Fault Zoning Map issued by the State Geologist for the area or based on other substantial evidence of a known fault? *(Sources #: 3, 8, 14, 17, 22, 24, 25)*

No impact. A review of geologic maps for the project area indicates that the site is not located within an Alquist-Priolo Earthquake Fault Zone.

ii. Strong seismic ground shaking? *(Sources #: 8, 17, 22, 23, 24, 25, 29)*

Less than Significant Impact. The project site is located in Santa Clara County within a seismically active area. The San Andreas Fault is located roughly 4 miles northeast of the project site, resulting in the high probability that the project site will be subject to very strong seismic shaking during the next major earthquake on the San Andreas Fault. The engineering design of the treatment skid reduces the risk of damage from seismic shaking. The equipment does not pose a public safety risk in the event of damage during a seismic event; therefore, the impact is less than significant.

iii. Seismic-related ground failure, including liquefaction? *(Sources #: 8, 12, 14, 16, 17, 22, 23, 29)*

Less than Significant Impact. The project site is located in a seismically active region. The project includes installation of dechlorination equipment on a graded pad that could be subject to ground shaking during a seismic event. The soils beneath the graded pad are unknown and could be subject to liquefaction. However, no permanent building foundations are required for the project and resulting structural damage to the dechlorination equipment would not be significant. See Response 6.a.ii above.

iv. Landslides? *(Sources #: 12, 16, 17, 23, 24)*

No Impact. The dechlorination units would be installed at the Pump Station facility which is located on the Santa Clara valley floor. The project site is not located in or near an area subject to landsliding.

b. Result in substantial soil erosion or the loss of topsoil? *(Sources #: 12, 16, 17, 23, 24)*

Less than Significant Impact. Equipment installation will require minor ground disturbance as described in Section 2.4. Best Management Practices will be used to control erosion and runoff. The project will not result in soil erosion or loss of topsoil.

c. Be located on a geologic unit or soil that is unstable, or that would become unstable as a result of the project, and potentially result in on- or off-site landslide, lateral spreading, subsidence, liquefaction or collapse? *(Sources #: 8, 12, 16, 17, 21, 23, 24, 25, 29)*

No impact. The soils within the project area are not unstable and the project will not cause any soil instability.

d. Be located on expansive soil, as defined in Table 18-1-B of the Uniform Building Code (1994), creating substantial risks to life or property? *(Sources #: 12, 14, 16, 17, 21, 23, 24, 29)*

Less than Significant Impact. The soil types where the dechlorinator and pipelines will be installed are unknown and could be expansive. However, no permanent building foundations are required for the project and structural damage to the dechlorination equipment potentially resulting from expansive soils would not be significant.

e. Have soils incapable of adequately supporting the use of septic tanks or alternative wastewater disposal systems where sewers are not available for the disposal of wastewater? *(Sources #: 12, 16, 21, 27)*

No impact. The project does not propose the installation of new septic tanks.

	Potentially Significant Impact	**Less Than Significant with Mitigation Incorporation**	**Less Than Significant Impact**	**No Impact**
3.7. HAZARDS AND HAZARDOUS MATERIALS — Would the project:				
a) Create a significant hazard to the public or the environment through the routine transport, use, or disposal of hazardous materials?	9	9	±	9
b) Create a significant hazard to the public or the environment through reasonably foreseeable upset and accident conditions involving the release of hazardous materials into the environment?	9	9	±	9
c) Emit hazardous emissions or handle hazardous or acutely hazardous materials, substances, or waste within one-quarter mile of an existing or proposed school?	9	9	9	±
d) Be located on a site which is included on a list of hazardous materials sites compiled pursuant to Government Code Section 65962.5 and, as a result, would it create a significant hazard to the public or the environment?	9	9	9	±
e) For a project located within an airport land use plan or, where such a plan has not been adopted, within two miles of a public airport or public use airport, would the project result in a safety hazard for people residing or working in the project area?	9	9	9	±
f) For a project within the vicinity of a private airstrip, would the project result in a safety hazard for people residing or working in the project area?	9	9	9	±
g) Impair implementation of or physically interfere with an adopted emergency response plan or emergency evacuation plan?	9	9	9	±
h) Expose people or structures to a significant risk of loss, injury or death involving wildland fires, including where wildlands are adjacent to urbanized areas or where residences are intermixed with wildlands?	9	9	9	±

ENVIRONMENTAL SETTING:

Hazardous substances have certain chemical and physical properties that may pose a substantial present or future hazard to human health or the environment when improperly handled, stored, disposed or otherwise managed. These substances are commonly used in commercial, agricultural, and industrial applications, and to a limited extent in residential areas. There are no known hazardous material sites identified in the project area based on a review of the Cortese List (pursuant to Government Code Section 65962.5).

DISCUSSION:

Will the proposed project:

a. **Create a significant hazard to the public or the environment through the routine transport, use, or disposal of hazardous materials?** *(Source #: 12, 13, 16, 18, 19, 27, 33)*

Less than Significant Impact. The project involves construction and operation of a dechlorination facility to produce recycled water for release to Upper Silver Creek that complies with Title 22 and NPDES standards. Liquid bisulfate or similar dechlorinating compound will be added to the treated recycled water using automated metering pumps. The compound will be stored on site in double containment tanks to minimize risk of accidental spills. Handling and storage of fuels, flammable materials, and construction related hazardous materials are governed by California Occupational Safety and Health (OSHA) standards for storage and fire prevention.

b. **Create a significant hazard to the public or the environment through reasonably foreseeable upset and accident conditions involving the release of hazardous materials into the environment?** *(Source #: 12, 13, 16, 18, 19, 27, 33)*

Less than Significant Impact. Liquid bisulfate or similar dechlorinating compound would be stored on site in double containment tanks to minimize risk of accidental spills. Construction related hazardous materials such as fuels would be stored according to state and federal regulations.

The Material Safety Data Sheet for Sodium Bisulfite Solution states: "Emergency Overview: A pale yellow aqueous solution with a pungent sulfur-like odor. Non-combustible but excessive heat may liberate sulfur dioxide gas that is toxic and corrosive. The solution itself is relatively non-toxic and poses little immediate hazard to fire fighting personnel in an emergency situation. Solution is mildly acidic and can pose a threat to water courses in an emergency situation."

c. **Emit hazardous emissions or handle hazardous or acutely hazardous materials, substances, or hazardous waste within one-quarter mile of an existing or proposed school?** *(Source #: 12, 13, 14, 16, 21, 27)*

No Impact. The proposed project does not involve the emission or handling of hazardous materials. The site is not within a quarter-mile of an existing or proposed school. The nearest school is James Smith Elementary located roughly 0.4 miles from the project site.

d. Be located on a site which is included on a list of hazardous materials sites compiled pursuant to Government Code Section 65962.5 and, as a result, would it create a significant hazard to the public or the environment? *(Source #:4)*

No impact. No hazardous material site is known to occur on or in the vicinity of the project site. The project site is not on the Department of Toxic Substance Control's Hazardous Waste and Substance Site List (Cortese List).

e. For a project located within an airport land use plan or, where such a plan has not been adopted, within two miles of a public airport or public use airport, would the project result in a safety hazard for people residing or working in the project area? *(Source #: 10, 11, 12, 16, 21)*

No Impact. The nearest public airport to the project site is Reid Hillview Airport in San Jose. This airport is a general aviation airport and has an adopted Airport Master Plan. The airport is located approximately 2.5 miles north of the project site. The project site is not located within the land use plan area of the airport. The proposed stream flow augmentation project at the Pump Station would not result in an airport safety hazard for the people using the site.

f. For a project within the vicinity of a private airstrip, would the project result in a safety hazard for people residing or working in the project area? *(Source #: 10, 11, 12, 16, 21)*

No Impact. There are no private airstrips near the project vicinity.

g. Impair implementation of or physically interfere with an adopted emergency response plan or emergency evacuation plan? *(Source #: 12, 16, 21)*

No Impact. The project would not impair implementation of or physically interfere with an adopted emergency response plan or emergency evacuation plan.

h. Expose people or structures to a significant risk of loss, injury or death involving wild land fires, including where wild lands are adjacent to urbanized areas or where residences are intermixed with wild lands? *(Source #: 11, 12, 13, 16, 21)*

No Impact. The project would not expose people or structures to a significant risk or loss, injury or death involving wildland fires. The project site is located within an industrialized compound surrounded by urbanized areas and grass parkland. There are no wildland areas with a fire risk near the project site.

	Potentially Significant Impact	**Less Than Significant with Mitigation Incorporation**	**Less Than Significant Impact**	**No Impact**
3.8. HYDROLOGY AND WATER QUALITY -- Would the project:				
a) Violate any water quality standards or waste discharge requirements?	9	±	9	
b) Substantially deplete groundwater supplies or interfere substantially with groundwater recharge such that there would be a net deficit in aquifer volume or a lowering of the local groundwater table level (e.g., the production rate of pre-existing nearby wells would drop to a level which would not support existing land uses or planned uses for which permits have been granted)?	9	9	9	±
c) Substantially alter the existing drainage pattern of the site or area, including through the alteration of the course of a stream or river, in a manner which would result in substantial erosion or siltation on- or off-site?	9		9	±
d) Substantially alter the existing drainage pattern of the site or area, including through the alteration of the course of a stream or river, or substantially increase the rate or amount of surface runoff in a manner which would result in flooding on- or off-site?	9	9	±	9
e) Create or contribute runoff water which would exceed the capacity of existing or planned stormwater drainage systems or provide substantial additional sources of polluted runoff?	9	9	9	±
f) Otherwise substantially degrade water quality?	9	9	±	9
g) Discharge unregulated, emerging contaminants?	9	9	±	9
h) Place housing within a 100-year flood hazard area as mapped on a federal Flood Hazard Boundary or Flood Insurance Rate Map or other flood hazard delineation map?	9	9	9	±

i) Place within a 100-year flood hazard area structures which would impede or redirect flood flows?	9	9	9	±
j) Expose people or structures to a significant risk of loss, injury or death involving flooding, including flooding as a result of the failure of a levee or dam?	9	9	9	±
k) Inundation by seiche, tsunami, or mudflow?	9	9	9	±

ENVIRONMENTAL SETTING:

Upper Silver Creek is located in south San Jose. Its upper reach originates in the eastern foothills south of Yerba Buena Road. The lower reach of the stream passes through Silver Creek Linear Park and then becomes a concrete lined drainage channel passing beneath US Highway 101 and through residential development before discharging to Coyote Creek. The proposed release of recycled water to Upper Silver Creek would occur through an existing storm drain outfall from the Pump Station. This segment of Upper Silver Creek at the release location has steep banks and is heavily vegetated (Figure 7, Photo 2a). The channel widens downstream as it approaches the Greenyard Road overcrossing where the channel becomes concrete (Figure 7, Photos 3 and 4). Upper Silver Creek flows to Coyote Creek from a culvert. The water flow in Upper Silver Creek is intermittent.

Regulatory Standards. The principal standards that apply are the SCVWD'S own policies for surface and groundwater protection, and for surface water, the California Department of Fish and Game, and the Regional Water Quality Control Board (RWQCB) Basin Plan, and particularly standards set under NPDES, Waste Discharge Requirements.

Surface Water Quality. Water quality of Upper Silver Creek and Coyote Creek is heavily impaired. A study of water quality in Coyote Creek found water temperatures to be elevated, heavy concentrations of metals and pathogens (TetraTech, 2001).

The proposed project will include a detailed water quality survey of project affected streams. This will establish baseline conditions.

Groundwater Quality. The creek is located in a transitional zone between the unconfined and confined aquifer of the Santa Clara Valley groundwater subbasin. The point of confluence with Coyote Creek and downstream is located in the confined zone (SCVWD, Groundwater Management Unit Memo dated March 15, 2005).

The 2005 Stanford study sampled Recycled Water at the Yerba Buena Pump Station, one groundwater site, and surface water in six sites on Upper Silver Creek and Coyote Creek (See Figure 5. Water Quality Sampling Sites, and detailed results in Appendix A, Results of the 2005 Baseline Study for Coyote Creek Stream Augmentation Project). Table 4 shows average water quality parameter values from several monthly samples. Table 5 shows where trace compounds were detected; due to less complete sampling, averages are not presented here, quantified results are in Appendix A.

Table 4.
Baseline Water Quality Monitoring Results 2005
(See Discussion section for an analysis of the results)

Parameter		**Recycled Water***	**Ground Water**	**Surface Water**
General Water Quality				
Bicarbonate Alkalinity	mg/L	176	574	411
Carbonate Alkalinity	mg/L	0	0	25
Hydroxide Alkalinity	mg/L	0	0	0
Total Alkalinity	mg/L	176	573	383
Chloride	mg/L	**184**	63	156
Conductivity	umhos	1223	1353	1260
PH	pH Units	7.3	7.2	8.4
Dissolved Organic Carbon	mg Carbon/L	**6.6**	3.3	4.1
Ammonia as Nitrogen	mg/L	ND	ND	ND
Nitrate as Nitrogen	mg/L	**8.3**	ND	1.1
Total Suspended Solids	mg/L	0.3	2.5	13.6
Total Filterable Residue at 180C	mg/L	695	754	729
Metals				
Boron	ug/L	**474**	221	296
Calcium	mg/L	52	134	41
Calcium as $CaCO_3$	mg/L	130	335	103
Copper	ug/L	ND	ND	ND
Iron	ug/L	ND	840	ND
Magnesium	mg/L	32	71	92
Potassium	mg/L	**15.9**	ND	4.5
Sodium	mg/L	**146**	58	99
Zinc	ug/L	ND	ND	ND
Aluminum	ug/L	ND	72	ND
Arsenic	ug/L	ND	ND	7.3
Barium	ug/L	ND	180	187
Cadmium	ug/L	ND	ND	ND
Lead	ug/L	ND	ND	ND
Manganese	ug/L	37	697	ND
Nickel	ug/L	11	19	12
Selenium	ug/L	ND	ND	ND
Silver	ug/L	ND	ND	ND
Total Chromium	ug/L	ND	ND	ND
Mercury	ug/L	ND	ND	ND

Table 4.
Baseline Water Quality Monitoring Results 2005 (Continued)

Parameter		**Recycled Water***	**Ground Water**	**Surface Water**
Herbicides and Pesticides				
2,4,5-TP	ug/L	ND	ND	ND
2,4-D	ug/L	ND	ND	ND
Aciflurfen	ug/L	ND	ND	ND
Bentazon	ug/L	ND	ND	ND
Dalapon	ug/L	ND	ND	ND
Dicamba	ug/L	ND	ND	ND
Dinoseb	ug/L	ND	ND	ND
Pentachlorphenol	ug/L	ND	ND	ND
Picloram	ug/L	ND	ND	ND
Trihalomethanes				
THM (method 502.2)				
Bromodichloromethane	ug/L	57.3	ND	ND
Bromoform	ug/L	6.2	ND	ND
Chloroform	ug/L	69.7	ND	1.0
Dibromochlormethane	ug/L	36.0	ND	ND
Total Trihalomethanes	ug/L	166.7	ND	0.5
Haloacetic Acids				
Bromochloroacetic acid	ug/L	14.0	1.0	1.0
Dibromoacetic Acid	ug/L	4.0	ND	ND
Dichloroacetic Acid	ug/L	18.0	ND	1.0
Monobromoacetic Acid	ug/L	3.0	ND	ND
Monochloroacetic Acid	ug/L	2.5	ND	ND
Total haloacetic Acids	ug/L	68.3	ND	1.7
Trichloroacetic Acid	ug/L	44.0	ND	2.0
Microbes				
E. Coli	MPN/100mL	NM	NM	711
Fecal Coliforms	MPN/100mL	NM	NM	992
Total Coliforms	MPN/100mL	NM	NM	5381

ND = Not Detected or reported as below detection limits.
NM = Not Measured
***Bold type** shows where Recycled Water value is more than 50% greater than Surface Water average.

Source: Stanford University, Coyote Creek Background Study.xls Nov. 2005
Summary: TRA

Table 5.
Water Quality Monitoring Results 2005
Trace Contaminant Detection

	Recycled Water	**Ground Water**	**Surface Water**
Pharmaceuticals			
Acetaminophen	-	-	-
Caffeine	-	-	✓
Carbamazepine	-	-	-
Carisoprodol	✓	-	-
Gemfibrozil	-	-	-
Ibuprofen	-	-	-
Iminostilbene	✓	-	-
Ketoprofen	-	-	-
Naproxen	-	-	-
Primidone	-	-	-
Propanolol	-	-	-
Hormones			
Estradiol	-	-	-
Estriol	-	-	-
Estrone	-	-	-
Ethynylestradiol	-	-	-
Organophophates (fire retardants)			
Tris(3-chloropropyl)phosphate	✓	✓	✓
Tris(2,3-dichloropropyl)phosphate	✓	✓	✓
Plasticizers			
Bisphenol A (BPA)	-	✓	-
N-butyl benzenesulfonamide (NBBS)	✓	✓	✓
Herbicide			
Oxadiazon	-	-	✓
Alkylphenol polyethoxylates		-	
APEOs	-	-	-
Alkylphenols (nonyl-, octyl-)	-	-	-
A+CAPECs3	✓	-	-
Halogenated APEMs4	✓	-	-
Disinfection Byproduct		-	-
N-Nitrosodimethylamine (NDMA)	✓	-	-
Perfluorochemicals (PFCs)	✓	✓	✓

✓ Detected
- Not detected above detection limits.

Source: Stanford University, Appendix A

Discussion:

Will the proposed project:

a. **Violate any water quality standards or waste discharge requirements?** *(Source #: 16, 21, 24)*

Less Than Significant with Mitigation Incorporation: Release of tertiary treated water to surface waters is subject to NPDES permit issued by RWQCB. Recycled water produced for this project meets the criteria set forth in Title 22, California Code of Regulations, for the production of disinfected tertiary treated recycled water. Table 3 presents the results from three sample of the recycled water from the Yerba Buena Pump Station (RW-1).

Regulated Chemicals

The recycled water carries chlorination byproducts, notably the Haloform, Haloacetic Acids and N-Nitrosodimethylamine (NDMA). The Haloforms as Trihalomethane and the NDMA are listed by the State of California pursuant to Proposition 65 as carcinogens. They are the subject of wide study throughout the U.S. where chlorine is used to disinfect potable water or wastewater.

Proposition 65 lists Oxadiazon and the older "tris" flame retardants. Oxadiazon was found only in the surface water baseline. The newer "tris" flame retardants (Tris(2,3-dichloropropyl)phosphate and Tris(3-chloropropyl)phosphate are not listed and are found in recycled water, groundwater and surface water baseline.

Among other things, Proposition 65 also prohibits companies that do business within California knowingly discharging listed chemicals into sources of drinking water. This prohibition does not apply to the proposed project because the surface receiving waters are not used for drinking water and geological analysis determined that the groundwater at the project site is not used for sources of drinking water. Groundwater monitoring is proposed and if Proposition 65 chemicals appear, the stream flow augmentation will be discontinued.

The main objective in the pilot program is to observe the effect of stream processes on trace organic constituents. The stream system and the treated water will be monitored monthly at six locations. If levels of regulated compounds are too high, the release will be reduced or discontinued.

Temperature

The District proposes to regulate the release into Upper Silver Creek based on the biotic standard of a warm water fishery. Release volume will be adjusted so as to prevent water temperature downstream of the release from rising above 75 °F. The measurement will be made at a point approximately 100 feet downstream of the storm drain outfall to allow adequate mixing.

Water temperature modeling indicates that this 75 °F limit will allow a treated water release of 0.5 to 1.0 cfs depending on temperature of the receiving water and incoming recycled water.

At present, summer flows in Upper Silver Creek are low, generally under 1 cfs and reflect infiltration of irrigation water along the creek. Creek temperature during the proposed release period was measured to be between 59 ^{o}F and 66 ^{o}F. In the summer, temperatures rise a few degrees along the natural channel portion of Upper Silver Creek, but once flow enters the open concrete channel, temperatures rise rapidly to the range 60 ^{o}F to 86 ^{o}F (See Appendix A, Results of the 2005 Baseline Study for Coyote Creek Stream Augmentation Project).

Temperature in Coyote Creek ranges from 62 ^{o}F to 78 ^{o}F in the period from May to October (See Appendix A).

Simple temperature models suggest that at low flows on the order of a few cfs, the water temperature of Upper Silver Creek where it joins Coyote Creek is determined mainly by ambient air temperature and sun intensity – on hot days in San Jose, flows in Upper Silver Creek will reach into the 80's. Coyote Creek also warms in warm weather; data suggest that the warm tributary flow into Coyote Creek adds 1 to 2 degrees to Coyote base temperature and the temperature falls slightly as the flow equilibrates downstream.

Increasing the tributary flow from Upper Silver Creek into Coyote Creek will increase the input of warm water. The proposed project release of up to 1 cfs may have the effect of increasing temperatures in Coyote Creek by approximately an additional degree Fahrenheit in the reach immediately below the confluence with Upper Silver Creek. As described under Biology, this stretch is not a cold water fishery during the summer and is not occupied by steelhead. Estimated project increases will have a less than significant effect.

Mitigation Incorporated in Project: Measures WQ-1 Groundwater Protection WQ-2 Surface Water Chemistry Protection, and WQ-3 Surface Water Temperature Protection described in Section 2.5 will provide effective response to observed potential for impact.

b. Substantially deplete groundwater supplies or interfere substantially with groundwater recharge such that there would be a net deficit in aquifer volume or a lowering of the local groundwater table level (e.g., the production rate of pre-existing nearby wells would drop to a level which would not support existing land uses or planned uses for which permits have been granted)? *(Source #: 14, 18, 26)*

No Impact. The project would not extract groundwater and, therefore, would not affect the quantity of subsurface water supplies. The project would not change the direction or rate of groundwater flow. The project does not involve the use of groundwater supplies and, therefore, does not impact the groundwater table or nearby wells.

The project will monitor groundwater quality to determine if surface release appears in the groundwater. If that occurs, the release will be stopped.

c. Substantially alter the existing drainage pattern of the site or area, including through the alteration of the course of a stream or river, in a manner which

would result in substantial erosion or siltation on- or off-site? *(Source #: 14, 18, 26)*

No Impact. The existing drainage pattern of the Pump Station and Upper Silver Creek channel receiving the project release will not be altered.

d. **Substantially alter the existing drainage pattern of the site or area, including through the alteration of the course of a stream or river, or substantially increase the rate or amount of surface runoff in a manner which would result in flooding on- or off-site?** *(Source #:14, 18, 26)*

Less than Significant Impact: The project will not create new areas of impervious surface that generate an increased rate or amount of surface runoff. The project would not alter existing drainage patterns. The actual point of release into Upper Silver Creek is through an existing storm drain. The volume of project during the dry season will be substantially similar to the storm flows that occur normally during the wet season. It is unlikely that the project flow will erode or alter the creek bed. Nonetheless, the project will require a Streambed Alteration Agreement from the California Department of Fish and Game.

e. **Create or contribute runoff water which would exceed the capacity of existing or planned storm water drainage systems or provide substantial additional sources of polluted runoff?** *(Source #: 16, 21, 26)*

No Impact. The project would not create new surface runoff or provide a new source of polluted runoff. The release of recycled water into Upper Silver Creek is minor and would occur during the dry months when creek flow volumes are low. The project would not exceed the capacity of an existing or planned storm water drainage system.

f. **Otherwise substantially degrade water quality?** *(Source #: 16, 21, 26)*

Less than Significant Impact. The SCVWD Groundwater Management Unit investigated the potential for the augmentation project to impact water quality. The release area along Upper Silver Creek is located in an unconfined section of the groundwater subbasin. The recycled water release from the Station is expected to recharge along a short segment of the creek between the point of release and where the channel becomes lined with concrete. Along this segment of naturalized channel, the recycled water may enter a groundwater zone of limited extent where a direct hydraulic connection to the main Santa Clara Valley groundwater subbasin is unlikely. A more thorough explanation is presented in the Groundwater Management Unit Memo Attachment B (Appendix B). Project operation will occur in summer months when creek flows are low. Groundwater travels in a northerly direction. Monitoring wells will be established to intercept recharge flows to determine if groundwater quality is being adversely affected.

The 2005 baseline survey showed no endocrine disruptor chemicals present in the recycled water. Small amounts of pharmaceuticals, flame retardant, perfluorinated compounds and chlorination byproducts were found. At present no standards are set for biological activity of the trace levels of compounds in recycled water. The proposed project will monitor the amount of substances released and follow their fate in the stream system. Part of the project objective is to observe the extent of biological or physical attenuation of trace compounds.

g. Discharge unregulated, emerging contaminants?

Less than Significant Impact. There is a specific concern that the release of even highly treated recycled water may carry trace levels of organic compounds that are contaminants of concern because of their potential toxicological or endocrine disrupting effect on aquatic organisms. These compounds, sometimes called emerging contaminants, are unregulated compounds for which there are no established State or Federal standards for aquatic life or human health. Standardized EPA-approved detection methods have not been established for these compounds; however, academic research laboratories have developed methods to detect these compounds in the low nanogram per Liter range.

The complete results of the 2005 baseline survey for emerging contaminants can be found in Appendix A. Of note are the data tables showing which of the emerging contaminants were detected (Table 8 and Table 14). The baseline survey found pre-existing trace levels of some of these contaminants in the receiving waters of the project site. This is consistent with past studies that show these trace contaminants already exist in streams all around the country (Kolpin et al, 2002). The baseline survey results found no hormones—the class of compounds known to be the most significant endocrine disruptors (Pickering, 2003)—detected in the recycled water above detection limits. Small amounts of pharmaceuticals, flame retardants, perfluorinated compounds and chlorination byproducts were found in the recycled water. During the project, attenuation mechanisms can be expected to reduce the concentrations of these compounds during flow in the stream. These mechanisms include sorption, volatilization, biodegradation, dilution, photolysis, and phytodegradation (Gurr and Reinhard, 2006, Tixier et al., 2003, Gross et al, 2004, Lin et al, 2006, and Williams et al. 2003).

NDMA was detected in recycled water at levels above the State Proposed Public Health Goal for NDMA in drinking water (OEHHA, 2006). There are no criteria established for NDMA in aquatic environments. However, studies have shown that NDMA photodegrades when exposed to bright sunshine conditions—conditions that are present at this project site (Stefan and Bolton, 2002).

Given the non-detection of compounds that have been known to show acute toxicity (i.e., non-detection of hormones), and the non-detection of most of the pharmaceuticals, no or minimal impact to the aquatic environment from these compounds is expected. For the compounds that were detected, it is important to recognize that the concentrations will be diluted two-fold when recycled water is added to the existing creek water, and attenuation mechanisms are expected to act immediately on these compounds. Furthermore, chronic toxicity impacts due to prolonged exposure from the trace concentrations existing after augmentation are minimal due to the short term duration of exposure during the project. The proposed project will monitor the amount of

substances released and follow their fate in the stream system. Part of the project objective is to observe the extent of biological or physical attenuation of trace compounds.

In summary, while analytical methods in research labs have improved to the point that detection of unregulated compounds at trace levels is possible, the toxicity or ecological effects of such trace quantities (often in the parts per trillion range) is not available to determine whether these trace levels have an environmental impact. So there is no threshold of significance to determine impacts to water quality from these emerging contaminants. Nonetheless, the reasons discussed above point towards no or minimal impact to the aquatic environment from the existence of unregulated, emerging contaminants in the recycled water to be used for augmentation.

h. Place housing within a 100-year flood hazard area as mapped on a federal Flood Hazard Boundary or Flood Insurance Rate Map or other flood hazard delineation map? *(Source #: 12, 13, 14, 20 , 26)*

No Impact. The project does not involve construction of housing.

i. Place within a 100-year flood hazard area structures which would impede or redirect flood flows? *(Source #: 12, 13, 14, 20, 26)*

No Impact. The project site is located at the Yerba Buena Pump Station in Silver Creek Linear Park adjacent to Upper Silver Creek. The dechlorination units would be located near the existing pump facilities outside of the 100-year flood zone for the creek. The equipment would not impede or redirect flood flows of Upper Silver Creek.

j. Expose people or structures to a significant risk of loss, injury or death involving flooding, including flooding as a result of the failure of a levee or dam? *(Source #: 10, 12, 13, 14, 20, 26)*

No Impact. The project site is located at the Yerba Buena Pump Station in Upper Silver Creek Linear Park adjacent to Upper Silver Creek. The dechlorination units would be located near the existing pump facilities outside of the 100-year flood zone for the creek. The project site is not within an inundation zone of a levee or dam.

k. Inundation by seiche, tsunami, or mudflow? (*Source #: 10, 12, 13, 14, 20, 26)*

No Impact. The project site is not located in area that is subject to inundation by seiche, tsunami, or mudflow.

	Potentially Significant Impact	**Less Than Significant with Mitigation Incorporation**	**Less Than Significant Impact**	**No Impact**
3.9. LAND USE AND PLANNING -- Would the project:				
a) Physically divide an established community?	9	9	9	±
b) Conflict with any applicable land use plan, policy, or regulation of an agency with jurisdiction over the project (including, but not limited to the general plan, specific plan, local coastal program, or zoning ordinance) adopted for the purpose of avoiding or mitigating an environmental effect?	9	9	9	±
c) Conflict with any applicable habitat conservation plan or natural community conservation plan?	9	9	9	±

ENVIRONMENTAL SETTING:

The project would release dechlorinated recycled water from the Yerba Buena Pump Station into Upper Silver Creek. The Pump Station is located in Silver Creek Linear Park in the City of San Jose. Upper Silver Creek and a recreational trail pass across the entrance driveway from Yerba Buena Road to the Pump Station. The area immediately north and west of the project site is urbanized. Lower density residential development, the Ranch Golf Course, and Silver Creek Valley Country Club occur to the south and east of the project site.

Several public agencies have regulatory authority over the release of recycled water into Upper Silver Creek. The Regional Water Quality Control Board (RWQCB) is responsible for protecting the quality of state waters and their beneficial uses. The California Department of Fish and Game (CDFG) is responsible for protecting fish, wildlife, and plant resources in streams, rivers and lakes. Both CDFG and US Fish and Wildlife Service (USFWS) are responsible for protecting special status plant and wildlife species that may occur in project impact zone. Likewise, NOAA reviews impacts to protected fisheries as a trustee agency.

Regional Water Quality Control Board, Basin Plan. The San Francisco Bay Basin Plan identifies cold freshwater habitat, fish migration, fish spawning, and warm freshwater habitat as existing beneficial uses for Coyote Creek. The Basin Plan does not identify beneficial uses for Upper Silver Creek. The Basin Plan regulates the water quality of discharges to the bay for the purpose of protecting the beneficial uses through the National Pollutant Discharge Elimination System (NPDES) program. The Basin Plan does not identify beneficial uses for Upper Silver Creek.

California Department of Fish and Game.

Fish and Game Code, Section 1602.

The Department of Fish and Game is responsible for conserving, protecting, and managing California's fish, wildlife, and native plant resources. Fish and Game Code section 1602 requires any person, state or local governmental agency, or public utility to notify the Department before beginning any activity that will do one or more of the following: 1) substantially obstruct or divert the natural flow of a river, stream, or lake; 2) substantially change or use any material from the bed, channel, or bank of a river, stream, or lake; or 3) deposit or dispose of debris, waste, or other material containing crumbled, flaked, or ground pavement where it can pass into a river, stream, or lake. Fish and Game Code section 1602 applies to all perennial, intermittent, and ephemeral rivers, streams, and lakes in the state. (Source: http://www.dfg.ca.gov/1600/qa.html).

The proposed project would augment the natural stream flow of Upper Silver Creek and Coyote Creek likely requiring a 1602 Streambed Alteration Agreement. The Streambed Alteration Agreement would be a means for CDFG to review the project and ensure no adverse impacts to the stream channel or to sensitive species would occur.

California Endangered Species Act

CDFG also has oversight over the project through the California Endangered Species Act of 1984 which provides for the recognition and protection of rare, threatened, and endangered species of plants and animals. The Act requires state agencies to consult with the CDFG to ensure that state-authorized or funded actions do not jeopardize the continued existence of a listed species. CDFG may authorize the taking of a listed species through a Memorandum of Understanding that establishes the extent of take permitted by CDFG and establishes required mitigation measures.

In addition to the Streambed Alteration Agreement, CDFG would also review the project in relation to its impact on listed species and determine whether a Memorandum of Understanding is required. The special status species that could potentially be present within Upper Silver Creek and/or Coyote Creek, and therefore potentially impacted by this project are: 1) California Tiger Salamander (CTS); 2) California Red-legged frog (CRLF); 3) Western Pond Turtle (WPT); and 4) Steelhead. See Biology discussion in Section 4.0.

City of San Jose, General Plan. The Stream Flow Augmentation Project would release treated tertiary water into Upper Silver Creek from the South Bay Water Recycling (SBWR) Yerba Buena Pump Station located in San Jose. SBWR is run by a division of the City of San Jose. The San Jose 2020 General Plan specifies that creeks and natural riparian corridors should be preserved whenever possible. Habitat areas that support Species of Concern should be retained to the greatest extent feasible. The General Plan also states that City should protect groundwater recharge areas, particularly creeks and riparian corridors, and promote the use of reclaimed water when feasible, for irrigation and in groundwater recharge areas. The City of San Jose does not have regulatory authority over the proposed Stream Flow Augmentation Project.

US Fish and Wildlife Service, Federal Endangered Species Act. The federal ESA prohibits the take of endangered or threatened wildlife species. "Take" is defined as harassing, harming (includes significantly modifying or degrading habitat), pursing hunting, shooting, wounding, killing, trapping, capturing, or collecting wildlife species or any attempt to engage in such conduct. Actions that result in take can result in civil or criminal penalties. The federal ESA would be triggered by the proposed project if it results in the take of threatened or endangered species. The California red-legged frog, California tiger salamander, and steelhead are federal Threatened Species. The potential for impact to these species is described in Biology.

DISCUSSION:

Will the proposed project:

a. **Physically divide an established community?** *(Source #: 10, 12, 13, 14, 20)*

No Impact. The project is to augment stream flows in Upper Silver Creek and Coyote Creek with tertiary recycled water. Dechlorination equipment and pipelines would be installed at an existing recycled water Pump Station facility. The project would not result in changes to the existing adjacent land uses. The project will not divide an established community.

b. **Conflict with any applicable land use plan, policy, or regulation of an agency with jurisdiction over the project (including, but not limited to the general plan, specific plan, local coastal program, or zoning ordinance) adopted for the purpose of avoiding or mitigating an environmental effect?** *(Source #: 1, 2, 11, 12, 13, 18, 20, 26)*

No Impact. The project has been designed in consultation with the California Department of Fish and Game and the Regional Water Quality Control Board as the two public agencies that regulate the stream resources potentially affected by the project. The land use plans and policies relevant to the project are described in the environmental setting above. The project is consistent with the policies of the RWQCB Basin Plan by avoiding the elevation of receiving waters temperatures to a harmful level (see Responses to Hydrology above). The project will avoid potential impacts to federal and state special status species (see Responses to Biology above) and is therefore consistent with the federal Endangered Species Act and California Endangered Species Act. The project is also consistent with the San Jose General Plan by protecting the natural resources within the riparian corridor of Upper Silver Creek and promoting the use of recycled water.

c. **Conflict with any applicable habitat conservation plan or natural community conservation plan?** *(Source #: 14, 21)*

No impact. The project site is not located in a habitat conservation plan or natural community conservation plan area.

	Potentially Significant Impact	**Less Than Significant with Mitigation Incorporation**	**Less Than Significant Impact**	**No Impact**
3.10. MINERAL RESOURCES -- Would the project:				
a) Result in the loss of availability of a known mineral resource that would be of value to the region and the residents of the state?	9	9	9	±
b) Result in the loss of availability of a locally-important mineral resource recovery site delineated on a local general plan, specific plan or other land use plan?	9	9	9	±

ENVIRONMENTAL SETTING:

Mineral resources found and extracted in Santa Clara County include construction aggregate deposits such as sand, gravel, and crushed stone. The San Jose General Plan does not identify any significant mineral resource area along the Upper Silver Creek or Coyote Creek corridors.

DISCUSSION:

Will the proposed project:

a. **Result in the loss of availability of a known mineral resource that would be of value to the region and the residents of the state?** *(Source #: 12, 13, 14, 20, 26)*

No Impact. Construction of the project will not result in the loss of availability of known mineral resources of regional or local importance. No locally important mineral resources are designated in the vicinity of the Yerba Buena Pump Station according to the San Jose General Plan. The installation of equipment at the Pump Station and the release of recycled water into Upper Silver Creek would not result in the loss of mineral resources which are of regional or state-wide importance.

b. **Result in the loss of availability of a locally important mineral resource recovery site delineated on a local general plan, specific plan or other land use plan?** *(Source #: 12, 13, 14, 20, 26)*

No Impact. No locally important mineral resources are designated at this site in the San Jose General Plan. The installation of equipment at the Pump Station and the release of recycled water into Upper Silver Creek would not result in the loss of locally important mineral resources.

	Potentially Significant Impact	**Less Than Significant with Mitigation Incorporation**	**Less Than Significant Impact**	**No Impact**
3.11. NOISE -- Would the project result in:				
a) Exposure of persons to or generation of noise levels in excess of standards established in the local general plan or noise ordinance, or applicable standards of other agencies?	9	9	9	±
b) Exposure of persons to or generation of excessive groundborne vibration or groundborne noise levels?	9	9	9	±
c) A substantial permanent increase in ambient noise levels in the project vicinity above levels existing without the project?	9	9	9	±
d) A substantial temporary or periodic increase in ambient noise levels in the project vicinity above levels existing without the project?	9	9	±	9
e) For a project located within an airport land use plan or, where such a plan has not been adopted, within two miles of a public airport or public use airport, would the project expose people residing or working in the project area to excessive noise levels?	9	9	9	±
f) For a project within the vicinity of a private airstrip, would the project expose people residing or working in the project area to excessive noise levels?	9	9	9	±

ENVIRONMENTAL SETTING:

The major noise source at the Pump Station vicinity is the intermittent vehicle traffic on Yerba Buena Road. Much of the land surrounding the Pump Station project site is recreational which does not generate significant noise levels. Noise is generally defined as unwanted sound. Sound levels are usually measured and reported in decibels (dB), a unit that describes the amplitude, or extent, of the air pressure changes which produce sound. City of San Jose noise guidelines for residential areas and public parks are more restrictive than for industrial areas. An exterior noise level of 60 dBA Ldn is acceptable for parks and playgrounds whereas 70 dBA Ldn is acceptable for industrial areas. Acceptable noise levels for the project site reflect the recreational use of Silver Creek Linear Park.

DISCUSSION:

Will the proposed project:

a. **Exposure of persons to or generation of noise levels in excess of standards established in the local general plan or noise ordinance, or applicable standards of other agencies?** *(Source #: 10, 12, 13, 14, 20)*

No Impact. Short-term construction noise would be generated during minor grading and equipment installation at the Yerba Buena Pump Station. The nearest sensitive receptors are the occasional users of the recreational path in front of the Pump Station entrance driveway and the residences located off Yerba Buena Road north of the Pump Station. The nearest residences are 300 feet away. The use of equipment at the site would result in a temporary increase in noise levels. The construction period is expected to last one month. The equipment noise would occur during a small part of this time; it would be intermittent and occur during business hours.

In operation, the equipment is enclosed and powered by electric motors. The project would not generate or expose people to a permanent increase in noise levels or to noise levels in excess of standards. Therefore, the project would not result in significant adverse noise impacts.

b. **Exposure of persons to or generation of excessive ground borne vibration or ground borne noise levels?** *(Source #: 10, 12, 13, 14, 20)*

No Impact. There are no sources of ground vibration, such as may occur from railroad lines or blasting activity along the stream flow augmentation corridor.

c. **A substantial permanent increase in ambient noise levels in the project vicinity above levels existing without the project?** *(Source #: 12, 13, 14, 20)*

No Impact. Once equipment installation at the Pump Station is completed, the project would not affect ambient noise levels.

d. **A substantial temporary or periodic increase in ambient noise levels in the project vicinity above levels existing without the project?** *(Source #: 12, 13, 14, 20)*

Less than Significant Impact. The project will not create a substantial permanent or periodic increase in ambient noise levels. Installation of the dechlorination equipment and recycled water pipelines would result in short-term, localized increases in ambient noise levels from equipment used during grading. Noise levels generated by construction equipment are typically rated below 70 dBA at a distance of 300 feet.

e. **For a project located within an airport land use plan or, where such a plan has not been adopted, within two miles of a public airport or public use airport, would the project expose people residing or working in the project area to excessive noise levels?** *(Source #: 10, 12, 13, 14, 20)*

No Impact. The nearest airport to the project site is the Reid Hillview Airport located 2.5 miles to the north. The Pump Station and project stream flow corridor is outside of the airport safety zone and overflight area of airport traffic. The project would not expose people to excessive noise levels associated with the Reid Hillview Airport.

f. **For a project within the vicinity of a private airstrip, would the project expose people residing or working in the project area to excessive noise levels?** *(Source #: 10, 12, 13, 14, 20)*

No Impact. The proposed project is not within the vicinity of a private airstrip and would not expose people to excessive noise levels from private airstrips.

	Potentially Significant Impact	Less Than Significant with Mitigation Incorporation	Less Than Significant Impact	No Impact
3.12. POPULATION AND HOUSING -- Would the project:				
a) Induce substantial population growth in an area, either directly (for example, by proposing new homes and businesses) or indirectly (for example, through extension of roads or other infrastructure)?	9	9	9	±
b) Displace substantial numbers of existing housing, necessitating the construction of replacement housing elsewhere?	9	9	9	±
c) Displace substantial numbers of people, necessitating the construction of replacement housing elsewhere?	9	9	9	±

DISCUSSION:

Will the proposed project:

a. **Induce substantial population growth in an area, either directly (for example, by proposing new homes and businesses) or indirectly (for example, through extension of roads or other infrastructure)?** *(Source #: 10, 12, 14, 20)*

No Impact. The project would not affect population projections, housing supply, or induce substantial growth in the area. The project would not induce population growth in the community.

b. **Displace substantial numbers of existing housing, necessitating the construction of replacement housing elsewhere?** *(Source #: 10, 12, 14, 20)*

No Impact. The project involves equipment installation at an existing Pump Station facility and augmenting stream flows in Upper Silver Creek and Coyote Creek with tertiary recycled water. Development of the project would not displace any existing housing.

c. **Displace substantial numbers of existing people, necessitating the construction of replacement housing elsewhere?** *(Source #: 10, 12, 14, 20)*

No Impact. The stream flow augmentation project is located at an existing Pump Station facility located in a county park. There is no housing affected by the project.

	Potentially Significant Impact	Less Than Significant with Mitigation Incorporation	Less Than Significant Impact	No Impact
3.13. PUBLIC SERVICES --				
a) Would the project result in substantial adverse physical impacts associated with the provision of new or physically altered governmental facilities, need for new or physically altered governmental facilities, the construction of which could cause significant environmental impacts, in order to maintain acceptable service ratios, response times or other performance objectives for any of the public services:				
Fire protection?	9	9	9	±
Police protection?	9	9	9	±
Schools?	9	9	9	±
Parks?	9	9	9	±
Other public facilities?	9	9	9	±

DISCUSSION:

Will the proposed project:

a. **Would the project result in substantial adverse physical impacts associated with the provision of new or physically altered governmental facilities, need for new or physically altered governmental facilities, the construction of which could cause significant environmental impacts, in order to maintain acceptable service ratios, response times or other performance objectives for any of the public services:**

1. **Fire protection?** *(Source # 12, 14, 20)*

No Impact. The proposed project involves the installation of dechlorination equipment and pipelines at the Yerba Buena Pump Station and the release of recycled water into the storm drain that releases to Upper Silver Creek. The project would not increase the need for fire protection services or create an adverse impact on fire protection services.

2. Police protection? *(Source # 12, 14, 20)*

No Impact. The proposed equipment installation at the Pump Station and the release of recycled water into Upper Silver Creek would not increase the need for police protection services or create an adverse impact on police protection services.

3. Schools? *(Source # 12, 14, 20)*

No Impact. The proposed equipment installation at the Pump Station and the release of recycled water into Upper Silver Creek would not result in increased number of students served by local schools.

4. Parks? *(Source # 12, 14, 20)*

No Impact. The proposed equipment installation at the Pump Station and the release of recycled water into Upper Silver Creek would not result in an increased number of residents in the area using community parks.

5. Other public facilities? *(Source # 12, 14, 20)*

No Impact. No other public facilities would be adversely affected by the proposed project.

	Potentially Significant Impact	Less Than Significant with Mitigation Incorporation	Less Than Significant Impact	No Impact
3.14. RECREATION --				
a) Would the project increase the use of existing neighborhood and regional parks or other recreational facilities such that substantial physical deterioration of the facility would occur or be accelerated?	9	9	9	±
b) Does the project include recreational facilities or require the construction or expansion of recreational facilities which might have an adverse physical effect on the environment?	9	9	9	±

DISCUSSION:

Will the proposed project:

a. **Would the project increase the use of existing neighborhood and regional parks or other recreational facilities such that substantial physical deterioration of the facility would occur or be accelerated?** *(Source #: 10, 12, 14, 20)*

No Impact. The project would not increase the visitor use of Silver Creek Linear Park, or nearby community parks in San Jose, or generate demand for recreational facilities. The project would not affect existing recreational opportunities or affect access to existing recreation areas.

b. **Does the project include recreational facilities or require the construction or expansion of recreational facilities which might have an adverse physical effect on the environment?** *(Source #: 10, 12, 14, 20)*

No Impact. The project would not adversely affect recreational opportunities. The project would not increase the use of existing recreational facilities or expand a recreational facility.

	Potentially Significant Impact	Less Than Significant with Mitigation Incorporation	Less Than Significant Impact	No Impact
3.15. TRANSPORTATION/TRAFFIC -- Would the project:				
a) Cause an increase in traffic which is substantial in relation to the existing traffic load and capacity of the street system (i.e., result in a substantial increase in either the number of vehicle trips, the volume to capacity ratio on roads, or congestion at intersections)?	9	9	9	±
b) Exceed, either individually or cumulatively, a level of service standard established by the county congestion management agency for designated roads or highways?	9	9	9	±
c) Result in a change in air traffic patterns, including either an increase in traffic levels or a change in location that results in substantial safety risks?	9	9	9	±
d) Substantially increase hazards due to a design feature (e.g., sharp curves or dangerous intersections) or incompatible uses (e.g., farm equipment)?	9	9	9	±
e) Result in inadequate emergency access?	9	9	9	±
f) Result in inadequate parking capacity?	9	9	9	±
g) Conflict with adopted policies, plans, or programs supporting alternative transportation (e.g., bus turnouts, bicycle racks)?	9	9	9	±

DISCUSSION:

Will the proposed project:

a. **Cause an increase in traffic which is substantial in relation to the existing traffic load and capacity of the street system (i.e., result in a substantial increase in either the number of vehicle trips, the volume to capacity ratio on roads, or congestion at intersections)?** *(Source #: 12, 14, 20)*

No Impact. The project site is located at the Yerba Buena Pump Station which is surrounded by a county park. The proposed equipment installation at the Pump Station and the release of recycled water into Upper Silver Creek would not have an adverse impact upon existing transportation systems or generate an increase in traffic on local roads.

b. **Exceed, either individually or cumulatively, a level of service standard established by the county congestion management agency for designated roads or highways?** *(Source #: 12, 14, 20)*

No Impact. The project is the installation of dechlorination equipment at the Pump Station and the release of recycled water into Upper Silver Creek. The project would not generate any new vehicle traffic. No level of service standards for roads or highways would be exceeded, either individually or cumulatively, as a result of this project.

c. **Result in a change in air traffic patterns, including either an increase in traffic levels or a change in location that results in substantial safety risks?** *(Source #: 10, 12, 14, 20)*

No Impact. The project will not affect air traffic patterns.

d. **Substantially increase hazards due to a design feature (e.g., sharp curves or dangerous intersections) or incompatible uses (e.g., farm equipment)?** (*Source #: 10, 12, 14, 20, 26)*

No Impact. The proposed stream flow augmentation project would not create transportation safety hazards from design features. Neither public nor private roads are affected by the project.

e. **Result in inadequate emergency access?** *(Source #: 11, 12, 14, 20, 26)*

No Impact. The proposed stream flow augmentation project construction would not impact existing emergency access to nearby uses.

f. **Result in inadequate parking capacity?** *(Source #: 11, 12, 14, 20, 26)*

No Impact. The proposed stream flow augmentation project would not affect parking.

g. **Conflict with adopted policies, plans, or programs supporting alternative transportation (e.g., bus turnouts, bicycle racks)?** *(Source #: 11, 12, 14, 20, 26)*

No Impact. The proposed stream flow augmentation project would not affect alternative transportation policies or programs.

	Potentially Significant Impact	**Less Than Significant with Mitigation Incorporation**	**Less Than Significant Impact**	**No Impact**
3.16. UTILITIES AND SERVICE SYSTEMS -- Would the project:				
a) Exceed wastewater treatment requirements of the applicable Regional Water Quality Control Board?	9	9	±	9
b) Require or result in the construction of new water or wastewater treatment facilities or expansion of existing facilities, the construction of which could cause significant environmental effects?	9	9	±	9
c) Require or result in the construction of new storm water drainage facilities or expansion of existing facilities, the construction of which could cause significant environmental effects?	9	9	9	±
d) Have sufficient water supplies available to serve the project from existing entitlements and resources, or are new or expanded entitlements needed?	9	9	±	9
e) Result in a determination by the wastewater treatment provider which serves or may serve the project that it has adequate capacity to serve the project's projected demand in addition to the provider's existing commitments?	9	9	9	±
f) Be served by a landfill with sufficient permitted capacity to accommodate the project's solid waste disposal needs?	9	9	9	±
g) Comply with federal, state, and local statutes and regulations related to solid waste?	9	9	9	±

DISCUSSION:

Will the proposed project:

a. **Exceed wastewater treatment requirements of the applicable Regional Water Quality Control Board?** *(Source #: 11, 14, 20, 26)*

Less than Significant Impact. The project is the augmentation of stream flow in Upper Silver Creek/Coyote Creek corridor by the release of recycled water from the SJ/SC Water

Pollution Control Plant. The recycled water used for release has been treated in accordance with RWQCB standards as described in Land Use (see above). The water quality impacts of the project are identified in Hydrology. The project would not create a new source of wastewater.

b. Require or result in the construction of new water or wastewater treatment facilities or expansion of existing facilities, the construction of which could cause significant environmental effects? *(Source #: 11, 14, 20, 26)*

Less than Significant Impact. The project requires that the recycled water be dechlorinated prior to release to Upper Silver Creek. A dechlorination unit will be installed at the Pump Station as described in Project Description (Section 2.0). The ground disturbance impacts associated with equipment installation are minor. The potential impacts of releasing recycled water into Upper Silver Creek are evaluated in Biology and Hydrology responses above.

c. Require or result in the construction of new storm water drainage facilities or expansion of existing facilities, the construction of which could cause significant environmental effects? *(Source #: 11, 14, 20, 26)*

No Impact. The recycled water would be released into an existing storm drain line that flows into Upper Silver Creek. The site of the equipment installation is not environmentally sensitive. The ground disturbance associated with grading a pad for the dechlorinator is minor. There are no significant environmental effects associated with construction of the proposed facilities.

d. Have sufficient water supplies available to serve the project from existing entitlements and resources, or are new or expanded entitlements needed? *(Source #: 14, 20, 26)*

Less than Significant Impact. The South Bay Water Recycling (SBWR) system consists of over 100 miles of pipe serving the cities of Milpitas, Santa Clara and San José. During the summer months, an average of 10.9 million gallons of recycled water are produced and distributed to over 500 customers per day. The proposed project would use roughly 0.6 million gallons per day – about 5% of the total. The treatment plant and pipelines have the capacity to serve this demand without diminishing availability to other established recycled water users.

e. Result in a determination by the wastewater treatment provider which serves or may serve the project that it has adequate capacity to serve the project's projected demand in addition to the provider's existing commitments? *(Source #: 14, 20, 26)*

No Impact. The proposed stream flow augmentation project will not generate new volumes of wastewater requiring treatment service. The capacity of the local wastewater treatment plant serving the local community is not affected by the proposed project.

f. Be served by a landfill with sufficient permitted capacity to accommodate the project's solid waste disposal needs? *(Source #: 14, 20, 26)*

No Impact. There is no solid waste generated by the proposed project. The project will not affect the capacity of the landfill that serves the local community.

g. Comply with federal, state, and local statutes and regulations related to solid waste? *(Source #: 14, 20, 26)*

No Impact. There is no solid waste generated by the proposed project. The project is not affected by federal, state and local regulations related to solid waste.

	Potentially Significant Impact	**Less Than Significant with Mitigation Incorporation**	**Less Than Significant Impact**	**No Impact**
3.17. MANDATORY FINDINGS OF SIGNIFICANCE --				
a) Does the project have the potential to degrade the quality of the environment, substantially reduce the habitat of a fish or wildlife species, cause a fish or wildlife population to drop below self-sustaining levels, threaten to eliminate a plant or animal community, reduce the number or restrict the range of a rare or endangered plant or animal or eliminate important examples of the major periods of California history or prehistory?	9	±	9	9
b) Does the project have impacts that are individually limited, but cumulatively considerable? (“Cumulatively considerable” means that the incremental effects of a project are considerable when viewed in connection with the effects of past projects, the effects of other current projects, and the effects of probable future projects)?	9	9	9	±
c) Does the project have environmental effects which will cause substantial adverse effects on human beings, either directly or indirectly?	9	9	9	±

DISCUSSION:

a. **Does the project have the potential to degrade the quality of the environment, substantially reduce the habitat of a fish or wildlife species, cause a fish or wildlife population to drop below self-sustaining levels, threaten to eliminate a plant or animal community, reduce the number or restrict the range of a rare or endangered plant or animal or eliminate important examples of the major periods of California history or prehistory?**

Less than Significant with Project Design. The project has the potential to degrade the water quality of the Upper Silver Creek and Coyote Creek reaches and thus impair sensitive biological resources associated with the creek corridor. The project has been designed to minimize potential adverse impacts by restricting the release of recycled water to minimal flows, conducting the project during the summer months when creek temperatures are normally elevated and when biological resources are less impacted by increased temperatures. Monitoring temperature levels will ensure that the project does not exceed safe temperature thresholds for warm water ecosystems. The project would not reduce the number or restrict the range of rare or endangered plant or animal species. The project does not have the potential to eliminate important examples of the major periods of California history or prehistory.

Mitigation Incorporated in Project: Measure WQ-3 Surface Water Temperature Protection described in Section 2.5 will provide effective response to observed potential for impact.

b. Does the project have impacts that are individually limited, but cumulatively considerable? ("Cumulatively considerable" means that the incremental effects of a project are considerable when viewed in connection with the effects of past projects, the effects of other current projects, and the effects of probable future projects)?

No Impact. The proposed project does not involve increased impacts to the environment which are cumulatively considerable. The effect of other actions affecting Upper Silver Creek and Coyote Creek are accounted for in the baseline study of existing conditions and the biotic survey. No other projects are known that would affect these creek reaches during the proposed project time frame.

c. Does the project have environmental effects which will cause substantial adverse effects on human beings, either directly or indirectly?

No Impact. The project would not have environmental effects that will cause substantial adverse effects on humans, either directly or indirectly.

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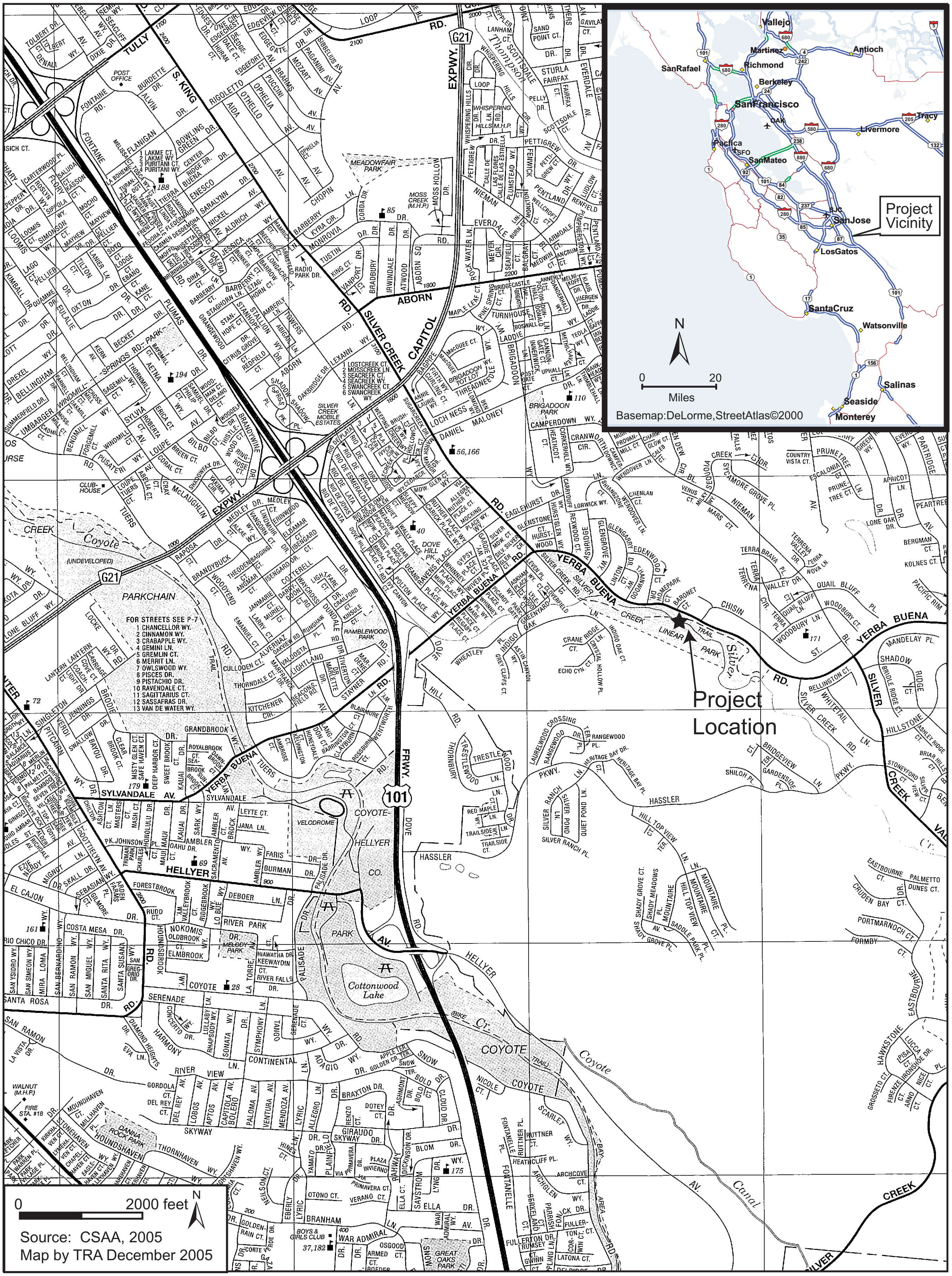
5.0 MAPS AND FIGURES

Figure 1. Project Location



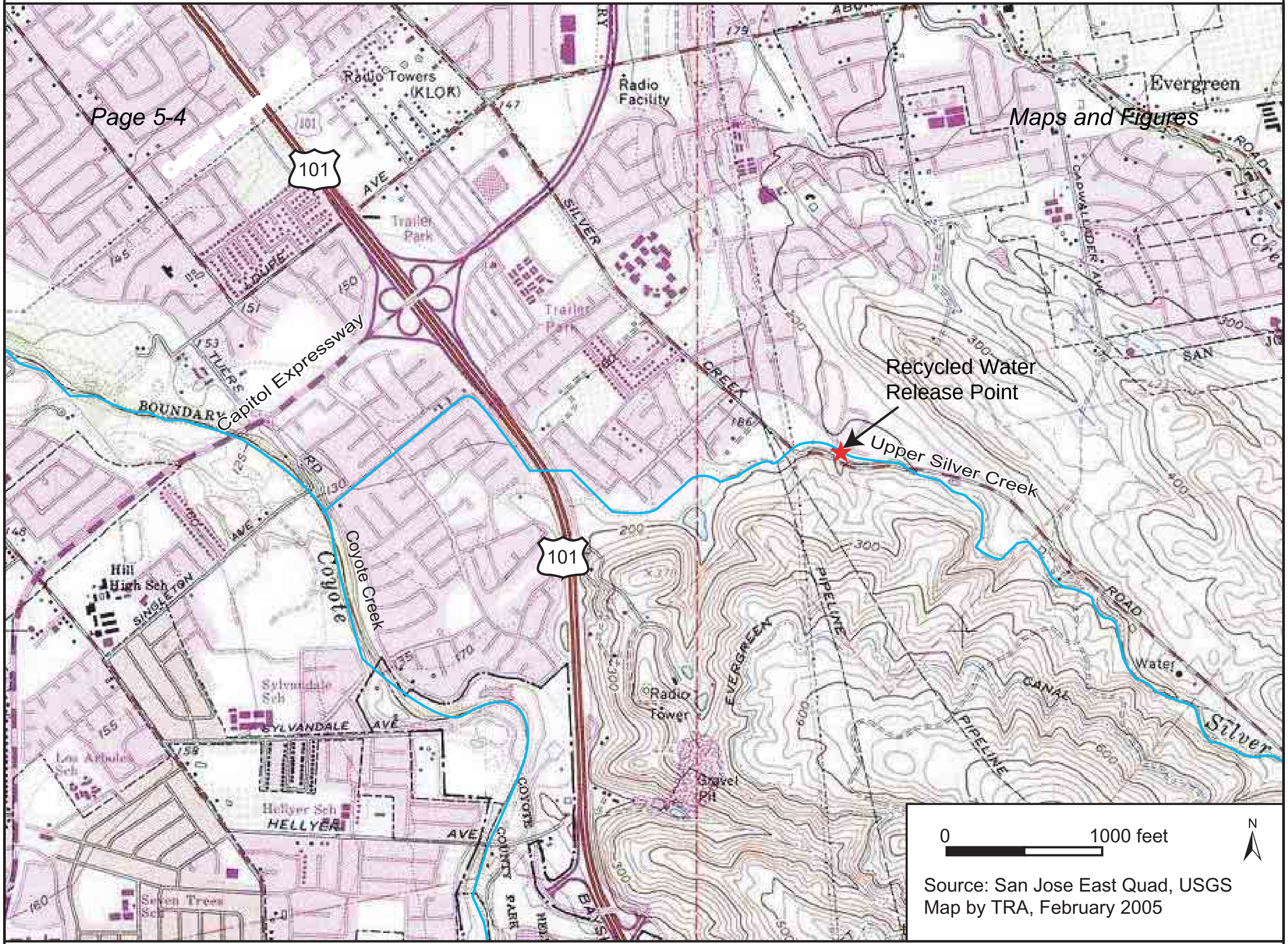
Basemap:DeLorme,StreetAtlas©2000

Source: CSAA, 2005
Map by TRA December 2005

Figure 2. Vicinity Aerial Photograph

Source: Western Mapping Center (WMC), 1998
Map by TRA December 2005

Figure 3. USGS Topographic Map



Source: San Jose East Quad, USGS
Map by TRA, February 2005

Figure 4. Project Facilities Schematic

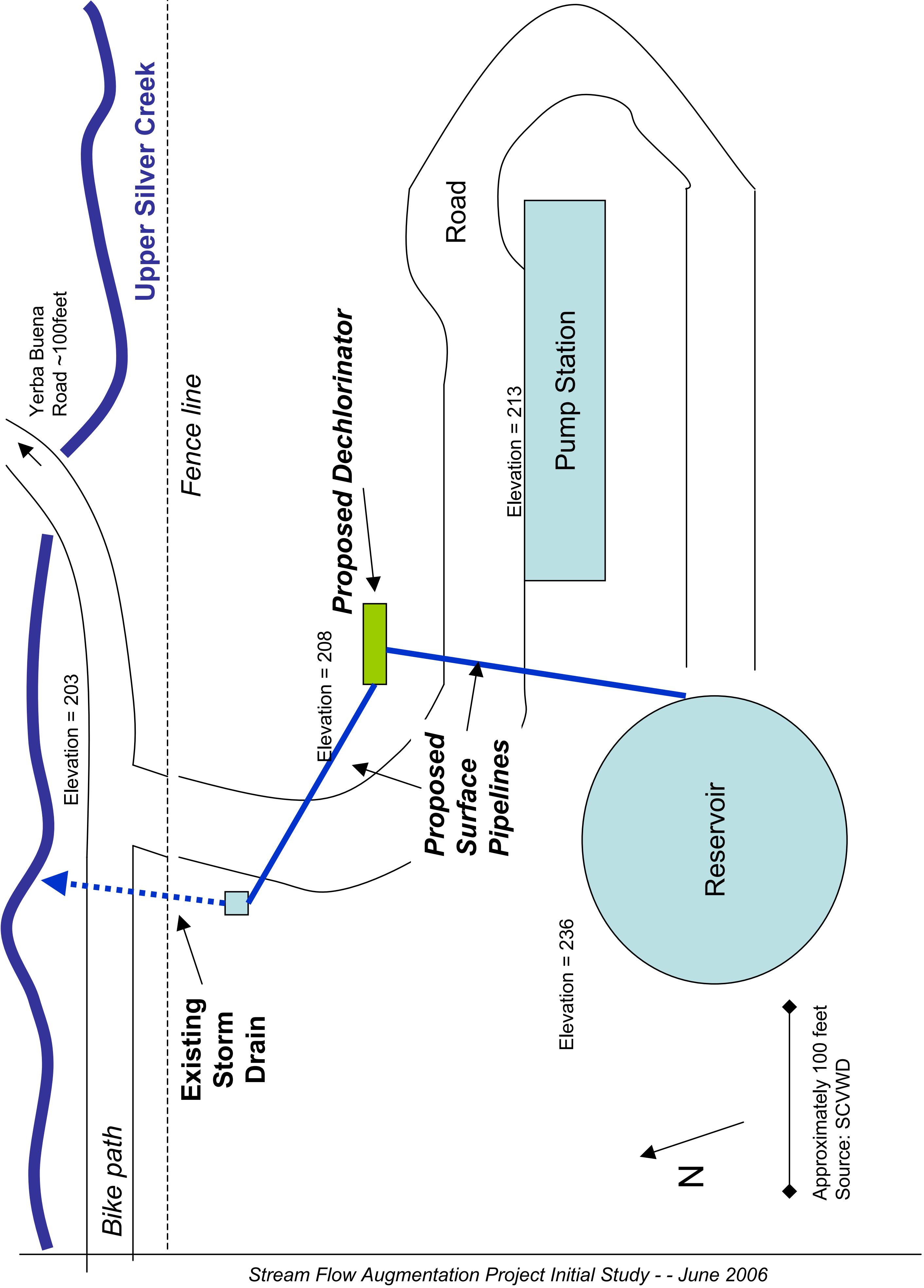


Figure 5. Water Quality Sampling Sites

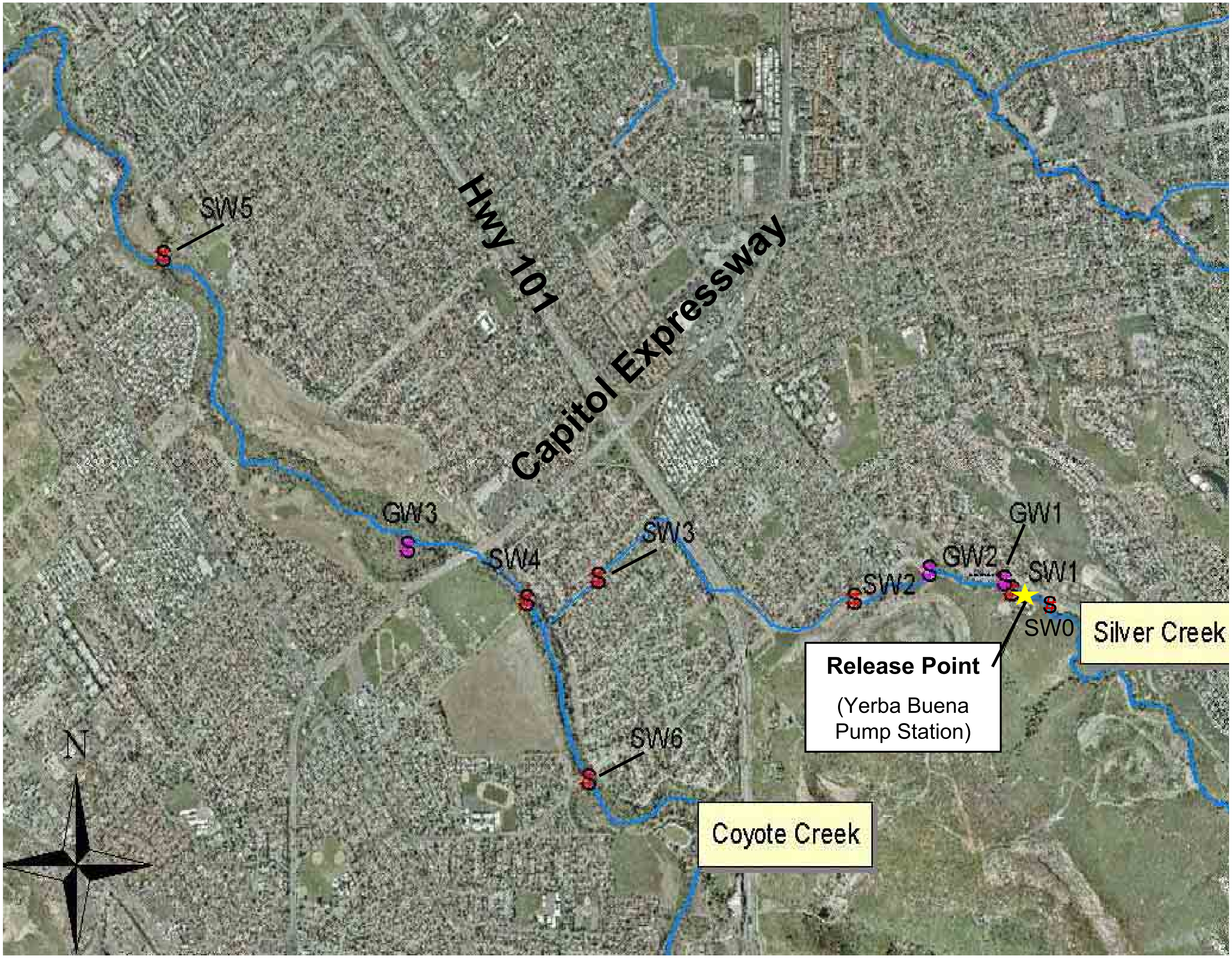
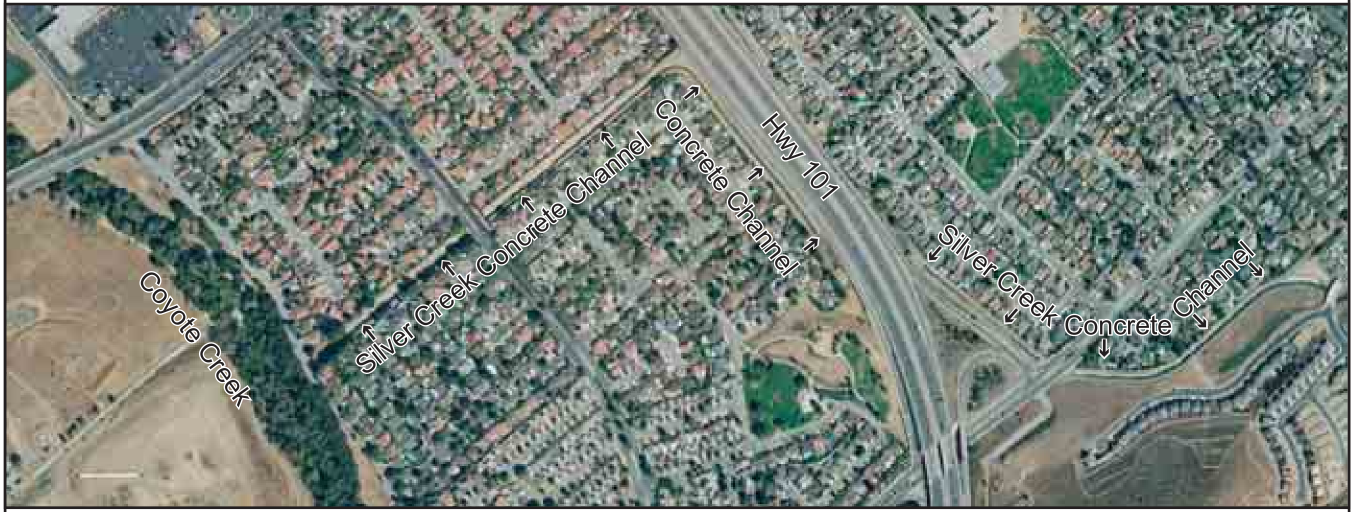


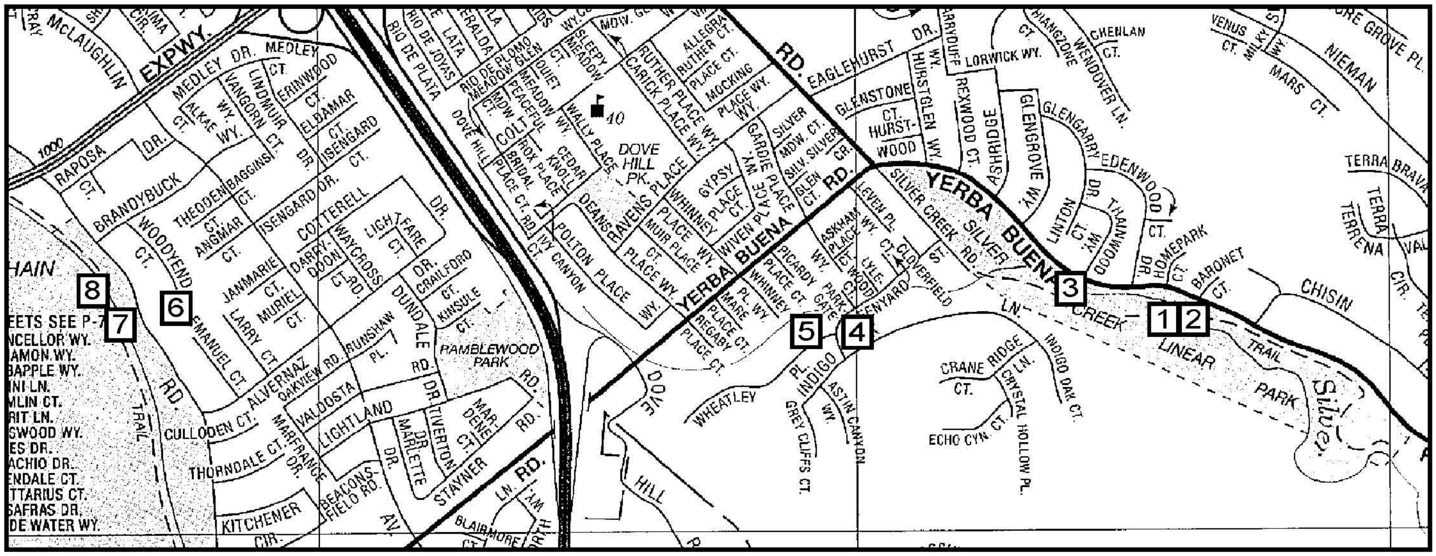
Figure 6. Upper Silver Creek Characteristics



The lower reach of Upper Silver Creek from Greenyard Street to Coyote Creek is an open concrete drainage channel. The ditch is surrounded by residential development. There is no vegetation on the banks or adjacent to the channel to provide canopy cover.

The riparian corridor along this segment of Upper Silver Creek is evidenced by the tree line. Creek Channel is lined with cattails near Greenyard Bridge.

Figure 7. Project Site and Stream Corridor Photographs



Map of photograph locations. Number on map corresponds to photos below.

Photo 1a – Yerba Buena Pump Station. Concrete storm drain inlet is visible to the right of the entrance driveway.

Photo 1b – Storm drain flows beneath foot trail and discharges to Upper Silver Creek. Trail and trees line creek corridor.

Photo 2a – Upper Silver Creek at Yerba Buena storm drain outfall. Proposed location of recycled water release.

Photo 2b – Upper Silver Creek bank opposite from Yerba Buena storm drain outfall.

Photo 3 – Upper Silver Creek downstream of recycled water release point.

Photo 4 – Upper Silver Creek drainage looking upstream from Greenyard Street overcrossing.

Photo 5a – Upper Silver Creek looking downstream from Greenyard Street overcrossing where channel becomes concrete.

Photo 5b – Upper Silver Creek looking upstream at the Greenyard Street Overcrossing.

Photo 6 – Upper Silver Creek is channelized through a residential area. It enters a culvert at Tures Road which outfalls to Coyote Creek.

Photo 7 – Outfall of Upper Silver Creek at its confluence with Coyote Creek.

Photo 8a – Coyote Creek downstream of confluence with Upper Silver Creek. Photo looks upstream from low vehicle crossing.

Photo 8b – Coyote Creek looking downstream from low vehicle crossing.

APPENDIX A
RESULTS OF THE 2005 BASELINE STUDY FOR COYOTE CREEK STREAM AUGMENTATION PROJECT
Stanford University, Dr. Martin Reinhard Research Group
December 15, 2005

Technical Memo

Date: 12/15/05

To: Alice Ringer, Project Manager, Santa Clara Valley Water District

From: Stanford University, Dr. Martin Reinhard Research Group

RE: Results of the 2005 Baseline Study for Coyote Creek Stream Augmentation Project

Introduction

This technical memorandum presents the results of the 2005 baseline analysis of Coyote and Silver Creek waters (surface and ground water) and recycled waters from the San Jose/Santa Clara Water Pollution Control Plant (SJ/SC WPCP) for the Coyote Creek Stream Flow Augmentation Project.

The results presented here meet the goals set out in Task 3 of the project workplan[1], which are stated as follows:

> Task 3 Baseline Data Collection and Analysis
>
> *Sub Tasks:*
>
> Characterization of SJ/SC WPCP Effluent
>
> SJ/SC WPCP effluent will be the water used to augment Coyote Creek stream flow. For Task B3, a detailed characterization of contaminants in the effluent will be conducted. The effluent will be screened for the target compounds listed in Table 4. Based on the findings of the characterization (presence or absence of trace contaminants) the suite of compounds to be analyzed during the study will be selected. A previous study in 2001 and 2002 showed the absence of target hormones and pharmaceuticals in SJ/SC WPCP effluent water. These findings will have to be verified for the timeframe of this study.
>
> Baseline Analysis of Water Quality at Coyote Creek Sampling Locations
>
> To characterize the baseline conditions in Coyote Creek with no stream flow augmentation, water samples taken at the sampling locations will be analyzed for the target analytes (discussed below in Section 2 of this Work Plan). Sampling frequency is explained below.
>
> Baseline Analysis of Potentially impacted Groundwater Quality
>
> Prior to augmentation, water quality in the shallow aquifer potentially connected hydrologically to the Coyote Creek study reach will be characterized to determine baseline concentrations of the selected analytes.
>
> Deliverable: Technical memorandum reporting on baseline data collection and analysis.

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[1] Workplan: Impact Evaluation of Stream Flow Augmentation with Tertiary Recycled Water in Coyote Creek, August 2004. Submitted to The Metropolitan Water District of Southern California, Agreement No. 41808, Santa Clara Valley Water District.

Sampling Locations, Analytes, and Schedule

The waters sampled for the baseline study include recycled water from the SJ/SC WPCP, surface water from Silver and Coyote creek, and groundwater from a well near Coyote Creek (further groundwater sampling is expected to occur in early 2006 after the construction of two additional wells near Silver Creek). Because the planned site of recycled water discharge has been modified since the drafting of the original project workplan[1], the chosen well and surface water locations differ from those described in the workplan. 2006 recycled water discharge will occur at Silver Creek, a tributary to Coyote Creek, near the Yerba Buena Recycled Water Pump Station. The sampling sites along Silver and Coyote creek will allow the monitoring of contaminant levels in both creeks following augmentation. Table 1 gives the names and descriptions of the sampling sites, and Figure 2 shows a map of the surface water sites and groundwater wells.

Table 1. Project sampling sites and descriptions.

SURFACE WATER SAMPLING POINTS:	
Site Name	**Description**
SW1	1) Discharge point at Yerba Buena Pump Station
SW2	2) Silver Creek upstream of concrete channel
SW3	3) Silver Creek downstream of concrete Channel
SW4	4) East bank of Coyote Creek near Singleton after Silver Creek confluence
SW5	5) Stonegate on Coyote
SW6	6) Coyote Creek control-- Yerba Buena Bridge upstream of confluence.
GROUNDWATER WELLS:	
Site Name	**Description**
GW1	1) Near discharge point at Yerba Buena Pump Station
GW2	2) Downstream on Silver at Silver Creek Line Park
GW3	3) After confluence at Coyote Creek
RECYCLED WATER:	
Site Name	**Description**
RW1	1) Recycled water from SJ/SC WPCP at Yerba Buena Pump Station

Figure 1. Map of Silver and Coyote Creeks with surface and groundwater sites. Creeks flow north.

The trace organic contaminants monitored as part of the baseline study are shown in Table 2. In addition to samples taken and analyzed for trace organic contaminants and dissolved organic carbon (DOC) by Stanford University, field measurements were taken of water quality parameters including pH, dissolved oxygen (DO), and conductivity. Further water quality parameters were monitored by the Santa Clara Valley Water District (SCVWD) laboratories, including cations and anions, metals, trihalomethanes (THMs), haloacetic acids (HAAs), and select herbicides and pesticides (data not presented here).

Generally, water samples were collected at each site (surface water sites 1-6, groundwater well 3, and recycled water) at least three times, spaced approximately five weeks apart, in summer and fall of 2005 for each analyte. Table 3 shows the sampling events and dates for the trace organic contaminants monitored by Stanford. Exceptions to the general schedule are the infrequency of the groundwater samplings for all analytes (since well construction was behind schedule) and the two (instead of three) surface water sampling events for perfluorochemicals (PFCs) (since the analyte group was added to the project late in the baseline study).

Table 2. Trace organic contaminants monitored by Stanford University in the recycled, surface, and ground water as part of the baseline study.

Pharmaceuticals	Organophophates (fire retardants)	Disinfection Byproduct
Acetaminophen	Tris(3-chloropropyl)phosphate	N-Nitrosodimethylamine (NDMA)
Caffeine	Tris(2,3-dichloropropyl)phosphate	
Carbamazepine		Perfluorochemicals (PFCs)
Carisoprodol	Plasticizers	PFBS
Gemfibrozil	Bisphenol A	PFHxS
Ibuprofen	N-butyl benzenesulfonamide	PFOS
Iminostilbene		PFDS
Ketoprofen	Herbicide	6:2 FtS
Naproxen	Oxadiazon	PFHpA
Primidone		PFOA
Propanolol	APEOs[1] & APEMs[2]	PFNA
	APEOs	PFDA
Hormones	Alkylphenols (nonyl-, octyl-)	FOSA
Estradiol	A+CAPECs[3]	EtFOSAA
Estriol	Halog. APEMs[4]	
Estrone		
Ethynylestradiol		
[1] Alkylphenol polyethoxylates (AP1EO, AP2EO, AP3EO)		
[2] Alkylphenol polyethoxylate metabolites		
[3] Sum of alkylphenol ethoxycarboxylates and carboxyalkylphenol ethoxycarboxylates (both metabolites of APEOs).		
[4] Sum of halogenated (chlorine or bromine) alkylphenols, APEOs, and A+CAPECs		

Table 3. Complete list of sampling events for trace organic contaminants in the recycled, surface, and ground waters.

Perfluorochemicals

Recycled Water	Surface Water	Ground Water
Jul-05	Oct-05	Oct-05 (GW3)
Aug-05	Nov-05	Future sampling planned
Oct-05		
Nov-05		

NDMA

Recycled Water	Surface Water	Ground Water
Jul-05 (Montse)	Aug-05	Aug-05
Aug-05	Oct-05	Oct-05
Oct-05	Nov-05	Future sampling planned
Nov-05		

Other trace contaminants: Pharmaceuticals, hormones, organophosphates, plasticizers, oxadiazon, APEMs

Recycled Water	Surface Water	Ground Water
May-05	May-05	Jul-05 (GW3)
Jul-05	Jul-05	Aug-05 (GW3)
Aug-05	Aug-05	Future sampling planned

Sample Collection and Analysis Methods

Pharmaceuticals, Hormones, Organophosphates, Plasticizers, Oxadiazon, and APEMs (analyzed together)

1.0 Sample Collection

For recycled, surface, and ground water, three to four liters were collected in 1 L amber glass bottles (rinsed three times with sample water) and packed on ice in coolers. To recycled water, 1 mL of a sodium thiosulfate solution was added to quench chlorination.

2.0 Sample Preparation

Following return to the Stanford laboratory later the same day of collection, samples were stored at 4°C. For analysis, liters obtained from the same site were mixed to promote homogeneity and were filtered using 0.2 μm nylon filters and adjusted to pH 2.3. A blank of Milli-Q purified water was also prepared. As described in the project workplan but modified here to reflect method changes, C-18 cartridges with 1.0 g sorbent (Alltech, IL, USA, extract-clean columns, 8 mL) for the May analysis, C-18 with 2.0 g sorbent for the July analysis, and phenyl cartridges with 1.0 g sorbent (Phenomenex Strata End-Capped, 6 mL) for the August analysis were used to extract the target contaminants from 1 L samples by solid phase extraction (SPE). Each site was analyzed in replicate. SPE was performed using a 16-port vacuum extraction manifold. Cartridges were conditioned sequentially with 6 mL acetone, 6 mL acetonitrile, and 10 mL Milli-Q water (pH 2). The samples were then loaded through the cartridges by applying a vacuum at a flow rate of 10 mL/min or less. The cartridges were then washed with Milli-Q water and dried under vacuum. Analytes were eluted with 5 mL acetonitrile followed by 5 mL acetone. The extract was concentrated by evaporation on a sand block at 30-40ºC to 30-50 μL and divided into three fractions. To one fraction, 10 μL of a 20 mg/L internal standard solution (chrysene-d_{12}) was added for neutral compounds analysis (some APEMs, some pharmaceuticals, oxadiazon, NBBS, BPA, and organophosphates). The second aliquot was used to analyze for acidic compounds (carboxylated APEMs, some pharmaceuticals). In this aliquot, carboxylic acids were converted into their respective propyl esters by adding 10 μL of 90/10 (v/v) *n*-propanol/acetylchloride to the evaporated samples and heating for 1 hour at 85ºC. After propylation, the samples were evaporated to near dryness and 10 μL of the chrysene-d_{12} internal standard solution was added. The third fraction (for hormones, BPA, and some pharmaceuticals) was similarly derivatized but by silylation using 10 μl of MTBSTFA and heated for 3 hours at 95ºC, followed by internal standard addition. In the August analysis, the silylation fraction was not prepared due to method problems, but the analytes normally measured using this fraction were instead monitored in the neutral or propylation fraction (i.e., not the optimal fraction but detection possible nevertheless). Two exceptions were acetaminophen and propanolol, pharmaceuticals which are only detectable using the silylation preparation; thus these two analytes were not measured in the recycled, surface, and ground waters in August 2005 of the baseline study.

3.0 Quantitation

As described in the project workplan but with differences noted here, quantitation was performed by gas chromatography-mass spectrometry (GC-MS) by sample injection onto an Agilent 6890N GC with a 5973 MSD. A DB-5 capillary column (30 m x 0.32 mm I.D., film thickness 0.25 μm; Agilent, Wilmington, DE, USA) or an equivalent column was employed using helium as the carrier gas.

All analytes in the neutral and propylated fractions were monitored in the total ion current (TIC) mode (mass range m/z = 50 – 550; scan time 0.5 s) and quantified using their base ions. Compounds in the silylated fraction were monitored using single-ion monitoring (SIM) mode of their base ions. Since APs, APEOs, APECs, and CAPECs occur as complex mixtures, the different isomers are manually differentiated with respect to the number of ethoxy groups and the length of their alkyl-chain (i.e., octyl or nonyl). APECs and CAPECs, which produce many of the same mass spectral fragments, are generally reported as the sum of the APECs and CAPECs (denoted as A+CAPECs). Because no commercial standards were available for tris(3-chloropropyl)phosphate or some of the pharmaceuticals including iminostilbene, these compounds were tentatively identified in the samples by comparing the spectral characteristics of the sample peak with spectral characteristics in the NIST (National Institute of Standards and Technology) mass spectral library.

Concentrations of the individual compounds were determined *semi-quantitatively* by comparing the base ion with the m/z 240 ion of the internal standard, chrysene-d_{12}. Thus, all reported concentrations are based on the assumption that the response factors for the internal standard and the analyte are the same. Exceptions were the compounds caffeine, carisoprodol, NBBS, octylphenol, and tris(2,3-dichloropropyl)phosphate, for which the response factors between chrysene-d_{12} and the compounds were determined in one calibration from 2005. Hence, these concentrations are quantitatively reported. Detection limits for the analytes, if known, are noted below with each set of results.

N-Nitrosodimethylamine (NDMA)

1.0 Sample Collection

For recycled, surface, and ground water, three to four liters were collected in 1 L amber glass bottles (rinsed three times with sample water) and packed on ice in coolers. For the August analysis, the same water samples were analyzed simultaneously for both NDMA and the group of analytes pharmaceuticals, APEMs, etc. described previously.

2.0 Sample Preparation

Following return to the Stanford laboratory later the same day of collection, samples were stored at 4°C. For analysis, liters obtained from the same site were mixed to promote homogeneity and were filtered using 0.2 or 0.45 μm nylon filters. A blank of MilliQ purified water was also prepared.

NDMA was extracted from 500mL or 1L of sample water (each site analyzed in replicate) by solid phase extraction (SPE) with a 16-port vacuum extraction manifold using reservoirs packed with activated charcoal (method under development at Stanford)[2]. Activated charcoal was washed with MilliQ water at the same pH as the sample, dried overnight at 110ºC, and 1.0 g was packed into empty 8 mL SPE reservoirs fitted with a frit and filter at the base. The sorbent was wetted with MilliQ water before loading the water sample under vacuum at a flow rate less than 5 mL/min. After loading the water sample, the bottles were rinsed three times with MilliQ which served to wash the charcoal. The cartridges were drained except for a small amount of water left behind, which was eluted into 15 mL glass collection vials. NDMA was eluted from the charcoal using 2 mL acetonitrile (two times), 2 mL methanol (two times), and 2 mL acetone (two times). The extract was evaporated on a sand bath at 37ºC leaving 1-2 mL of solvent-free water. 0.3 mL of 110 ppb internal standard, NDMA-d6, was added to 1.0 mL of extract and stored at 4ºC until analysis.

For the August sample preparation, SPE for NDMA was run in series with SPE for the pharmaceuticals, APEMs, etc., by placing the activated charcoal cartridge in series with the phenyl cartridge. Thus the same water samples were loaded through both. Therefore in this case, the water samples analyzed for NDMA had been acidified to pH 2.3 in keeping with the method used for pharmaceuticals, APEMs, etc.

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[2] Lopez Mesas, M., Plumlee, M. H., Reinhard, M. Method Development for the Extraction of Creek and Wastewater Samples, *to be submitted for publication.*

For instrumental analysis, the concentrated extracts following elution had to be returned to a pH of 5 – 9 by adding a small amount of concentrated NaOH.

3.0 Quantitation

NDMA was quantified using liquid chromatography-tandem mass spectrometry (LC-MS/MS) by injecting 50 μL at a flow rate of 0.15 ml/min onto a liquid chromatograph from Shimadzu LC-10AD *VP* with a Shimadzu SIL-10AD *VP* autosampler (Columbia, MD) equipped with a triple quadrupole mass spectrometer from Applied Biosystems API3000 (Foster City, CA). The current instrument detection limit is 1 ppb and instrument reporting limit is 2 ppb NDMA, from which the method detection limit (assuming full recovery) is 4 ng/L for 500 mL of loaded water sample.

Perfluorochemicals (PFCs)

1.0 Sample Collection

Water samples of recycled, surface, and ground waters were collected (60 to 250 mL) in polypropylene bottles, after rinsing bottles three times with the sample water, and packed on ice in coolers until returned to the Stanford laboratory.

2.0 Sample Preparation

Each water sample was prepared for replicate analysis. Sample preparation involved the addition of a sample aliquot to a methanol-containing microcentrifuge tube, centrifugation, and transfer of the mixture to a vial containing a 70:30 (v/v) mixture of methanol and 0.01% aqueous ammonium hydroxide[3]. An internal standard solution containing ^{13}C-labelled PFCs was added for quantitation.

3.0 Quantitation

PFCs were quantified using liquid chromatography-tandem mass spectrometry (LC-MS/MS) by large-volume injection[4] of 490 μL onto a liquid chromatograph from Shimadzu LC-10AD *VP* with a Shimadzu SIL-10AD *VP* autosampler (Columbia, MD) equipped with a triple quadrupole mass spectrometer from Applied Biosystems API3000 (Foster City, CA). Calibration standards containing each of the 10-11 PFCs analyzed in the study were carefully matched in solution makeup to the sample preparation method, to minimize matrix effects and to achieve a linear calibration curve[3].

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[3] Higgins, C.P.; Field, J.A.; Criddle, C.S.; Luthy, R.G. Quantitative Determination of Perfluorochemicals in Sediments and Domestic Sludge. *Environ. Sci. Technol*. **39**(11), 3946-3956.

[4] Schultz, M. M., Barofsky, D. F., Field, J. A. 2005. Quantitative Determination of Fluorinated Alkyl Substances by Large-Volume-Injection Liquid Chromatography Tandem Mass Spectrometry – Characterization of Municipal Wastewaters. *Environ. Sci. Technol*, submitted for publication 2005.

Analytical Results

Presented below are the *detections* determined for each analyte or analyte group in all sample waters (recycled, surface, and ground waters) and sites. Following these brief summaries is a larger table (Table 14) in the section "Data Summary" featuring the array of results for all waters and sites and reporting both the detections and the non-detects.

Pharmaceuticals

Most of the pharmaceuticals included in the project analyte list (Table 2) were not detected in much of the baseline 2005 study. Tables 4 and 5 show the detections of two pharmaceuticals, carisoprodol and iminostilbene, in the recycled water and caffeine in the creek water. Carisoprodol and iminostilbene were both detected in July and August, but not in May for the recycled water. In a previous investigation (not required as part of project workplan) these same two pharmaceuticals were identified in the SJ/SC WPCP secondary effluent in June 2005. No other pharmaceuticals were detected in the recycled water. Note that all measurements only reflect the particular day and time sampled; pharmaceutical concentrations emitted in wastewater effluents are quite variable even over a single day.

Caffeine was detected at three creek sites, spanning both Silver and Coyote Creeks, but only in July. Caffeine has been demonstrated for use as a marker for wastewater contamination of surface waters[5]. No pharmaceuticals were detected in the groundwater (well 3, sampled in July and August) or other surface sites for the other sampling events. The detection limits noted in the tables were determined from a statistical analysis of a calibration curve.

Table 4. Detection of two pharmaceuticals in Yerba Buena Pump Station recycled water in both July and August 2005. The detection limit of iminostilbene is not known as a standard was not available.

Recycled Water 2005	July	August	DL*
Carisoprodol (ng/L)	217	195	60
Iminostilbene (ng/L)	98	96	--
Carisoprodol: muscle relaxant, blocks pain			
Iminostilbene: intermediate in synthesis of analgesics and antipsychotic agents			

*DL: detection limit

Table 5. Detection of caffeine in three sites along Silver and Coyote Creek in July of 2005.

Surface Water July 2005	SW 3 (Silver)	SW 4 (Coyote)	SW 5 (Coyote)	DL*
Caffeine (ng/L)	72	19	23	10
Caffeine: stimulant added to analgesics to enhance effect				

*DL: detection limit

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[5] Buerge, I. J., et al. Caffeine, an Anthropogenic Marker for Wastewater Contamination of Surface Waters. Environ. Sci. Technol. **2003**, *37*, 691-700.

Plasticizers: N-butyl benzenesulfonamide (NBBS) and Bisphenol-A (BPA)

NBBS, a plasticizer used in nylon production that is commonly found in US water bodies and is reportedly neurotoxic[6], was found in recycled, creek and ground waters throughout the baseline 2005 study (Figure 2). Creek concentrations were generally similar to recycled water concentrations, with the exception of May when the creek levels at sites 3, 4, 5, and 6 were higher than the recycled water. A detection limit of 7 ng/L was determined based upon the statistical analysis of a calibration curve. NBBS was tentatively identified in July SW5 and August GW3 but concentrations fell below the detection limit. Note that all measurements only reflect the particular day and time sampled; the groundwater, for instance, appears to be lower in NBBS concentration than the surface and recycled waters for the particular day and time sampled.

A single detection of BPA, 18 ng/L, was found in the July 2005 groundwater well 3 (GW3). BPA is a plasticizer used in polycarbonate plastic and epoxy resins and is considered estrogenic. The detection limit for this analyte has not been determined.

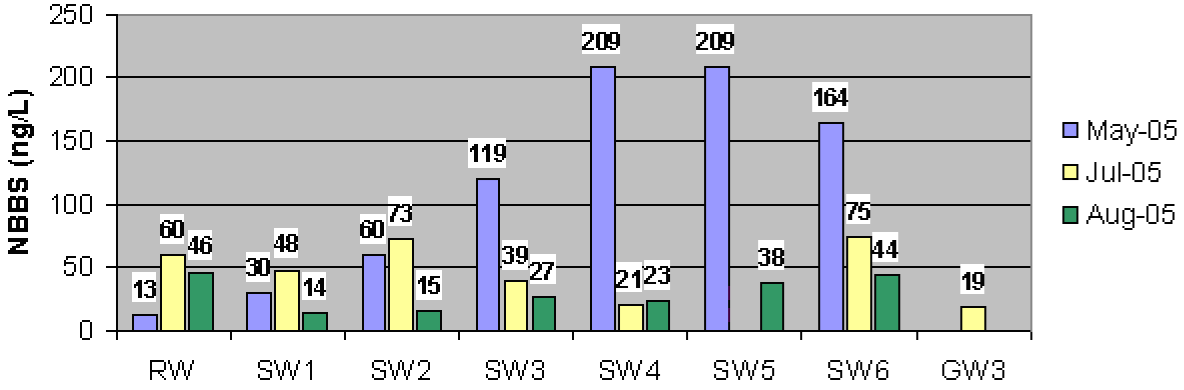

Figure 2. Concentrations of NBBS at all sites for the three sampling events (May, July, and August). Note that the groundwater well 3 was not sampled in May. Detection limit is 7 ng/L.

Organophosphates

Tris(3-chloropropyl)phosphate and tris(2,3-dichloropropyl)phosphate are organophosphates used as fire retardants. Both are on the EU priority list for carcinogenic suspicion. Figures 3 and 4 show the results for tris(3-chloropropyl)phosphate and tris(2,3-dichloropropyl)phosphate, respectively. Tris(3-chloropropyl)phosphate appears fairly consistently through most of the sampling sites and throughout May, July, and August, except for the May recycled water and May surface water sites 4, 5, and 6. Additionally, the compound does not appear in the groundwater in August (not measured in May). Note the log scale; concentrations are much higher in the recycled water than in the natural waters, and are also higher in the creek than in the groundwater. Tris(2,3-dichloropropyl)phosphate in Figure 4 appears more sporadically, with a concentration on the order of μg/L noted in May surface water site 1. Because a standard was available for tris(2,3-dichloropropyl)phosphate, a detection limit of 10 ng/L was determined based upon the statistical analysis of a calibration curve. For the groundwater July sample, tris(2,3-dichloropropyl)phosphate was detected but fell below the statistical detection limit for quantitative accuracy.

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[6] Duffield, P. et al, 1994

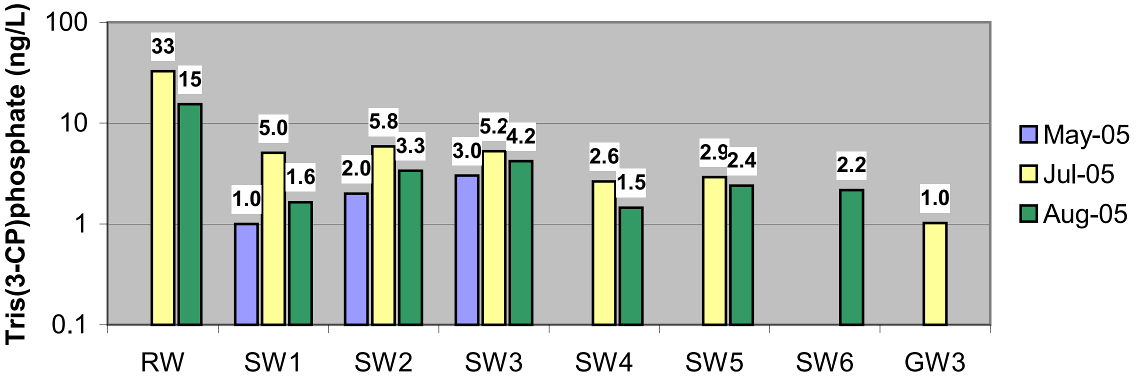

Figure 3. Tris(3-chloropropyl)phosphate concentrations for the baseline 2005 study. Detection limit unknown (no standard available).

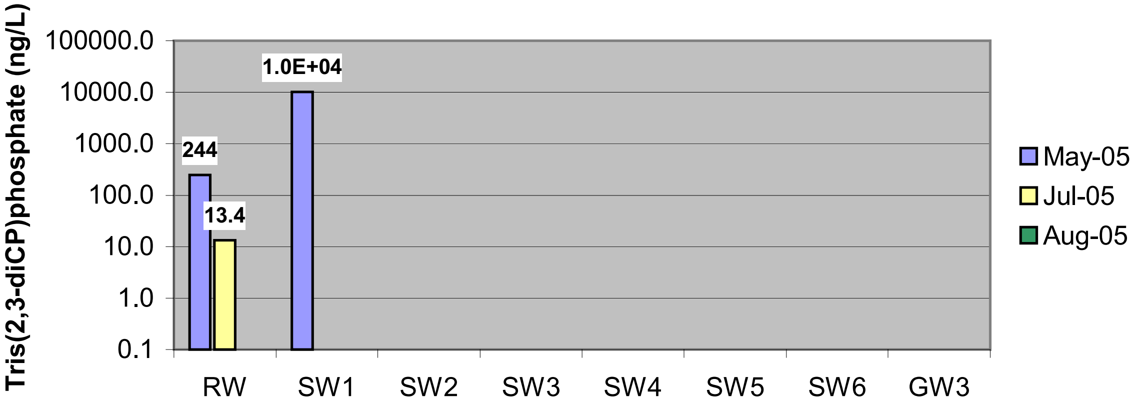

Figure 4. Tris(2,3-dichloropropyl)phosphate concentrations for the baseline 2005 study. Detection limit is 10 ng/L.

Oxadiazon

The herbicide oxadiazon was added to the project analyte list after its discovery in preliminary analyses of the Coyote Creek surface water. It was not found in the recycled or ground water, and was only found in the surface water during the 2005 baseline study in one month (July) at the three sites on Silver Creek, as shown in Table 6.

Table 6. Concentration of oxadiazon found at Silver Creek sites in July 2005 surface water. Detection limits have not been determined.

Surface Water July 2005	SW 1 (Silver)	SW 2 (Silver)	SW 3 (Silver)
Oxadiazon (ng/L)	12	12	3
Oxadiazon: herbicide applied in CA (600 pounds in Santa Clara County, 2003 (www.pesticideinfo.org)); developmental/reproductive toxin, suspected carcinogen			

APEMs: A+CAPECs and Halogenated APEMs

Figure 5 shows the results for summed metabolites of alkylphenol ethoxylates (APEMs), which are metabolites of nonionic surfactants. Of the large family of APEMs, carboxylated APEMs (A+CAPECs: alkyl- and carboxyalkyl ethoxycarboxylates) and halogenated APEMs were detected in the recycled water each time it was sampled. Halogenated APEMs are chlorinated and brominated forms of the APEMs produced during wastewater disinfection. Halogenated APEMs made up 10, 19, and 5% of the total APEMs for May, July, and August, respectively. Detection limits are largely unknown because pure standards are not available for most of these compounds; however the detection limit for individual APECs (and assumed to be the same for CAPECs) applied in this study is approximately 0.5 ng/L. No APEMs were detected in surface or ground waters.

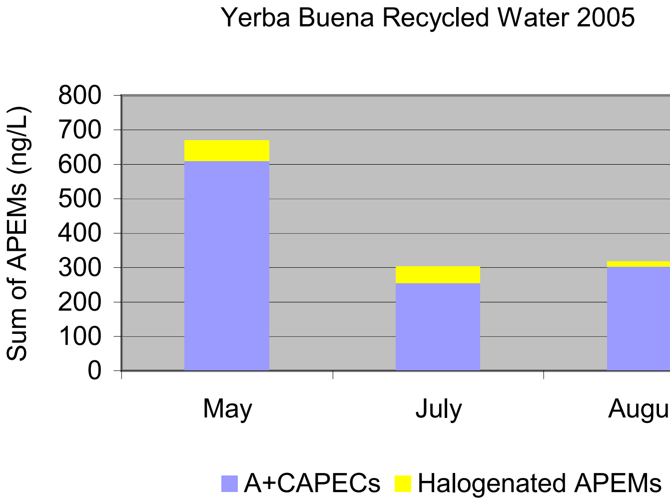

Figure 5. The sum of APEMs detected for the recycled water for the baseline 2005 study, which consisted entirely of A+CAPECs and halogenated APEMs.

N-Nitrosodimethylamine (NDMA)

NDMA was added to the project analyte list to expand the monitoring set and because it has recently received much attention, particularly in California. NDMA is a disinfection byproduct formed during chloramination of waters containing dimethylamines and is considered a "probable carcinogen." Other nitroso- compounds with differing alkyl amines are also likely carcinogens, including NDEA, NDBA, NDPA, and NMEA. As shown in Table 7, NDMA was only found in the recycled water (all sampling events) and not found in the surface or ground waters.

Table 7. Concentrations of NDMA for baseline 2005 study. Detection limit is 4 ng/L.

NDMA (ng/L)	RW	SW 1 (Silver)	SW 2 (Silver)	SW 3 (Silver)	SW 4 (Coyote)	SW 5 (Coyote)	SW 6 (Coyote)
June	51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
August	46	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
October	61	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
November	111	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

*DL: detection limit

Perfluorochemicals (PFCs)

Perfluorochemicals are a group of compounds which were added to the project analyte list, like NDMA, to expand the analyte set. They have hydrocarbon-based structures that are partially or fully fluorinated, and the parent compounds are used for many purposes such as textile and paper coatings, fire fighting foams, and fluoropolymer manufacturing. They can be found in products from the commonly used brands/products Teflon, Scotchguard, Gore-Tex, and Stainmaster. There are many persistent degradation products of which 10 were chosen for this project because of their frequent occurrence in wastewaters and/or relevance to other research.

Table 8 gives a summary of the results and shows the 10 compounds monitored (11 in the first sampling rounds, but PFBS was eliminated when it became undetectable after method improvements were made). Note that unlike the other analytes included in the study, the surface water was only surveyed during two events (instead of three) late in the study (October and November) because the analyte group was added to the project late and method optimization was necessary. The total PFCs gives a summation of all PFCs detected in each sample. The compounds were found in the recycled and surface waters, with higher concentrations (three to four times for the higher level PFCs) in the recycled water than in the surface water. The detection limits are shown and improved during the study sampling due to method development that took place at the same time.

Additionally, Table 8 shows a test of Teflon tubing compared to the groundwater well 3 October result. The groundwater was sampled with Teflon tubing, which is not recommended for perfluorochemical analysis but was carried out since perfluorochemicals were not considered during project planning. One to two months after sampling, the same Teflon tubing was obtained and rinsed with MQ water; one 60 mL sample in polypropylene was taken and analyzed for Perfluorochemicals in replicate. The results show that indeed some perfluorochemicals may originate from the tubing, including PFOS, PFOA, and PFNA. Of these, PFOS was detected in the groundwater (at approximately three times greater concentration). Additionally, PFHxS was detected in the groundwater and not in the tubing. PFOS should be considered a tentative groundwater identification since it was detected in the test of the Teflon tubing.

Table 8. Perfluorochemical concentrations (ng/L) for the baseline 2005 study, also showing the detection limits applicable to each sample set. Additionally, results for the groundwater sample and test of the Teflon tubing used to sample the groundwater are shown. Sample names include site and date.

Sample	Date Sampled	PFBS (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	PFDS (ng/L)	6:2 FtS (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	FOSA (ng/L)	EtFOSAA (ng/L)	**Total PFCs (ng/L)**
Detection Limit	n/a	42	1.0	2.1	2.1	4.2	1.0	1.0	1.0	1.0	1.0	2.1	
RW_0705	Aug-05	50	20	341	7.7	n.d.	13	103	15	4.6	2.1	30	587
RW_0805	Aug-05	44	8	258	6.1	5.3	12	113	14	4.5	1.7	21	488
Blank_1005	Oct-05	n.d.	n.d.	n.d.	n.d.	n.d.	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	2.0
RW_1005	Oct-05	n.d.	7.9	160	n.d.	n.d.	n.d.	67	12	3.8	2.2	14	266
SW1_1005	Oct-05	n.d.	9.5	77	n.d.	n.d.	n.d.	27	3.7	7.3	4.3	n.d.	129
SW2_1005	Oct-05	n.d.	9.2	57	4.2	n.d.	8.2	26	3.2	4.3	5.2	7.2	124
SW3_1005	Oct-05	n.d.	9.2	62	n.d.	n.d.	n.d.	28	3.8	4.6	4.5	n.d.	112
SW4_1005	Oct-05	n.d.	1.7	12	n.d.	n.d.	n.d.	4.4	10	n.d.	n.d.	n.d.	28
SW5_1005	Oct-05	n.d.	2.1	15	n.d.	n.d.	n.d.	5.6	n.d.	n.d.	n.d.	4.9	28
SW6_1005	Oct-05	n.d.	n.d.	4.2	n.d.	n.d.	8.0	n.d.	n.d.	n.d.	n.d.	n.d.	12
Detection Limit	n/a	n/a	1.0	1.0	1.0	4.2	1.0	0.4	0.4	0.4	0.2	1.0	
Blank_1105	Nov-05	n.m.	n.d.	n.d.	1.9	n.d.	n.d.	0.6	n.d.	n.d.	n.d.	1.7	4.2
RW_1105	Nov-05	n.m.	6.7	201	4.5	7.3	6.8	83	14	4.9	2.8	19	350
SW1_1105	Nov-05	n.m.	4.8	52	3.0	n.d.	4.3	19	2.4	5.1	2.4	2.5	95
SW2_1105	Nov-05	n.m.	4.5	50	3.9	n.d.	4.7	19	2.3	5.1	3.2	2.1	94
SW3_1105	Nov-05	n.m.	n.d.	67	5.1	n.d.	5.1	20	3.5	5.7	3.7	4.1	114
SW4_1105	Nov-05	n.m.	n.d.	7.3	n.d.	n.d.	n.d.	3.1	0.6	0.7	0.3	1.3	13
SW5_1105	Nov-05	n.m.	n.d.	7.2	2.7	n.d.	n.d.	3.1	1.1	0.8	0.6	3.2	19
SW6_1105	Nov-05	n.m.	n.d.	2.3	1.2	n.d.	n.d.	1.1	n.d.	n.d.	n.d.	1.4	5.9

Sample	Date Sampled	PFBS (ng/L)	PFHxS (ng/L)	PFOS (ng/L)	PFDS (ng/L)	6:2 FtS (ng/L)	PFHpA (ng/L)	PFOA (ng/L)	PFNA (ng/L)	PFDA (ng/L)	FOSA (ng/L)	EtFOSAA (ng/L)	**Total PFCs (ng/L)**
Detection Limit	n/a	42	1.0	2.1	2.1	4.2	1.0	1.0	1.0	1.0	1.0	2.1	
GW3_1005	Nov-05	n.d.	8.4	26	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	34
Teflon Test	Dec-05	n.m.	n.d.	8.4	n.d.	n.d.	n.d.	2.7	3.0	n.d.	n.d.	n.d.	14

The contribution of the different PFCs was calculated and is shown in Figures 6,7, and 8, perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA) largely make up the majority of the PFCs for both the surface and recycled water. Perfluorobutanesulfonate (PFBS) and 1H,1H,2H,2H-perfluorooctane sulfonate (6:2 FtS) appear in the recycled water but not in the surface water (note PFBS was not measured for November surface water). The pie charts represent an average of all measurements for the sites; levels of individual PFCs and distributions were quite consistent for both recycled and surface water.

Figure 9 shows the total PFCs plotted with distance along Silver and Coyote creeks for October and November. The results between the two months are consistent and show that Silver Creek, the first three points, has higher levels of PFCs than Coyote creek, the lower three points. The result for the upstream control of Coyote Creek (Site 6, river mile 1.0) confirms that Coyote Creek has lower levels of PFCs. Site 4 (river mile 1.7) is just downstream of the confluence of Silver and Coyote Creek, and shows the lower PFC levels that occur after mixing.

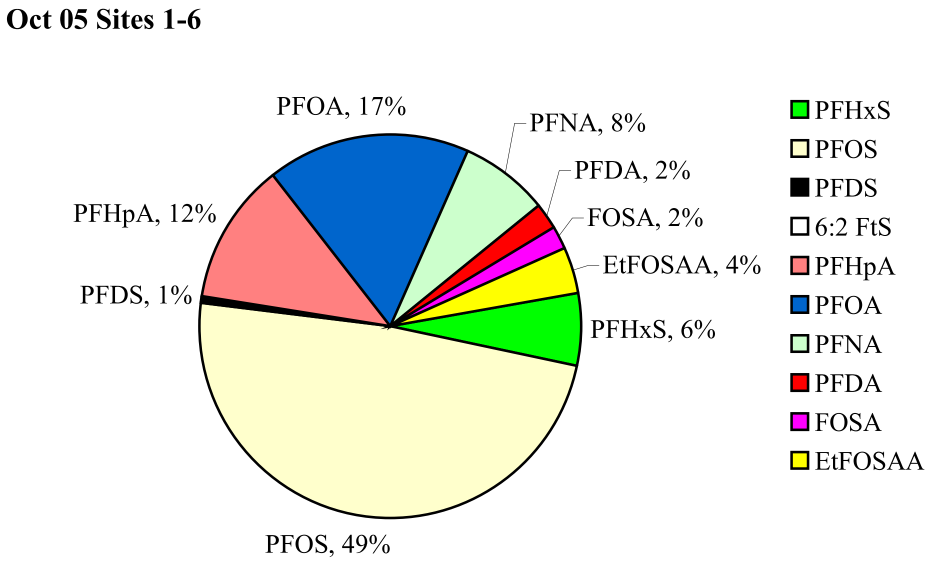

Figure 6. Percentage contributions of 11 PFCs for average of surface water sites 1-6 in October 2005.

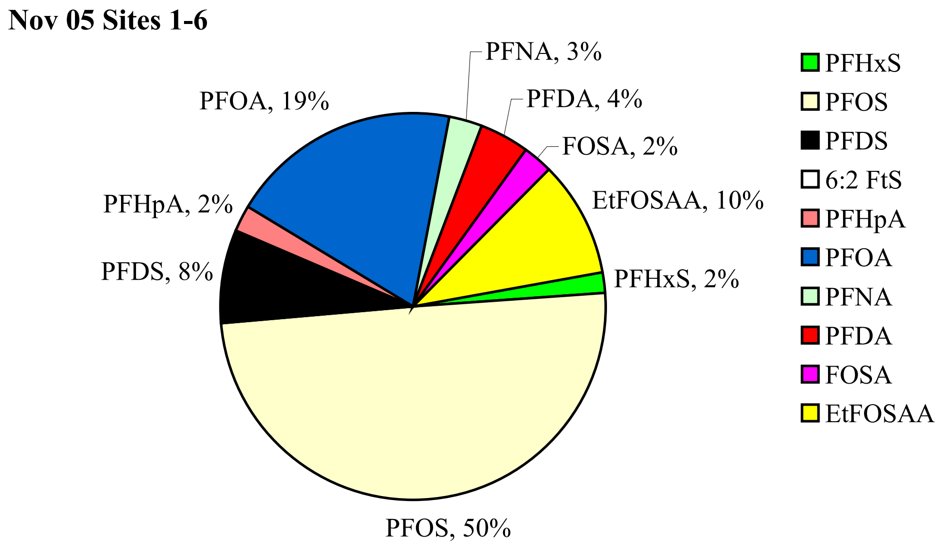

Figure 7. Percentage contributions of 10 PFCs for average of surface water sites 1-6 in November 2005.

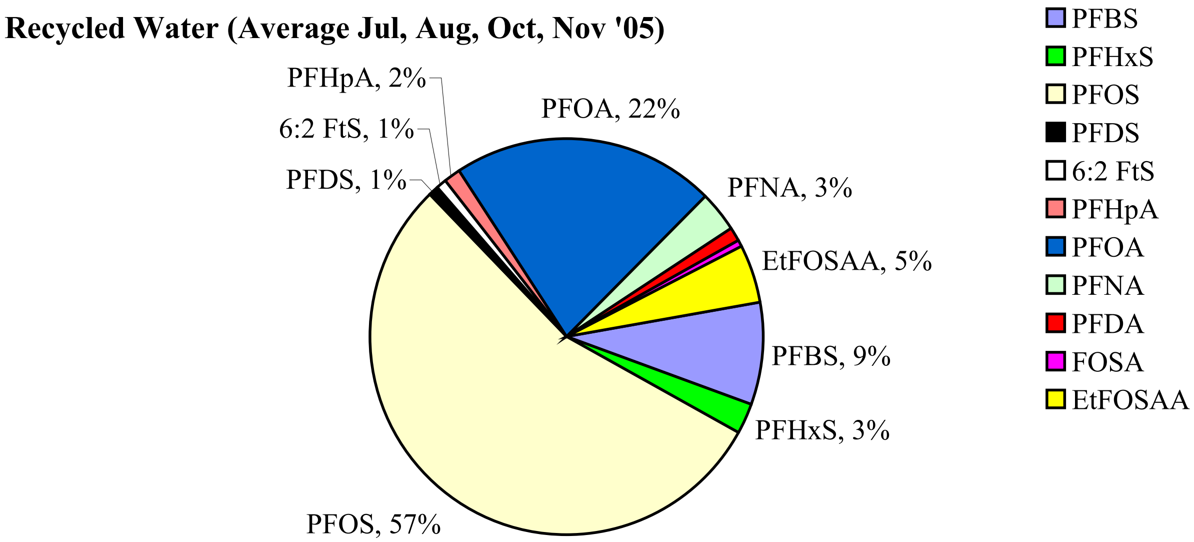

Figure 8. Percentage contributions of 10 PFCs for average of recycled water in July, August, October, November 2005.

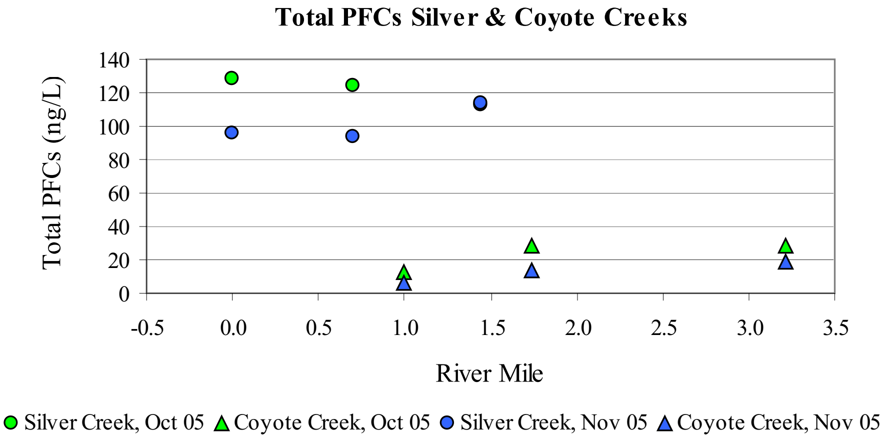

Figure 9. Total PFCs plotted with river mile along Silver and Coyote Creek. The green points indicate October results, the blue indicate November results.

General Water Quality

Dissolved Organic Carbon (DOC)

DOC measurements of the recycled, surface, and ground water were made within 28 days (usually less) of sample collection (250 mL glass bottles). Water samples were analyzed for DOC using a Shimadzu TOC analyzer. Samples were prepared by filtration using a 0.45 μm nylon membrane, in accordance with the definition of dissolved organic carbon. Specifically, non-purgeable organic carbon (NPOC) was measured, because the samples were acidified (to pH 2 using HCl) and purged of carbon dioxide before measurement. Standards were prepared with oven-dried potassium hydrogen phthalate (KHP) in MilliQ water, as per manufacturer's guidelines, and adjusted to pH 2 using HCl for preservation.

The measurements for each month and site, reported as the average of two replicate measurements, are given in Table 9. Between May and October, the DOC at each site was fairly consistent as shown by the average and standard deviations given at the right of the table and in Figure 10. The recycled water was generally 2-5 mg/L higher in DOC than surface water. The groundwater (not measured in May due to lack of well and in July due to oversight) was much lower in DOC than surface water, as expected. Figure 10 shows that the DOC concentration is typically higher in Silver Creek (first 3 sites) than in Coyote Creek.

Table 9. DOC values for the baseline 2005 study of recycled, surface, and groundwater. Each monthly value is an average of two replicate measurements.

Site	**Dissolved Organic Carbon (mg/L)**				**Average** (mg/L)	**Standard Deviation** (mg/L)
	May '05	July '05	Sep '05	Oct '05		
SW1	3.0	5.5	3.8	4.1	4.1	1.0
SW2	3.3	4.6	3.7	4.1	3.9	0.5
SW3	3.5	4.8	4.7	4.4	4.4	0.6
SW4	2.2	2.9	3.4	3.0	2.9	0.5
SW5	1.9	3.4	2.5	3.2	2.7	0.7
SW6	2.6	1.8	1.9	2.8	2.3	0.5
RW	n.m.	7.9	5.9	7.4	7.0	1.0
GW3	n.m.	n.m.	1.1	0.9	1.0	0.1

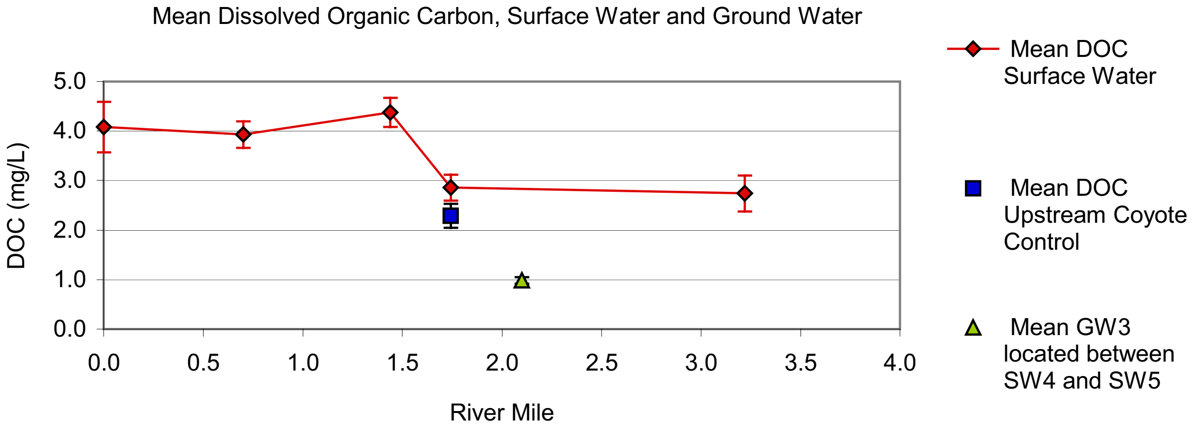

Figure 10. DOC for the baseline 2005 study plotted with river mile.

Recycled Water Chlorine Levels

Free chlorine and total chlorine were measured on-site of the recycled water during the May – August sample collection events (Table 10) using indicator strips according to the manufacturer's directions. Levels are reported as a single value or range depending on the interpretation of the strip color.

Table 10. Results for free and total chlorine in the recycled water collected at the Yerba Buena Pump Station for the baseline 2005 study.

Date	Recycled Water (mg/L)	
	Free Chlorine	Total Chlorine
May-05	0.1	0.2 - 0.5
Jul-05	0.0	0.15 - 0.2
Aug-05	0.0 - 0.1	0.0 - 0.05

Field Data: pH, Dissolved Oxygen (DO), Conductivity, Temperature

On-site parameters (Table 11) were measured in the field using portable equipment at the time of sample collection. A Hach Portable Multiparameter meter was used to obtain data on temperature, pH, conductivity and DO in May, July, August, and October. An additional temperature measurement was made of the recycled water in November.

Table 11. On-site field measurements for baseline 2005 study.

Date: 05/18/2005

Site	River mile *(miles)*	Mean Temp *(° F)*	pH *pH units*	DO *mg/L*	Conductivity *(uS/cm)*
Silver Creek					
SW1	0.0	58.6	8.69	9.2	1109
SW2	0.7	58.5	8.50	8.5	1107
SW3	1.4	60.4	8.59	15.6	1047
Coyote Creek					
SW6	1.0	64.1	7.90	5.3	624
SW4	1.7	62.6	8.19	7.8	730
SW5	3.2	64.2	7.14	7.1	717
Recycled Water					
RW1	n/a	n.m.	n.m.	n.m.	n.m.

Date: 7-20-05

Site	River mile *(miles)*	Mean Temp *(° F)*	pH *pH units*	DO *mg/L*	Conductivity *(uS/cm)*
Silver Creek					
SW1	0.0	66.5	8.59	9.9	1193
SW2	0.7	67.6	8.51	8.3	1170
SW3	1.4	85.8	9.28	16.5	1062
Coyote Creek					
SW6	1.0	74.3	7.95	6.7	602
SW4	1.7	77.6	8.74	7	717
SW5	3.2	76.6	8.29	7.2	739
Recycled Water					
RW1	n/a	80.6	n.m.	n.m.	n.m.

Date: 8-29-05

Site	River mile *(miles)*	Mean Temp *(° F)*	pH *pH units*	DO *mg/L*	Conductivity *(uS/cm)*
Silver Creek					
SW1	0.0	62.2	8.51	10.7	1164
SW2	0.7	66.8	8.53	8.9	1172
SW3	1.4	80.1	9.49	23.6	1054
Coyote Creek					
SW6	1.0	69.6	7.91	6	544
SW4	1.7	68.7	8.33	8.5	713
SW5	3.2	71.0	8.17	9.5	721
Recycled Water					
RW1	n/a	81.5	n.m.	n.m.	n.m.

Date: 10-3-05

Site	River mile *(miles)*	Mean Temp *(° F)*	pH *pH units*	DO *mg/L*	Conductivity *(uS/cm)*
Silver Creek					
SW1	0.0	60.4	8.72	10.8	1294
SW2	0.7	56.8	8.74	9.6	1224
SW3	1.4	62.2	9.12	20.5	1141
Coyote Creek					
SW6	1.0	61.7	7.82	7.3	547
SW4	1.7	63.9	8.49	9.2	635
SW5	3.2	62.5	8.17	7.6	632
Recycled Water					
RW1	n/a	n.m.	n.m.	n.m.	n.m.

Date: 11-2-05

Site		Mean Temp *(° F)*	pH *pH units*	DO *mg/L*	Conductivity *(uS/cm)*
Recycled Water					
RW1		72.9	n.m.	n.m.	n.m.

Anions: Chloride, Sulfate, Nitrate

The Stanford laboratory performed anions analyses for only the 1st sampling event of the baseline 2005 study (May, shown in Table 12 below), after which the SCVWD laboratories took over the analyses.

Water samples were analyzed for nitrate, chloride, and sulfate by ion chromatography (Dionex) using an ASHC-11 column. Samples were processed within the same day of collection, because nitrate must be measured within 24 hours[7].

The isocratic program consisted of 25 mM NaOH in degassed MilliQ water as the eluent at a flow rate of 1.5 mL/min. Since measurement occurred before filtration, samples were centrifuged to remove all particles. For quantification, external standards were used and samples were diluted to fall within the calibration range of approximately 50 to 500 μM.

Table 12. Results for chloride, sulfate, and nitrate May analyses for baseline 2005 study.

		Background May '05		
Site	River Mile	Cl^- (ppm)	SO_4^{2-} (ppm)	NO_3^- (ppm)
SW1	0.0	124	51	1.5
SW2	0.7	123	51	1.5
SW3	1.4	118	49	1.3
SW4	1.7	61	45	1.1
SW5	3.2	43	43	1.1
SW6	n/a	58	44	1.0

Data Summary

The following tables give summaries of the baseline 2005 study analytical data for the recycled, surface, and ground waters at all dates and sites surveyed showing both the detections, non-detections (“n.d.”), and occasional events in which certain analytes were not measured (“n.m.”).

Table 13 below gives a listing of the analytes which were detected and not detected in the three waters sampled. Table 14 reports the findings on the group of analytes which were surveyed at the earlier part of the study (May, July, and August) including pharmaceuticals, APEMs, and other compounds. NDMA and PFCs are not included in this table as they were surveyed in slightly different months and the complete data for these compounds can be found in Tables 7 and 8, respectively, earlier in this report.

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[7] *Standards Methods for the Examination of Water and Wastewater*, Edition 19*;* Eaton, A. D.; Clesceri, L.S.; Greenberg, A. E., Eds.; American Public Health Association: Washington, D.C., 1995, p 4-85.

Table 13. Summary of all of the analytes which were detected and not detected in the baseline 2005 study.

Recycled Water		Ground Water		Surface Water	
Found	**Not Found**	**Found**	**Not Found**	**Found**	**Not Found**
Carisoprodol	Acetaminophen	BPA	Caffeine	Caffeine	Acetaminophen
Iminostilbene	Caffeine	NBBS	Acetaminophen	NBBS	Carisoprodol
NDMA	Carbamazepine	Tris(3-chloropropyl)phosphate	Carisoprodol	Tris(3-chloropropyl)phosphate	Iminostilbene
		Tris(2,3-dichloropropyl)phosphate			
A+CAPECs	Gemfibrozil	PFCs	Iminostilbene	Tris(2,3-dichloropropyl)phosphate	Carbamazepine
Halog. APEMs	Ibuprofen		Carbamazepine	PFCs	Gemfibrozil
NBBS	Ketoprofen		Gemfibrozil		Ibuprofen
Tris(3-chloropropyl)phosphate	Naproxen		Ibuprofen		Ketoprofen
Tris(2,3-dichloropropyl)phosphate	Primidone		Ketoprofen		Naproxen
PFCs	Propanolol		Naproxen		Primidone
	Estradiol		Primidone		Propanolol
	Estriol		Propanolol		Estradiol
	Estrone		Estradiol		Estriol
	Ethynylestradiol		Estriol		Estrone
	BPA		Estrone		Ethynylestradiol
			Ethynylestradiol		NDMA
			NDMA		A+CAPECs
			A+CAPECs		Halog. APEMs
			Halog. APEMs		BPA

Table 14. Summary report of pharmaceuticals, hormones, APEMs, and other compounds monitored as part of the 2005 baseline study of the Yerba Buena Pump Station recycled water, Silver and Coyote Creeks sites 1-6, and groundwater monitoring well 3 near Coyote Creek.

Analyte	**Yerba Buena Recycled Water**			**SW 1 (Silver Creek)**			**SW 2 (Silver Creek)**			**SW 3 (Silver Creek)**			**SW 4 (Coyote Creek)**			**SW 5 (Coyote Creek)**			**SW 6 (Coyote Creek)**			**Groundwater Well 3**		
	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05	May-05	Jul-05	Aug-05
Pharmaceuticals (ng/L)																								
Acetaminophen	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.m.	n.d.	n.m.
Caffeine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**72**	n.d.	n.d.	**19**	n.d.	n.d.	**23**	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Carbamazepine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Carisoprodol	n.d.	**217**	**195**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Gemfibrozil	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ibuprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Iminostilbene	n.d.	**98**	**96**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ketoprofen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Naproxen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Primidone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Propanolol	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.d.	n.d.	n.m.	n.m.	n.d.	n.m.
Hormones (ng/L)																								
Estradiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Estriol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Estrone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Ethynylestradiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
APEOs[1] & APEMs[2] (ng/L)																								
APEOs	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Alkylphenols (nonyl-, octyl-)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
A+CAPECs[3]	**610**	**256**	**303**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Halog. APEMs[4]	**60**	**48**	**17**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.
Other (ng/L)																								
Bisphenol A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	**18**	n.d.
N-butyl benzenesulfonamide	**13**	**60**	**46**	**30**	**48**	**14**	**60**	**73**	**15**	**119**	**39**	**27**	**209**	**21**	**23**	**209**	**<d.l.**	**38**	**164**	**75**	**44**	n.m.	**19**	**<d.l.**
Tris(3-chloropropyl)phosphate	n.d.	**33**	**15**	**1.0**	**5.0**	**1.6**	**2.0**	**5.8**	**3.3**	**3.0**	**5.2**	**4.2**	n.d.	**2.6**	**1.5**	n.d.	**2.9**	**2.4**	n.d.	n.d.	**2.2**	n.m.	**1.0**	n.d.
Tris(2,3-dichloropropyl)phosphate	**244**	**13.4**	n.d.	**1.0E+04**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	**<d.l.**	n.d.
Oxadiazon	n.d.	n.d.	n.d.	n.d.	**12**	n.d.	n.d.	**12**	n.d.	n.d.	**3.4**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.m.	n.d.	n.d.

[1] Alkylphenol polyethoxylates (AP1EO, AP2EO, AP3EO)

[2] Alkylphenol polyethoxylate metabolites

[3] Sum of alkylphenol ethoxycarboxylates and carboxyalkylphenol ethoxycarboxylates (both metabolites of APEOs).

[4] Sum of halogenated (chlorine or bromine) alkylphenols, APEOs, and A+CAPECs

APPENDIX B
GROUNDWATER MANAGEMENT UNIT MEMORANDUM, SANTA CLARA VALLEY WATER DISTRICT

groundwater management
Santa Clara Valley Water District

MEMORANDUM

TO: Ray Wong,
Water Use Efficiency Unit

FROM Henry Barrientos
Groundwater Management Unit.

SUBJECT: Coyote Creek Stream Augmentation at Upper Silver Creek.

DATE: March 15, 2005

This memorandum addresses groundwater quality concerns for the Coyote Creek Streamflow Augmentation Pilot Project conducted by the Santa Clara Valley Water District (District) Water Use Efficiency Unit (WUEU) and Stanford University (Stanford), and also addresses groundwater monitoring program elements which the Groundwater Management Unit (GWMU) believes are necessary to assess any potential groundwater quality impacts resulting from this project.

Background

In 2003 the District developed and agreement with the Metropolitan Water District of Southern California (MWD) to subcontract from the MWD part of a research grant provided by the MWD form the California State Department of Water Resources (DWR). The grant was approved by the DWR with the condition that a premiere research laboratory would be used as a partner in the research. Stanford was the selected laboratory.

This project will investigate if large scale releases of tertiary treated recycled water into a streambed will be adequately filtered by streambed action and natural percolation or if it impacts the groundwater quality. The project is centered on Stanford's hypothesis that stream flow can improve water quality by natural attenuation of trace organics. The project ensures the protection of upper and lower aquifers in the groundwater basin and the stream water quality, while piloting the use of recycled water for streamflow augmentation.

Recycled water produced at the South Bay Water Recycling Plant (SBWRP) will be used to augment stream flows in Coyote Creek. The site selected for this project is located in the City of San Jose in the Upper Silver Creek area next to the SBWRP Pump Station (Station). A small water treatment skid will be installed next to the Station where recycled water will be dechlorinated and then discharged to Upper Silver Creek (Creek), a tributary to Coyote Creek, next to the existing Station as shown in Figure A (attached). The project will run for a period of 6 months, beginning in May 2006.

The Creek is located in a transitional zone between the unconfined and confined Santa Clara Valley (SCV) groundwater subbasin. The point of confluence with Coyote Creek and downstream is located in the confined zone. A more detailed description of the projects' research objectives can be found in the report "Groundwater Impact Evaluation Partnership for Using Tertiary Treated Recycled Water In a Large Scale Streamflow Augmentation Project" by the District, included as Attachment A.

Site Investigation and Findings

The GWMU was asked by the WUEU to review this project and determine if any groundwater quality impacts could occur as a result of the augmentation. The GWMU investigation included a review of historical data, a groundwater well database search, a site visit and a geologic investigation of the area in question.

Historical Data

According to the District's 1977 Groundwater Recharge Facilities Report, recharge was conducted in the Creek from the Evergreen Canal crossing to the Coyote Creek bypass area. Stream recharge length was 4.8 miles and its first year of operation was 1964. The Evergreen Canal was constructed in 1955 and abandoned in 1988, when recharge to the Creek was stopped. The estimated recharge rate for Silver Creek was 3 acre-feet per day (AF/day) in the summer and 1 AF/day in the winter. The turn out and distribution capacity was 5 cubic feet per second.

Well Database Search

The purpose of the well database search was to determine the presence of any groundwater wells in the areas closest to the discharge point and downstream. Existing wells could serve as water quality monitoring locations, and abandoned wells in the proximity of the Creek could serve as potential conduits for groundwater migrating to deeper water bearing zones.

The search resulted in no active wells in the area adjacent to the Creek, and abandoned/destroyed wells downstream, with historical depth to water data only for wells which were probably used for irrigation or water supply purposes. The historical data for these wells, show depth to water in the area northwest of the Creek ranging between 100 and 120 feet below ground surface (bgs), [50 to 60 feet above the National Geodetic Vertical Datum (NGVD29)]. Historical data for groundwater in the area northwest of the Creeks' confluence point with Coyote Creek ranges between 60 and 80 feet bgs [50 to 80 feet above the NGVD29]. Unfortunately no well construction information was found for these wells, and therefore first groundwater encountered in this area could not be established. It was also noted that from the confluence point and approximately 2,000 feet downstream along Coyote Creek, there are a number of active groundwater wells with water quality data, which could aid in monitoring groundwater quality downstream once the project begins (Figure B).

Site Visit

A site visit was conducted on January 13, 2005 by the GWMU and Stanford staff to further evaluate the area of discharge and confirm geologic formations and physical characteristics of the area. During the site visit staff observed the area adjacent to the creek along a footpath, upstream and downstream of the discharge point as bedrock hillside with clay-rich banks. This condition continues downstream to the start of the concrete lined portion of the Creek. The Creek bed appears to be clay rich with sand and some gravel in the bedload, and some sandy zones at the banks (Figure C).

Geologic Investigation

The geologic investigation is addressed in a memorandum by Seena Hoose of the GWMU dated March 1, 2005 included as Attachment B. The two objectives of this investigation were to determine whether the segment of the Creek receiving recycled effluent discharge is in the confined or unconfined area of the SCV groundwater subbasin, and second evaluate the potential for recharge reaching the main drinking water aquifers in the rest of the subbasin. The result of this investigation along with the field observations made on January 13 indicates that the discharge area in question is located in the unconfined area of the SCV groundwater subbasin. In addition, the discharge from the Station is expected to recharge along a short portion of the Creek between the discharge point and the concrete lined portion downstream, and enter a groundwater zone of limited extent where a direct hydraulic connection between the main SCV groundwater subbasin is unlikely. A more thorough explanation of these findings can be found in Attachment B.

Surface and Groundwater Monitoring Parameters

As stated above, the augmented segment of the Creek appears to be located in an unconfined zone of the SCV subbasin, consequently groundwater quality could potentially be impacted during the six months of operations. Therefore, monitoring parameters should be established prior to commencement of the project.

Water quality parameters should be based on California drinking water standards and water quality objectives in the San Francisco Bay Regional Water Quality Control Board's Water Quality Control Plan. A preliminary list of these parameters is illustrated in Table 1 (attached). These should be monitored prior to project commencement (baseline samples) and on a monthly basis there on after. District Ends Policy E2.1.5 states *"the groundwater basins are aggressively protected from contamination and the threat of contamination."* It should therefore be noted that in the event water quality indicators are exceeded as a result of this project (as evidenced by analytical data from the groundwater), stream augmentation should be suspended until the project can address and correct the causes of the negative impacts.

Discussion

Based on this investigation and historical site conditions, groundwater recharge will likely occur along the segment of the Creek from the Station discharge point to the concrete lined portion. Project operation will occur during the summer months when expected flows in the Creek are low, and groundwater is expected to travel in a northerly direction. Recharge from the Creek occurring next to the discharge point may be intercepted in the first water bearing zone by installing a well just north of the Creek. If recharge is occurring beyond this zone, groundwater is likely to travel to deeper zones which can be intercepted by installing a second well in the second to third water bearing zone downstream. In order to protect groundwater and to confirm no recharge is occurring further downstream after the Creeks' confluence with Coyote Creek, a third well could be used to intercept groundwater in the first water bearing zone north of Coyote Creek in what is known as a confined zone of the SCV subbasin.

Actual well depths and screen intervals can be determined in the field based on lithology as observed at each drilling location, and are estimated in the recommendations below.

Recommendations

The following is list of recommendations based on information provided to the GWMU by the WUEU as of the date of this memo; additional recommendations may be necessary should project specifications change at a later date:

- In order to properly monitor potential groundwater quality and migration occurring as a result of recharge in the Creek, a minimum of three wells should be installed on the north side of the Creek to monitor for groundwater quality conditions before and after the project begins. The first well should be located close to the discharge point not to exceed 100 feet in a northerly direction, and screened in the first encountered permeable zone (estimated between 30 to 50 feet bgs). The second well should be installed downstream of the discharge point at an easily accessible location (in proximity of the City parking lot identified in Figure B) not to exceed 150 feet to the north of the Creek, and screened in the second to third permeable zone (estimated between 50 and 100 feet bgs). The third well should be installed on the northeast side of the Creeks' confluence with Coyote Creek and downstream, not to exceed 100 feet in a perpendicularly direction from Coyote Creek, and screened in the first encountered permeable zone (estimated between 30 and 50 feet bgs). The latter can also be accomplished by using existing wells in the area depending on total well depth, screen interval, accessibility and approval from the respective well owner. In addition, one alternate well may be identified for use also. Preliminary sites for this option are under review by both the WUEU and GWMU staff.

- Groundwater quality data should be provided to the GWMU on a monthly basis, to coincide with the proposed monthly sampling.

- Should any of the parameters listed in Table 1 be detected in the shallow monitoring wells above their respective drinking water standard, stream augmentation should be suspended pending identification of the cause and possible remedies established.

- Groundwater samples should be collected and analyzed as baseline data before discharge to the Creek begins and monthly after start up. Groundwater sample collection should coincide with the scheduled surface water collection events.

Cc: Behzad Ahmadi, Seena Hoose.

Attachments:

Table 1: Groundwater Quality Monitoring Parameters;
Figure A: Upper Silver Creek; Figure B: Upper Silver Creek and Coyote Creek; Figure C: Upper Silver Creek
Attachment A: Groundwater Impact Evaluation Partnership for Using Tertiary Treated Recycled Water In a Large Scale Streamflow Augmentation Project" , SCVWD, December 2004.
Attachment B: Memorandum from Seena Hoose on Upper Silver Creek Augmentation with Recycled Water.

Table 1 Groundwater Quality Monitoring Parameters.

Parameter
General Water Quality
Temperature Conductivity pH TDS Total Alkalinity SAR (calculated parameter)
Cations and Anions
Sodium Potassium Calcium Magnesium Sulfate Chloride Bicarbonate Nitrate as NO_3
Metals and Trace Compounds
Aluminum Arsenic Barium Boron Cadmium Total Chromium Copper Iron Lead Mercury Manganese Nickel Selenium Silver Zinc
Miscellaneous
NDMA Organic Chemicals (VOCs, etc) EDC's (endosulfan sulfate, dioxin, methoxychlor, etc)

Notes: NDMA: N-nitrosodimethylamine, VOC: Volatile Organic Compounds,
EDCs: Endocrine Disrupting Chemicals (Surrogates may be used instead where applicable)

SBWRP Yerba Buena Pump Station

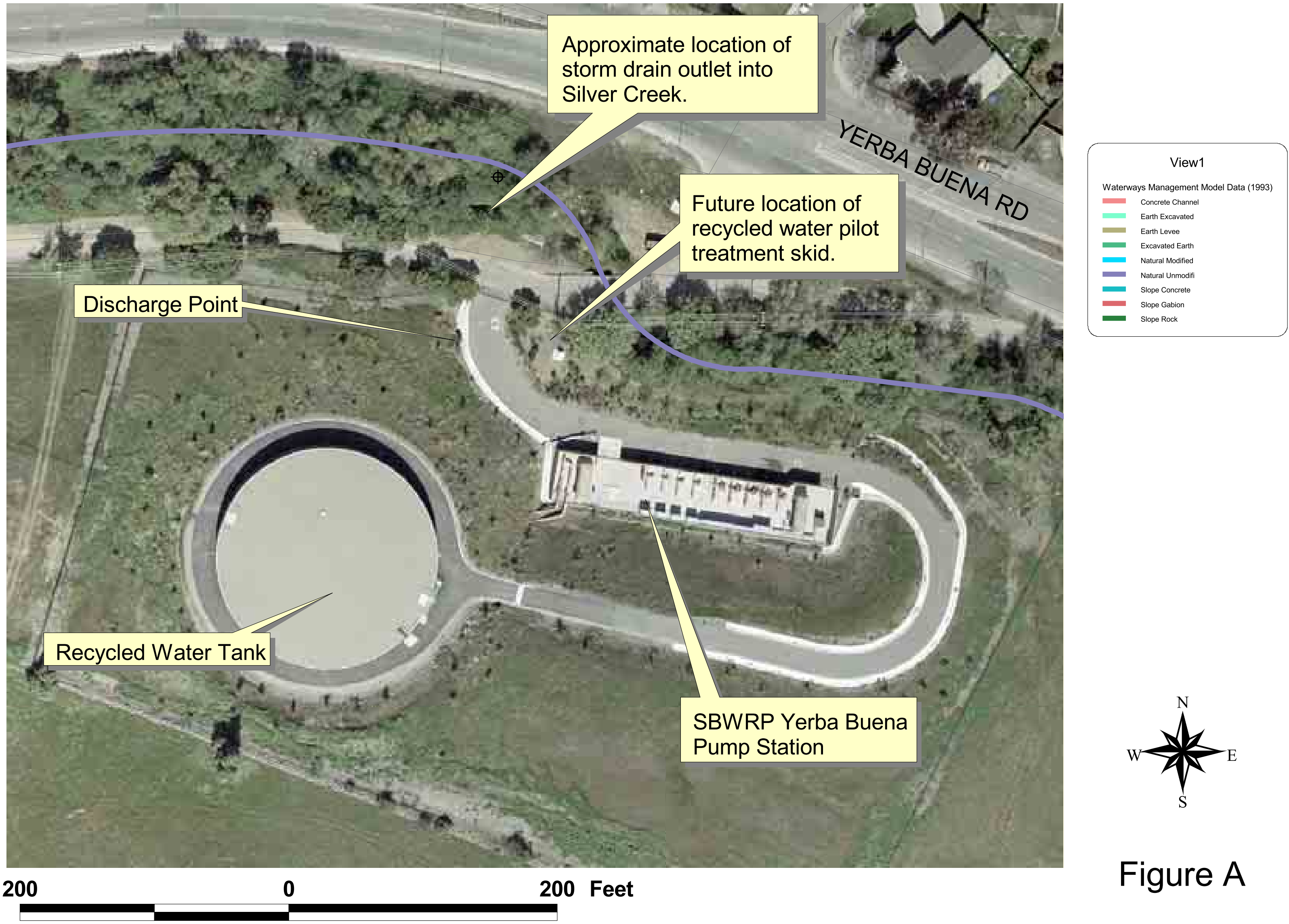


Figure A

UPPER SILVER CREEK & COYOTE CREEK

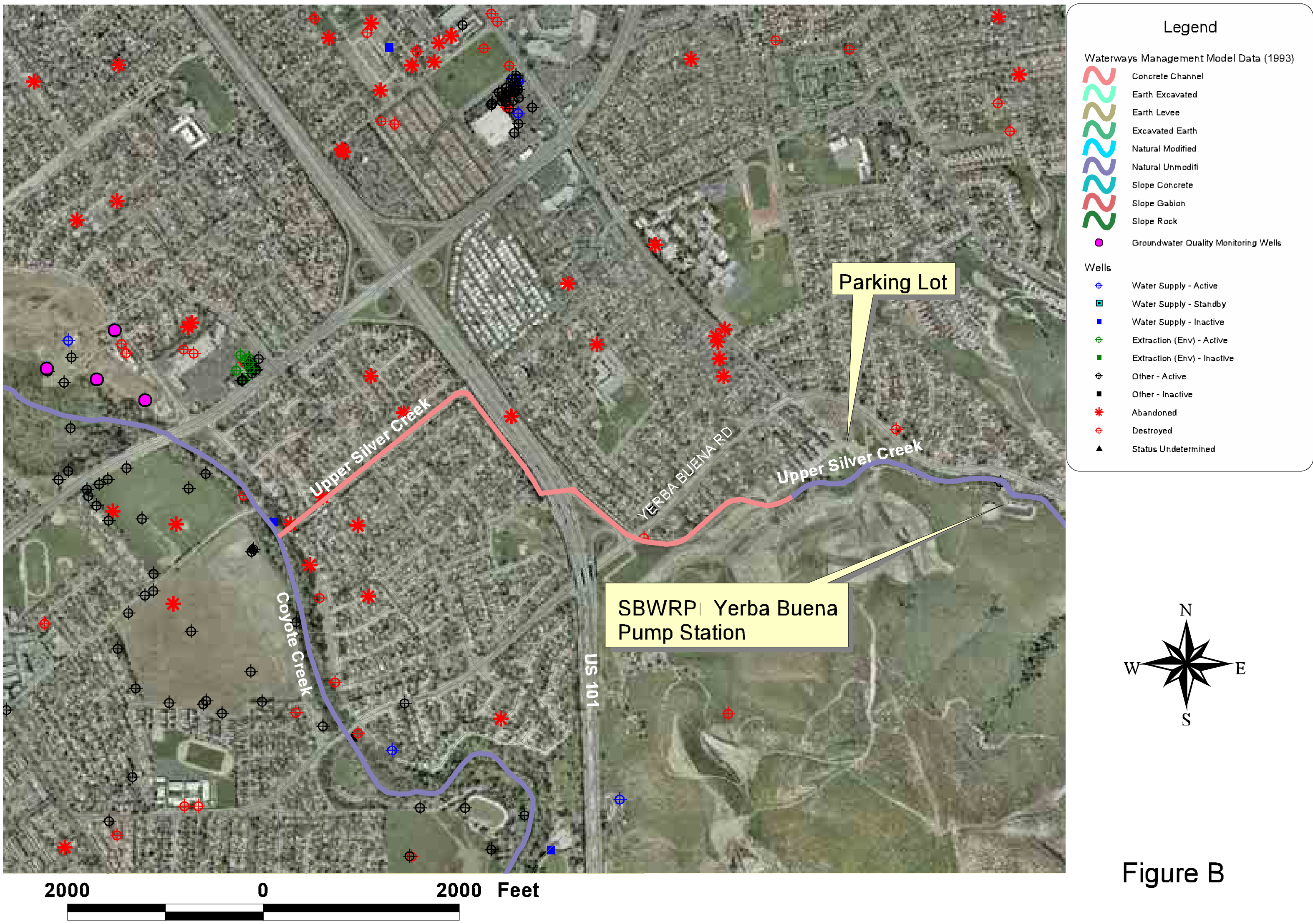


Figure B

UPPER SILVER CREEK

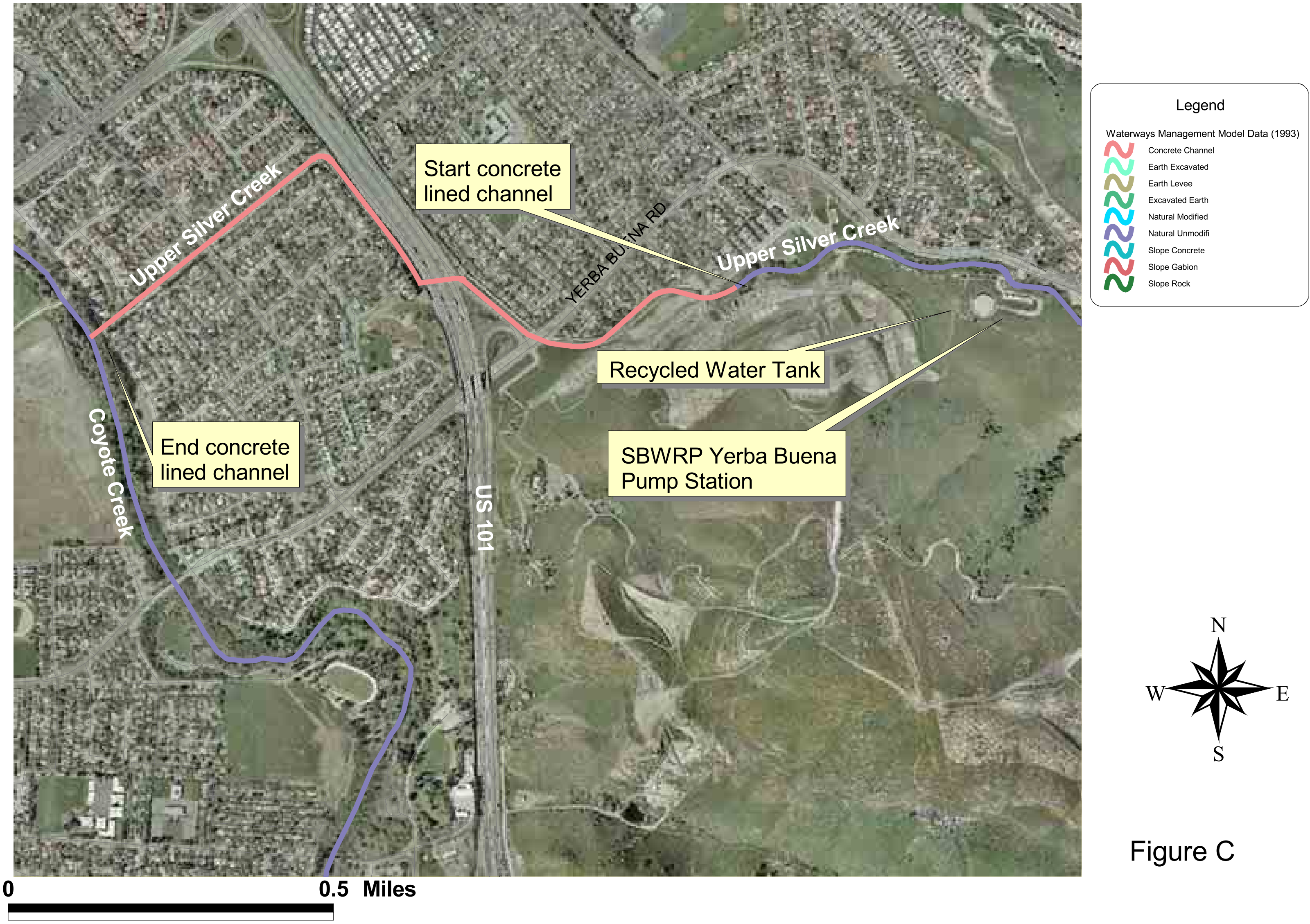


Figure C

ATTACHMENT A

Work Plan

Under Department of Water Resources Grant entitled

"Safe Drinking Water, Clean Water, Watershed Protection and Flood Protection Act"

For The Project

"Groundwater Impact Evaluation Partnership For Using Tertiary Treated Recycled Water In A Large-Scale Streamflow Augmentation Project"

Submitted to:

The Metropolitan Water District of Southern California

Agreement No. 41808

December 2004

Santa Clara Valley
Water District

TABLE OF CONTENTS

Section 1: Project Definition, Background, Objectives and Organization

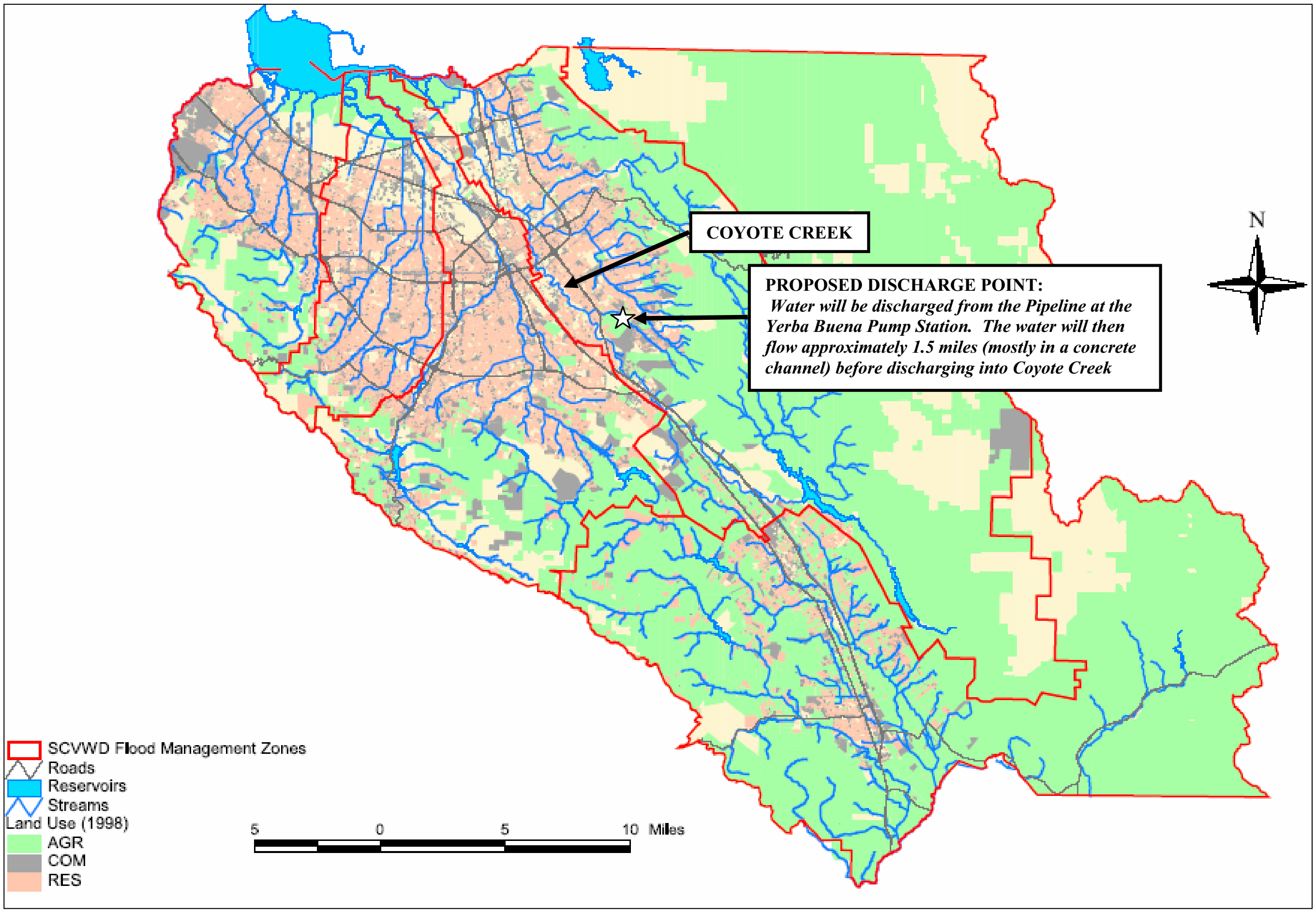
This project increases the potential for the expanded use of recycled water by the Santa Clara Valley Water District (District) in Santa Clara County, which is consistent with the desires and policies of the District Board of Directors (Board). It also has the potential to provide augmented creek flows for environment benefit as part of the "Environmental Stewardship" mission of the Board.

Project Definition

An increasing number of communities in California are turning towards water recycling as a means to meet the growing demand for water. The traditional solution to increase water supplies has been to import water from distant sources. However, this option has been vanishing with population growth spreading all across the Southwest. In cases where human uses have diminished the water source that an ecosystem depends on, one option is to treat impaired sources—including tertiary effluents—such that the treated water can replenish the water source. Re-used water must be protective of both stream ecology and groundwater, and comply with local and regional regulations. Currently there are limited data available to assess such water augmentation schemes *a priori*, and detailed, site-specific evaluations are needed.

This research-scale study will examine the use of recycled water produced at the San José/Santa Clara Water Pollution Control Plant (SJ/SC WPCP) to augment stream flows in Coyote Creek. The study proposes to add from 2 to 6 cfs of recycled water to Coyote Creek, corresponding to two to three times base summer flow (base flow readings are available elsewhere (SCVWD)). The source of Coyote Creek is located in the upper reaches of the Santa Clara Valley, and flows over 20 miles through suburban and urban areas to its mouth in south San Francisco Bay. Figure 1 is a regional map of Santa Clara County showing Coyote Creek. The proposed quantities of tertiary treated recycled water will be released into the stream approximately 15 miles upstream from the Bay.

The overall goal of the stream augmentation project is *to assess the potential impact of large-scale augmentation of the Coyote Creek flow with tertiary treated water on the water quality of the river and the underlying groundwater. If results indicate adverse effects, appropriate treatment methods will be evaluated. These treatment methods may include reverse osmosis treatment, soil treatment, or blending with higher quality water.*



COYOTE CREEK

PROPOSED DISCHARGE POINT:
Water will be discharged from the Pipeline at the Yerba Buena Pump Station. The water will then flow approximately 1.5 miles (mostly in a concrete channel) before discharging into Coyote Creek

Figure 1 Regional Map of Santa Clara County

Project Background

The City of San José previously proposed to augment stream flow in Coyote Creek by up to 400 percent with recycled water. Several relevant supporting studies were conducted for the City. Chief amongst these studies was the "Revised Initial Study" (Jones & Stokes, 2000), which evaluated the ecological and groundwater impacts of the augmentation. A primary objective of the San José scheme was to improve cold-water habitat in Coyote Creek, thus recycled water was to be dechlorinated and chilled significantly prior to release into the creek. For groundwater, the study noted that the Santa Clara groundwater basin, which contains the reach of Coyote Creek to be studied, is divided into three zones: a shallow unconfined aquifer, a regional aquitard, and beneath the aquitard a potable deep confined aquifer. Considering the location of the City's proposed outfall at Singleton Landfill, recycled water in Coyote Creek would only flow over the regional aquitard and infiltration to the potable deep aquifer would be unlikely. The report noted that there is a low probability of infiltration to the shallow aquifer due to the clayey composition of the creek bottom; nevertheless, monitoring of shallow aquifer water quality was recommended to confirm that no recharge with recycled water was taking place.

Another concern that arose during the City of San José project was the degradation of water quality due to trace organics and endocrine disruptors. The appearance of these compounds in the aquatic environment is a recent environmental concern because some of them are biologically active and viewed as potentially harmful to wildlife and human health.

In late October 2000, the City of San José obtained a permit from the California Regional Water Quality Control Board (RWQCB) to implement a demonstration stream flow augmentation project in Coyote Creek. The City decided not to proceed with the project and the RWQCB permit expired in June 2003.

Project Objectives

The objectives of this study are:

1. To assess the potential of fate mechanisms – including photochemical degradation, adsorption, and biotransformation – to remove specific contaminants from tertiary treated recycled water used for large-scale augmentation of stream flow in Coyote Creek. We will determine the specific contaminants to be analyzed based upon the results of a detailed characterization of the tertiary treated recycled water.
2. To assess the fate of contaminants during percolation from Coyote Creek into groundwater under stream flow augmentation conditions. An evaluation of Coyote Creek hydrology—specifically the interactions between surface flow and shallow and deep aquifers—will determine the boundaries of the assessment.
3. If results indicate adverse effects on groundwater or stream ecology, appropriate treatment methods for the augmentation water will be evaluated. These treatment methods may include Reverse Osmosis treatment, soil treatment, or blending with higher quality water.

For the current study, augmentation will be conducted with a lesser volume of water than previously proposed by the City of San José. The recycled water will be dechlorinated and potentially chilled prior to discharge into Coyote Creek.

A central hypothesis that will be tested during the research study is that natural biological, physical, and chemical action during stream flow can improve the stream's water quality, including by natural attenuation of trace organics. Likewise, natural action during the infiltration of surface water into groundwater can further improve the water quality of the infiltrating water.

A prior study conducted by Stanford University researchers suggests that the hypothesis will prove valid. With support from the Orange County Water District, Reinhard et al. conducted a similar study of water quality changes in the Santa Ana River in Southern California. (Reinhard and J. 2001) (Reinhard et al.1999). The Santa Ana River carries nearly 100 percent tertiary treated water during the summer months (Gross et al. 2004). In that study it was found that trace organic contaminants such as pharmaceuticals and alkylphenol ethoxylate metabolites (biological degradation products of nonionic detergents) are significantly attenuated during river transport suggesting that the river itself acts as an efficient treatment system. The subsequent infiltration of river water into the ground led to significant additional water quality improvement in terms of total organic carbon (dissolved and particulate) and trace organics.

Natural attenuation not withstanding, initial screening may reveal that a limited number of un-transformed trace organics are present. Analyses conducted by Reinhard and collaborators at Stanford University for the District's 2002 Advanced Recycled Water Treatment Feasibility Study determined the concentrations of a range of trace organics in effluent samples from the SJ/SC WPCP –the treatment plant that will be producing the recycled water for the stream flow augmentation. Data for the analyzed effluent are summarized in Table 1. The analyses found that alkylphenol ethoxy carboxylates (APEC) are typically the major group of trace contaminants in tertiary effluents with concentrations generally in the range of 1-20 micrograms per liter. Pharmaceutical compounds such as ibuprofen and naproxen were not found above the reporting limit. Chlorinated and brominated APECs have been identified previously in Palo Alto (Ball and Reinhard 1984). The findings at the SJ/SC WPCP facility are consistent with the 1984 findings that chlorination of tertiary effluent APEC compounds can convert APEC compounds into their chlorinated or brominated forms. Furthermore, analyses for hormones in SJ/SC WPCP effluent conducted by the David Sedlak Research Group at the University of California, Berkeley in August 2002 did not find four hormones known by other studies to occur in the environment in concentrations greater than the limits of quantification.

Based on studies similar to the Coyote Creek Stream flow Augmentation conducted in Southern California (Gross et al. 2004), results are hypothesized to confirm that water quality with respect to wastewater indicator compounds will improve during augmented Coyote Creek stream flow.

Table 1: Trace Organics Concentrations in the South Bay Water Recycling Program Tertiary Recycled Water (Source from Santa Clara Valley Water District's Advanced Recycled Water Treatment Feasibility Study in 2002)

Analysis Date	**Reporting Limit** *(μg/L)*	**12/1/01**	**3/2/02**	**6/2/02**	**7/2/02**
Neutrals (μg/L)					
NP/OP	0.003	-	n.d.	n.d	n.d
AP1EO	0.003	-	n.d.	n.d	n.d
AP2EO	0.003	-	n.d.	n.d	n.d
AP3EO	0.003	-	n.d.	n.d	n.d
Total APEO	0.003	-	n.d.	n.d	n.d
Halog. AP/APEO	0.003	-	0.026 [d]	n.d	n.d
Alkylphenol Ethoxy Carboxylates (APECs) (μg/L)					
m/z 235	0.0005	-	n.d.	n.d.	n.d.
m/z 249	0.0005	-	n.d.	n.d.	n.d.
m/z 279	0.0005	-	n.d.	n.d.	n.d.
Total APEC	0.0005	-	n.d.	n.d.	n.d.
Halog. APEC	0.0005	-	12.9 [b]	1.7	14.8
EDTA by HPLC	0.003	6	305	n.l.f.	n.l.f.
Pharmaceuticals (μg/L)					
Ibuprofen	0.005	n.d.	n.d.	n.d.	n.d.
Carba-mazepine	Tbd	n.d.	n.d.	n.d.	n.d.
Gemfibrozil	0.005	n.d.	n.d.	n.d.	n.d.
Ketoprofen	0.005	n.d.	n.d.	n.d.	n.d.
Naproxen	0.005	n.d.	n.d.	n.d.	n.d.
Others (μg/L)					
Bisphenol A	Tbd	n.l.f.	n.d.	n.l.f.	n.l.f.
Tris(3) phosphate	Tbd	n.l.f.	0.011	0.003	0.022
Tris(2,3) phosphate	Tbd	n.l.f.	0.01	0.01	0.32
N-butyl benzenesulfonamide	Tbd	n.l.f.	0.015	0.017	0.27
Caffeine	0.005	n.l.f.	n.d.	n.d.	n.d.

Hormones (ng/L)	6/20/02	8/27/02	11/4/02

Testosterone	n.d. (<0.5)	n.d. (<0.5)	n.d. (<0.5)
17β-Estradiol	n.d. (<0.5)	n.d. (<0.5)	n.d. (<0.5)
Estrone	n.d. (<1.0)	n.d. (<1.0)	n.d. (<1.0)
Medroxyprogesterone	n.d. (<1.0)	n.d. (<1.0)	n.d. (<1.0)

All data semi-quantitative except EDTA

EDTA-Analysis: HPLC-UV, ion-pair reversed-phase method with external calibration

All others: GC/MS or GC/MS/MS, Mode: EI, semi-quantitative with d_{12}-chrysene as internal standard

Trace: above detection limit, below reporting limit

Tris(3)phosphate: Tris(3-chloropropyl)phosphate, Tris(2,3)phosphate: Tris(2.3-dichloropropyl)phosphate

Halogenated APEOs and APECs:

Byproducts during chlorine disinfection.

Halog. APECs: halogenated (chlorinated or brominated) APECs; [a] 1.91 µg/L chlorinated and 0.15 µg/L brominated

[b] 11.43 µg/L chlorinated and 1.45 µg/L brominated;

Halog.AP/APEO: chlorinated AP and APEOs, [c] 0.006 µg/L AP, [d] 0.009 µg/L AP and 0.017 µg/L APEO

n.l.f.: not looked for

n.d.: not detected

Task Descriptions and Project Timeline

Task 1: Work Plan Preparation

This document fulfills the requirements of Task 1.

Deliverable: Project Work plan.

Task 2: Design and Installation of Monitoring Well(s) System

Sub Tasks:

Identify and Secure Needed Permits. Determine Augmentation Scheme, Groundwater Monitoring Requirements and Ecological Monitoring Requirements

In order to add recycled water to Coyote Creek, project personnel will identify and secure a variety of permits from different regulatory agencies as applicable. The permitting requirements may dictate several important factors in the study, including:

- Flow rate and temperature of augmentation water in relation to Coyote Creek base flow
- Groundwater monitoring requirements, including a plan detailing water quality parameters that must not be exceeded
- Ecological monitoring requirements, possibly including fisheries monitoring, benthic macroinvertebrate monitoring, and aquatic and riparian vegetation monitoring.

Select Recycled Water Outfall

Project personnel will work to select an outfall location along Coyote Creek that will optimize costs and data requirements. Specific items to be addressed include:

- proximity to a recycled water pipeline,
- known hydrogeology,
- available site for facilities such as dechlorinator, chiller, startup/testing equipment, etc.
- appropriate zoning.

Review of Historical Data and River Hydrology

The study will review historical data that is relevant and available to the study, specifically regarding the following:

- SJ/SC WPCP recycled water quality
- Groundwater quality of the shallow aquifers
- Coyote Creek hydrology and water quality
- Coyote Creek/Groundwater hydrogeology

Additionally, the hydrological conditions of Coyote Creek prior to augmentation along the study reach will be determined. Interactions between surface water and groundwater will be evaluated, and the flow rate between sampling locations will be calculated. Study methods will include the analysis of potential additions or subtractions of flow in Coyote Creek, including evaporation, percolation into or seepage from the shallow aquifer, or addition of water by tributaries. Indications for groundwater infiltration from the creek to the shallow aquifer will also be examined based on water table measurements and water quality anomalies along the river, and groundwater table changes due to flow changes. The hydrological information found may lead to the decision that a tracer study be proposed.

Select Surface Water Sampling Locations

Surface water sampling locations will be identified along Coyote Creek that will be accessible and meet project data requirements. A logical starting point for choosing sampling points will be recommendations detailed in the Jones & Stokes report (discussed below). Additionally, project personnel will work with the District's Groundwater Department to select groundwater sampling locations in the shallow aquifer.

Design and Installation of Well Systems

If groundwater wells are currently available and meet project data requirements, they will be utilized. Otherwise, locations will be determined where new wells will be needed, and wells will be designed and installed in accordance with Santa Clara Valley Water District well installation standards.

Deliverable: Technical memorandum reporting on all sub-tasks.

Task 3 Baseline Data Collection and Analysis

Sub Tasks:

Characterization of SJ/SC WPCP Effluent

SJ/SC WPCP effluent will be the water used to augment Coyote Creek stream flow. For Task B3, a detailed characterization of contaminants in the effluent will be conducted. The effluent will be screened for the target compounds listed in Table 4. Based on the findings of the characterization (presence or absence of trace contaminants) the suite of compounds to be analyzed during the study will be selected. A previous study in 2001 and 2002 showed the absence of target hormones and pharmaceuticals in SJ/SC WPCP effluent water. These findings will have to be verified for the timeframe of this study.

Baseline Analysis of Water Quality at Coyote Creek Sampling Locations

To characterize the baseline conditions in Coyote Creek with no stream flow augmentation, water samples taken at the sampling locations will be analyzed for the target analytes (discussed below in Section 2 of this Work Plan). Sampling frequency is explained below.

Baseline Analysis of Potentially impacted Groundwater Quality

Prior to augmentation, water quality in the shallow aquifer potentially connected hydrologically to the Coyote Creek study reach will be characterized to determine baseline concentrations of the selected analytes.

Deliverable: Technical memorandum reporting on baseline data collection and analysis.

Task 4 Facilities Construction and Recycled Water Release

Sub Tasks:

Construction and Operation of Recycled Water Supply Facilities and Infrastructure

The District will construct, install, and operate facilities (e.g., dechlorinator, cooling towers, and chillers) and associated infrastructure necessary for providing recycled water supply. The District will obtain all necessary permits required for this subtask.

Analyze Augmentation Conditions

The following analyses will be performed for Coyote Creek under augmentation flow conditions:

- Re-calculate river hydrological parameters based on addition of augmentation water
- Adjust sampling scheme according to augmented flow conditions
- Analyze selected contaminants at both Coyote Creek surface water sampling locations and applicable groundwater sampling locations.

Deliverable: Technical memorandum reporting on the findings of the release of the tertiary treated recycled water.

Task 5 Data Integration, Analysis and Reporting

Collected data will be analyzed, a summary report prepared, and the study will evaluate if groundwater protection is achieved. If the evaluation shows that groundwater is impacted, the study will determine the level of treatment necessary to ensure that the groundwater basin is not degraded due to the introduction of recycled water into Coyote Creek.

Deliverable: Final project report and technical memorandum reporting on the data analyses.

The project schedule of the Impact Evaluation of Stream Flow Augmentation With Tertiary Recycled Water Project is presented in Table 2.

Table 2: Impact Evaluation of Stream Flow Augmentation With Tertiary Recycled Water Project Schedule (Year/Quarter)

Task	***Year/quarter***	***4/4***	***5/1***	***5/2***	***5/3***	***5/4***	***6/1***	***6/2***	***6/3***	***6/4***	***7/1***
1	Work plan preparation	■									
2	Design and installation of monitoring well(s) system	■	■	■							
3	Baseline data collection and analyses		■	■	■	■					
4	Facilities construction and recycled water release		■	■	■	■	■	■	■	■	
5	Data integration, analysis, and reporting								■	■	■

Project Personnel and Responsibilities

Table 3 lists the institutions and the key participants involved in this project.

Table 3: Key Project Participants, their roles and contact information

Institution	Personnel	Role/ Responsibilities	Telephone (T), Fax (F), E-mail (E)
Project Owner Santa Clara Valley Water District 5750 Almaden Expressway San José, CA 95118 (Grant recipient)	Pamela John, P.E., T-4 *Senior Engineer*	Project Liaison with MWD	(T) (408) 265-2607 x3003 (F) (408) 979-5639 (E) pjohn@valleywater.org
	Ray Wong *Program Administrator*	Project Manager	(T) (408) 265-2607 x2288 (F) (408) 978-0156 (E) rwong@valleywater.org
	Behzad Ahmadi, P.E. *Groundwater Management Unit Manager*	Groundwater Monitoring Program	(T) (408) 265-2607 x2324 (F) (408) 978-0156 (E) bahmadi@valleywater.org
	Henry Barrientos *Groundwater Management Engineer*	Groundwater Monitoring Program	(T) (408) 265-2607 x2078 (F) (408) 978-0156 (E) hbarrientos@valleywater.org
	Debra Caldon *Watershed Unit Manager*	Environmental Planning and Review	(T) (408) 265-2607 x3057 (F) (408) 979-5639 (E) dcaldon@valleywater.org
	Don Arnold *Ecological Services Unit Manager*	Ecological Monitoring Program	(T) (408) 265-2607 x3007 (F) (408) 979-5657 (E) darnold@valleywater.org
City of San José **Environmental Services Dept.** **3025 Tuers Rd.** **San José, CA 95121**	Bob Wilson, P.E. *Senior Civil Engineer*	Recycled Water Facilities Manager	(T) (408) 277-3671 (F) (408) 277-4954 (E) bob.wilson@ci.sj.ca.us

Institution	Personnel	Role/ Responsibilities	Telephone (T), Fax (F), E-mail (E)
Stanford University **Department of Civil and Environmental Engineering** Terman Engineering Center Stanford, CA 94305-4020	Martin Reinhard, PhD *Professor*	Principal Investigator	(T) (650) 723-0308 (F) (650) 723-7059 (E) Reinhard@stanford.edu
	Montserrat Lopez-Mesas, PhD *Post-Doctoral Researcher*	Analytical Laboratory	(T) (650) 723-0315 (F) (650) 725-3162
	Angela Lin *Graduate Student*	Fate in Surface Water Research	(T) (650) 723-0315 (F) (650) 725-3162 (E) angelal@stanford.edu
	Megan Plumlee *Graduate Student*	Project Engineer	(T) (650) 723-0315 (F) (650) 725-3162 (E) meganp@stanford.edu
	Gary Hopkins *Field Operator*	Field Operations and Hydrology	(T) (650) 723-0315 (F) (650) 725-3162 (E) hopkins@ce.stanford.edu
	Chris Gurr *Graduate Student*	Logistics Liaison/Project Engineer	(T) (510) 866-8268 (F) (650) 725-3162 (E) cgurr@stanford.edu

Section 2: Experimental Design

Technical approach

Analysis of Historical Data. The District has routinely collected data relevant to this study for many years; a preliminary task for us will be to access and analyze this historical data. The study seeks to develop an understanding of regular variations in stream hydrology, water quality, or groundwater hydrology in the region of interest, and produce a written summary of the specific data that will impact the study. Variations are primarily expected from seasonal changes and rainfall in the watershed.

Baseline Study. In order to determine what changes in Coyote Creek are caused by augmentation, the study must first determine the initial conditions in the Creek. A full schedule of sampling (described below) will be conducted over the course of six months. For water quality baseline data, initial non-augmentation concentrations of all relevant contaminants and water quality parameters will be determined, as will base flow conditions in the Creek and any surface water/groundwater interactions we uncover.

Laboratory Studies. Stanford laboratories and libraries will be utilized to conduct a literature review and experimental fate studies of relevant contaminants. Bench-top studies will simulate both percolation and river conditions, and control for important variables. Results will permit project personnel to discern the existence and magnitude of different fate mechanisms, including photochemical degradation, adsorption, and biotransformation.

Augmentation Study. Data will be collected under augmentation conditions following a similar sampling regime to the baseline study. Information gleaned from the prior data sets—historical, baseline, literature, and laboratory—will be used to analyze the data collected during Coyote Creek augmentation, and make conclusions regarding the objectives of the study.

Water Quality Parameters

The on-site, inorganic, and trace organic water quality parameters that will be characterized are listed in Table 4. As a preliminary task project personnel will screen for a wide range of trace organics shown below, and then make a final selection of those compounds that are detected in sufficient quantities. A previous study in 2001 and 2002 showed the absence of target hormones and pharmaceuticals in SJ/SC WPCP effluent water. These findings will have to be verified for the timeframe of this study

Trace organic compounds

Of particular concern to this study are trace organic compounds. These include pharmaceuticals (gemfibrozil, ibuprofen, naproxen, ketoprofen, carbamazepine) and their metabolites, hormones (estrone, 17α-ethynyl estradiol, 17β-estradiol, estriol), the metabolites of alkylphenol polyethoxylates (APEMs), and N-butyl benzenesulfonamide (NBBS), and chlorinated tris-propylphosphates (TCPPs). The APEMs include alkylphenols (APs), short-chain alkylphenol polyethoxylates (APEOs), alkylphenol polyethoxycarboxylates (APECs) and carboxylated alkylphenol polyethoxycarboxylates (CAPECs).

Previous studies (March, June and July 2002) showed the presence of halogenated APEMs in SJ/SC WPCP effluents. Chlorinated APs and APEOs as well as chlorinated and brominated APECS were detected at concentrations up to 15 µg/L. These halogenated compounds are probably formed during chlorine disinfection in the presence of bromide. All other target compounds might also be present as halogenated derivatives, but as there are no commercial standards available their detection will be tentative.

N-nitroso dimethylamine (NDMA) is added to the list of target compounds because background studies confirmed its presence in the waters. Stanford University is currently developing a method to detect and quantify NDMA in environmental samples.

Table 4 Water Quality Parameters to be Screened and Selected

Parameter
On-Site
Temperature
Total dissolved solids (TDS)
Electrolytic conductivity
Dissolved oxygen (DO)
pH
Inorganic Compounds and DOC
Dissolved organic carbon (DOC)
Alkalinity
Chloride
Sulfate
Nitrate
Trace Organic Compounds
Gemfibrozil
Ibuprofen
Hydroxy-ibuprofen
Carboxy-ibuprofen
Naproxen
Desnaproxen
Ketoprofen
Carbamazepine
Estrone
17B-estradiol
Estriol
Alkyl phenols (nonyl, octyl)*
Alkylphenol polyethoxylates (AP1EO, AP2EO, AP3EO)*

Alkylphenol ethoxycarboxylates*
Carboxylated alkylphenol ethoxycarboxylates*
Tris(3-chloropropyl) phosphate
Tri(2,3-dichloropropyl) phosphate
N-butyl benzenesulfonamide
N-nitroso dimethylamine (NDMA)

*Including halogenated by-products

Rationale for Sampling Locations and Discharge Location

The objective is to choose sampling locations that permit the monitoring of a volume of Coyote Creek water for water quality changes as the volume flows from the augmentation outfall point towards San Francisco Bay. As stated above, sampling locations are not yet finalized; project personnel will establish surface water and groundwater sampling locations that will be both accessible and meet the study's data needs.

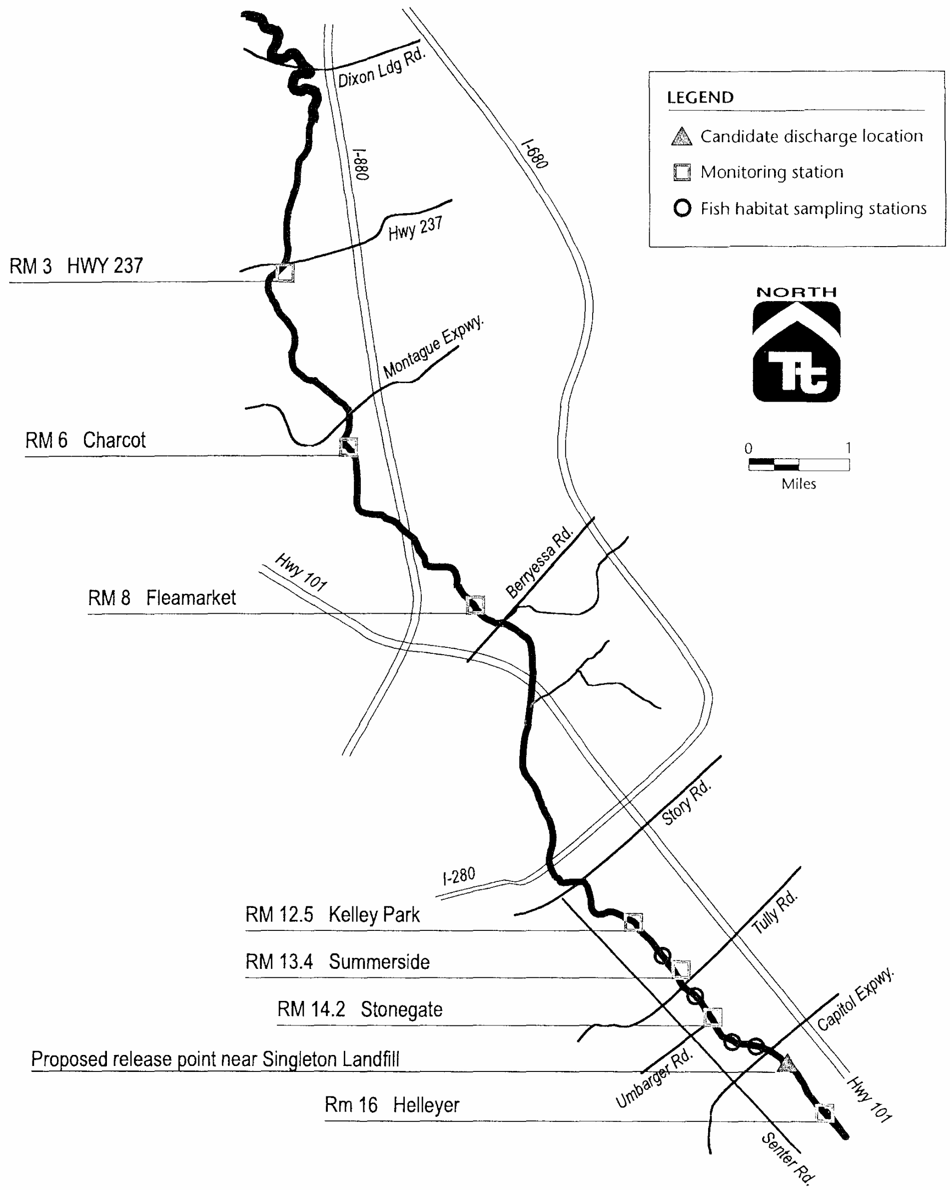
Key points in choosing sampling locations include:

- Selecting sites where access will not be an issue,
- Choose a control site upstream and up-gradient of the augmentation outfall,
- Ideally, between the sampling points there should be no additions/diversions that change the quality or quantity of water in Coyote Creek. If this is not feasible at least two adjacent locations will be selected that have no additions/diversions between them.

Additionally, if a site is found where Coyote Creek surface water infiltrates into the ground, wells will be installed directly in the infiltration flow path so that contaminant attenuation can be assessed as a function of distance and residence time.

As mentioned above in the description of Task 2, the Jones & Stokes *Revised Initial Study* is a logical starting point for choosing the recycled water outfall location and Coyote Creek surface water sampling locations. Cost and ownership issues may preclude the use of the discharge location suggested by Jones & Stokes. However, based upon an initial review, the Jones & Stokes outfall and sampling locations appear to be well-chosen and relevant to the current project. For these locations, one control point is proposed upstream of the augmentation outfall, and six locations are proposed downstream, ranging from a distance of ½ mile downstream to ten miles downstream. Figure 2 displays a map of the sampling locations proposed in the *Revised Initial Study*.

The *Revised Initial Study* does not make recommendations regarding groundwater sampling locations.



Jones & Stokes

Figure 2-5
Location of Water Quality Monitoring Stations
on Coyote Creek

Figure 2 Sampling Locations Proposed in the Jones & Stokes *Revised Initial Study*

Section 3: Sampling Approach

Sample Collection, Handling and Custody

The following procedure will be followed for sample collection, handling and custody:

1) Water samples will be collected in one-liter amber glass bottles with Teflon-coated caps. The bottles and caps will be triple-rinsed with sample before filling. The sample ports will be equipped with Teflon tubing to allow filling of the bottle from the bottom to the top.
2) A total volume of 4 L will be collected from each location during each sampling round.
3) Once filled, each bottle will be labeled with a unique sample identification number that specifies the date and time of the sample, the sample location within the system, sampler's initials, and any other pertinent information (e.g. field duplicate).
4) The bottles will then be placed on ice in a cooler and transported directly to Stanford University.
5) Upon arrival, the samples will be filtered immediately through 0.2 µm nylon filters (Nylon 66, 0.2 µm) from Sigma-Aldrich (Bellefonte, PA, USA) to inhibit microbial activity and to minimize cartridge clogging during solid phase extraction (SPE).
6) The samples will be stored at 4^{o}C, and processed within 48 hours of arrival.

Sampling and Monitoring Plan

Surface Water Sampling

Early in both the Baseline phase and Augmentation phase, a sub-study will be conducted to determine 24-hour variation. Four samples will be taken at one sampling location over the course of a day to determine if concentrations of the target compounds differ greatly depending on time of day.

In the Baseline phase, samples will be taken from each surface water sampling location on a once-per-month basis for a total of six months, beginning in summer 2005. Under augmentation conditions, samples will be taken from each surface water sampling location monthly for the duration of the augmentation.

Groundwater Sampling

Hydrological interactions between Coyote Creek surface water and groundwater have not yet been determined. Wells will be monitored monthly during the Baseline phase for a period of six months to determine baseline concentrations. During the augmentation phase, wells will be monitored every month for one year to determine if target compounds from augmentation have impacted groundwater quality.

Additionally, a sub-study analyzing percolation will be conducted in conjunction with relevant laboratory studies. At a to-be-determined location, wells will be installed with screens directly in the infiltration flow path so that contaminant attenuation can be assessed as a function of distance and residence time.

Section 4: Analytical Methods and Quality Control

A final decision of water quality parameters to be tracked during the study will be made based upon the results of the initial screening. A probable scenario is that general water quality parameters will be measured on-site using appropriate sensors. This includes dissolved oxygen (D.O.), pH, electrical conductivity, and temperature. Dissolved organic carbon (DOC) and nitrate and sulfate will be measured by Stanford University. Trace organics will be analyzed by either gas chromatography/mass spectroscopy (GC/MS) or liquid chromatography/tandem mass spectroscopy (LC/MS/MS) at Stanford University.

Table 5 Summary of Analytical Procedures

Characteristic	Method
On-Site Parameters Temperature Electrolytic Conductivity (E.C.) Dissolved Oxygen (D.O.) pH	Appropriate sensors
DOC	Combustion with IR detection
Anions: nitrate, sulfate	Ion Chromatography (IC)
Target Chemicals: Depending on results of screening, may include: Pharmaceuticals and metabolites, surfactant metabolites, plasticizer and flame retardants Hormones	Gas Chromatography/ Mass Spectroscopy (GC/MS) or Liquid Chromatography/Tandem Mass Spectroscopy (LC/MS/MS)

Analysis of On-site parameters

Dissolved oxygen (D.O.) concentration, pH, conductivity and temperature will be measured using appropriate environmental sensors by staff during sampling.

Analysis of Dissolved Organic Carbon (DOC)

The DOC measurements will be made on a Shimazu TOC analyzer (TOC-5050) using a combustion-nondispersive infrared method at 680 °C. Samples will be acidified with hydrochloric acid (HCL) to pH 2 and purged to remove carbon dioxide before measurement. Calibration standards are prepared with potassium hydrogen phthalate.

Analysis of Anions

Anions (e.g. sulfate, nitrate) will be analyzed using a Dionex Series DX 500 ion chromatograph (IC) equipped with a Dionex conductivity detector (series CD 25), a Dionex IonPac AS11-HC column (4 mm x 250 mm), and an AG110HC guard column (4 mm x 50 mm). Sodium hydroxide (25 mM) will be used as the eluant and external standards are used for quantification. If required, samples (200 µl) may be centrifuged and diluted prior to analysis.

Analysis of Trace Organic Compounds

Sample Preparation

Pharmaceuticals and Metabolites, APEMs, NBBS, TCPPs

Water samples are acidified to a pH of 2-2.3 using sulfuric acid. C-18 cartridges with 1.0 g sorbent (Alltech, IL, USA, extract-clean columns, 8 mL) are used to extract the target contaminants from 1 L samples. For samples >1 L, multiple cartridges are used and their eluants combined. SPE is performed using a 16-port vacuum extraction manifold. Cartridges are conditioned sequentially with 6 mL acetone, 6 mL acetonitrile, and 10 mL Milli-Q water (pH 2). The solvents are drawn through the cartridges by applying a slight vacuum. Water samples are drawn through the cartridge at a flow rate of 10 mL/min or less applying a slight vacuum. The cartridges are then washed with a small amount of Milli-Q water and dried using a stream of nitrogen for 1.5 to 2 h. Analytes are eluted with 5 mL acetonitrile, followed by 5 mL acetone. The extract is concentrated by a slight stream of purified nitrogen to 30 μL and divided into two aliquots.

To one aliquot, 10 μL of a 50 mg/L internal standard solution (chrysene-d_{12}) is added for analyzing the neutral compounds. The second aliquot is used to analyze for acidic compounds. In this aliquot, carboxylic acids are converted into their respective propyl esters by adding 10-20 μL of *n*-propanol/acetylchloride (90/10 volume per volume (v/v)) to the evaporated samples and heating for 1 hour at 85 °C. After propylation, the samples are evaporated to near dryness and 10 μL of the chrysene-d_{12} internal standard solution is added.

Hormones

C-18 cartridges (1.0 g sorbent, Alltech, IL, USA, extract-clean columns, 8 mL) are conditioned sequentially with 6 mL acetone, 6 mL methanol, and 10 mL Milli-Q water. The solvents are drawn through the cartridges by applying a slight vacuum. Water samples are drawn through the cartridge at a flow rate of 10 mL/min or less applying a slight vacuum. The cartridges are then washed with a small amount of Milli-Q water and dried using a stream of nitrogen for 1.5 to 2 h. Analytes are eluted with 5 mL methanol, followed by 5 mL acetone. The extract is concentrated to near dryness and reconstituted in a total of 200 μl of methanol.

Extracts from water samples containing more than 6.0 mg/L DOC require an additional clean-up step prior to analysis. Briefly, the SPE extracts are evaporated to near dryness, redissolved in 0.5 mL acetone and transferred to silica gel cartridges (Alltech, IL, USA, extract-clean columns silica, 1.0 g, 8 mL). The analytes are then eluted with 10 mL of a hexane/acetone (60/40, v/v) mixture, evaporated to near dryness and derivatized as described above.

GC/MS Analysis

An Agilent 6890 Series GC system coupled to a Varian 1200 Triple Stage Quadrupole Mass Spectrometer (MS) is used (Varian, Walnut Creek, CA, USA). A DB-5 capillary column (30 m x 0.32 mm I.D., film thickness 0.25 μm; Agilent, Wilmington, DE, USA) is employed using helium as the carrier gas. For the neutral and acidic fractions, the GC conditions are: injector temperature 275°C, constant flow mode of 2.6 mL/min, 1 µL splitless injection, 100°C isothermal for 5 min, increasing from 100°C to 280°C at 5°C/min, the final temperature is held for 4 minutes. MS conditions are: full scan mode, electron impact (EI) mode at ionization energy 70 eV, emission current 300 µA, ion source temperature 200°C, electron multiplier voltage 1500 V and transfer line 280°C.

APs, APEOs and APECs as well as tris(3-chloropropyl)phosphate, tris(2,3-dichloropropyl)phosphate and N-butyl benzenesulfonamide ware monitored in the total ion current (TIC) mode (mass range m/z = 50 – 550; scan time 0.5 s) and quantified using their base ions. Since APs, APEOs, APECs, and CAPECs occur as complex mixtures [23], the different isomers are manually differentiated with respect to the number (n) of ethoxy groups and the length of their alkyl-chain (i.e., octyl or nonyl). APECs and CAPECs, which produce many of the same mass spectral fragments, are generally reported as the sum of the APECs and CAPECs (denoted as A+CAPECs). No commercial standards are available for tris(3-chloropropyl)phosphate and tris(2,3-dichloropropyl)phosphate. These compounds are tentatively identified in the samples by comparing the spectral characteristics of the sample peak with spectral characteristics of the tris-chloropropylphosphates (TCPPs) in the NIST (National Institute of Standards and Technology) mass spectral library.

Pharmaceuticals (acids as propyl esters) are identified based on their retention time and at least two qualifier ions and are semi-quantified in the single-ion monitoring (SIM) mode using the base ion indicated in Table 2. Identification of carboxy-ibuprofen is based on the EI mass spectrum of the respective propyl ester and literature data. Hydroxy-ibuprofen is identified as the propyl ester of 2-[4-(2-methylpropenyl)phenyl] propionic acid . This compound is probably generated by dehydration of hydroxy-ibuprofen, a common reaction for tertiary alcohols under acidic conditions. The propyl ester of the main human metabolite of naproxen, 6-O-desmethyl-naproxen, is tentatively identified based on manual interpretation of the EI spectrum.

Concentrations of the individual compounds are determined *semi-quantitatively* by comparing the base ion with the m/z 240 ion of an internal standard, chrysene-d_{12}. Thus, the reported concentrations are based on the assumption that the response factors for the internal standard and the analyte are the same. The reporting limit for the pharmaceuticals is 5 ng/L (detection limit 1 ng/L). APECs are reported at 1 ng/L (detection limit 0.5 ng/L) and APs and APEOs have a reporting limit of 3 ng/L (detection limit 1 ng/L). As no standards were available, the reporting and detection limits for CAPECs were assumed to be the same as those for APECs.

LC/MS/MS Analysis

Analyses are carried out using a Shimadzu HPLC system consisting of an SIL-10ADvp auto sampler and a LC-10ADvp LC pump. Chromatographic separation is performed using a reversed-phase C18 column (50mm x 2.1mm, 5µm, Higgins Analytic, Foster City, CA). Detection is carried out by a Sciex API 3000 triple stage quadrupole mass spectrometer (Applied Biosystem, Toronto, Canada) using an atmospheric-pressure photoionization (APPI) interface. Nitrogen is generated by a Parker-Balston Nitrogen generator system (model N2-4000), and compressed air by a Parker-Balston Zero-Air generator (model 76-818) and air dryer from Parker-Balston (model 64-01). The mobile phase composition and the mass spectrometer parameters are listed in Table 6. The flow rate is 0.1ml/min (for APPI) with an injection volume of 50 µl. Toluene is used as a dopant at a flow rate of 10 µL/min for APPI. The MS-MS parameters are optimized in the continuous flow mode. After the best conditions for the isolation of each individual precursor ion is determined (Declustering potential (DP), collision energy (CE), and collision cell exit potential (CXP)), the nebulizer pressure, ion spray voltage, drying gas temperatures are optimized. The mass spectrometer is operated in the multiple reaction monitoring (MRM) mode with high resolution on the first analyzer and unit resolution on the second. A dwell time of 200 ms per monitored ion pair is used.

Table 6 LC/MS Parameter for Hormone Analysis

Parameter	
Solvent A	Water
Solvent B	Methanol
Ionization Mode	APPI Positive
Drying gas flow (L/min)	Nitrogen
Drying gas temperature (^oC)	400
Nebulizer pressure (psi)	Nitrogen
Capillary voltage (V)	1800

For all four hormones, 8-point calibration curves will be constructed using a least-square linear regression analysis from the direct injection of standard solutions. Limits of detection (LOD), representing the lowest concentration detected, will be experimentally determined from the lowest standard concentration (0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 2, 20 µg/L) in the linear range with a minimum signal-to-noise ratio of 3. LODs will be determined via direct injection of standard solutions without further pre-concentration and will represent the LOD of the instrument.

Quality Control Samples and Procedures for Laboratory Analyses

Blanks. For each sampling round there will be at least one preparation blank for the GC/MS and LC/MS/MS analyses. The preparation blank will consist of laboratory pure water and will be processed through all procedures, materials and labware used for sample preparation and analysis. Analytical results from blanks will indicate any contamination or bias resulting from the method.

Internal standards. An internal standard is a reference material added to a sample at a known concentration, and is used to calculate the concentration of an analyte. Chrysene-d_{12} will be used as the internal standard for all GC/MS analyses.

Sample replicates/duplicates. Precision will be determined using duplicate or replicate samples. Duplicate samples are collected in a common container and then transferred to two or more individual containers; replicates are collected sequentially in individual containers. At least one duplicate/replicate will be included in each sampling round for each type of laboratory analysis. Precision can be expressed as percent relative difference (%RD):

$$\%RD = 100\frac{|C1 - C2|}{0.5(C1 + C2)}$$

where

C1, C2 = individual measurements of duplicate/replicate samples

The acceptance limit for percent relative difference is less than or equal to 20%.

Surrogate spikes. Surrogate spike compounds are analytes that are typically not found within the sample matrix, and are added to a sample for validation of accuracy. Accuracy as measured by spike recovery is expressed as percent recovery (%R):

$$\%R = 100\left(\frac{C_M}{C_S}\right)$$

where

C_M = measured concentration of analyte

C_S = spiked concentration of analyte

The acceptance range for accuracy is typically 85%-115%. Surrogate spikes will be used periodically for LC/MS/MS and GC/MS analyses to determine accuracy.

Calibration curves and laboratory control samples. Calibration curves will be developed for IC, TOC analyzer, and LC/MS/MS analyses as described previously. The accuracy of these calibration curves will be tested periodically during the project using laboratory control samples (samples of known value). Accuracy can be evaluated using the equation for percent recovery shown above, where C_s represents the known concentration of the sample. The acceptance range for accuracy is typically 85%-115%.

Corrective action to address any quality control problems that arise may involve reanalysis of samples, collection and analysis of new samples, or use of supplementary information to validate the original data.

Instrument Maintenance

All analytical equipment housed at Stanford University (ion chromatograph, GC/MS, LC/MS/MS) is maintained by in-house professionals and/or contracted technicians as specified by the manufacturers. A maintenance log is kept for each instrument.

Section 5: Data Management, Validation and Analysis

Data will be collected and managed so that the objectives of the study can be fulfilled. Experimental data will be tabulated onto a standard form, and electronic files will be kept for grab samples and *in situ* measurements. This data will be accumulated and maintained in Excel spreadsheets for further analysis and graphing. All data will be backed up on a regular basis. Hard-copy reports for each test will be generated and maintained with other experiment data. Quality assurance data including calibration curves, reagent blanks, check standards, duplicates, and spikes will also be maintained.

Section 6: References

Ball, H. A. and M. Reinhard (1984). Discharge of Halogenated Octylphenol Polyethoxylate Residues in a Chlorinated Secondary Effluent. Water Chlorination. Chemistry, Environmental Impact, and Health Effects. R. L. Jolley, R. J. Bull, W. P. Daviset al. Chelsea, MI, Lewis Publishers, Inc. 5**:** 1505-1514.

Gross, B., J. Montgomery-Brown, A. Naumann and M. Reinhard, 2004. Occurrence and Fate of Pharmaceuticals and Alkylphenol Ethoxylate Metabolites in an Effluent Dominated River and Wetland. Environ. Tox. Chem. in press.

Jones & Stokes (2000). Initial Study/Mitigated Negative Declaration, Coyote Creek Streamflow Augmentation Pilot Project. Prepared for City of San José Environmental Services Department.

Reinhard, M., W.-H. Ding, J. Zhou and E. Orwin (1999). Organic Contaminant Behavior During Groundwater Recharge with Reclaimed Wastewater and Santa Ana River Water: A Laboratory and Field Evaluation. Stanford, CA 94305-4020, Department of Civil Engineering, Stanford University.

Reinhard, M. and D. J. (2001). Organic Contaminant Behavior During Wetland Treatment and Groundwater Recharge. SARWQH 1998-2000. Fountain Valley, CA., Orange County Water District.

SCVWD (Website Referenced November, 2004). http://alert.valleywater.org/gagestrm.html

Appendix A

Budget

Expense	Reimbursable	In-Kind	Total
Labor and labor additive	$ -	$ 60,000	$ 60,000
Equipment (non-consumables)	$ -	$ 40,000	$ 40,000
Materials & supplies	$ -	$ 50,000	$ 50,000
Consultants	$ 200,000	$ -	$ 200,000
Contractors (well drilling)	$ 100,000	$ 50,000	$ 150,000
Contractors (laboratory)	$ -	$ 100,000	$ 100,000
Subtotal	$ 300,000	$ 300,000	
Total			$ 600,000

ATTACHMENT B

MEMORANDUM

TO: Henry Barrientos

FROM: Seena Hoose, PG 4355

SUBJECT: Upper Silver Creek Stream-flow Augmentation with Recycled Water

DATE: March 1, 2005

OBJECTIVES

The first objective is to determine whether the segment of Upper Silver Creek from the bridge just upstream of the recycled water tank downstream to the beginning of the concrete lined channel is in the confined or the unconfined area of the north Santa Clara Valley groundwater sub-basin.

The second objective is to evaluate whether recharge from the segment of Silver Creek between the bridge just upstream of the recycled water tank and the concrete lined channel downstream is likely to reach the primary drinking water aquifers in the rest of the groundwater subbasin.

The segment of Upper Silver Creek under consideration is illustrated on the air photo on Figure B.

BACKGROUND AND OFFICE REVIEW

Two reports were written for the Evergreen Area in 2002. A memorandum titled Evergreen Area Groundwater Movement and Relationship to Main Basin was written by Seena Hoose and Cindy Kao on February 16, 2002. A report titled “Irrigation of Recycled Water in Evergreen and Potential to Impact Groundwater Quality in Santa Clara County” was written by Cindy Kao and Seena Hoose on May 20, 2002. These reports cover a larger area and are more generalized than the present evaluation, however they provide substantial information for this site specific evaluation.

Regional conditions and known faults from Kao and Hoose, 2002 are illustrated on Figure 2. The faults shown on fig. 2 are from Dibblee, 1972, and from east to west are the Quimby, Evergreen, and Silver Creek faults. These thrust faults are related to right lateral movement on the Calaveras Fault to the east, and are moving the bedrock from the east up toward the west, over the valley floor. Segments of the Quimby and Evergreen faults are shown as tectonically active on the Alquist-Priolo Fault Hazard Map, 1982. The Silver Creek fault appears to be a very complex thrust fault within a compressional system with a series of fault strands on both the east and west pushing up Evergreen Ridge. Silver Creek flows through the middle of the fault strands. Detailed studies have been performed on the Silver Creek Fault as required by the City of San Jose and Santa Clara County prior to land development. At the Silver Creek Golf and Country Club multiple active fault strands determined the placement of the golf course or roadways. These site specific maps were not readily obtainable for this evaluation. The thrust fault conditions explain the possible compartmentalization of groundwater resulting in a series of small groundwater micro-basins within the Evergreen Area.

Another line of evidence suggesting the lack of groundwater continuity between the Evergreen area and the central part of the Santa Clara subbasin is provided by the INSAR study done for the District (Ikehara, et. al., 1999). This study shows a small but measurable difference in land elevation between spring and fall, with the Evergreen area staying the same or rising slightly (14mm) and the central groundwater basin sinking slightly (-30 mm). The INSAR study report states, “The eastern extent of this deformation appears truncated by the Silver Creek fault. The fault, considered tectonically inactive, likely acts as a barrier to ground-water flow. The fault may have juxtaposed alluvial sediments of contrasting permeability and compressibility.”

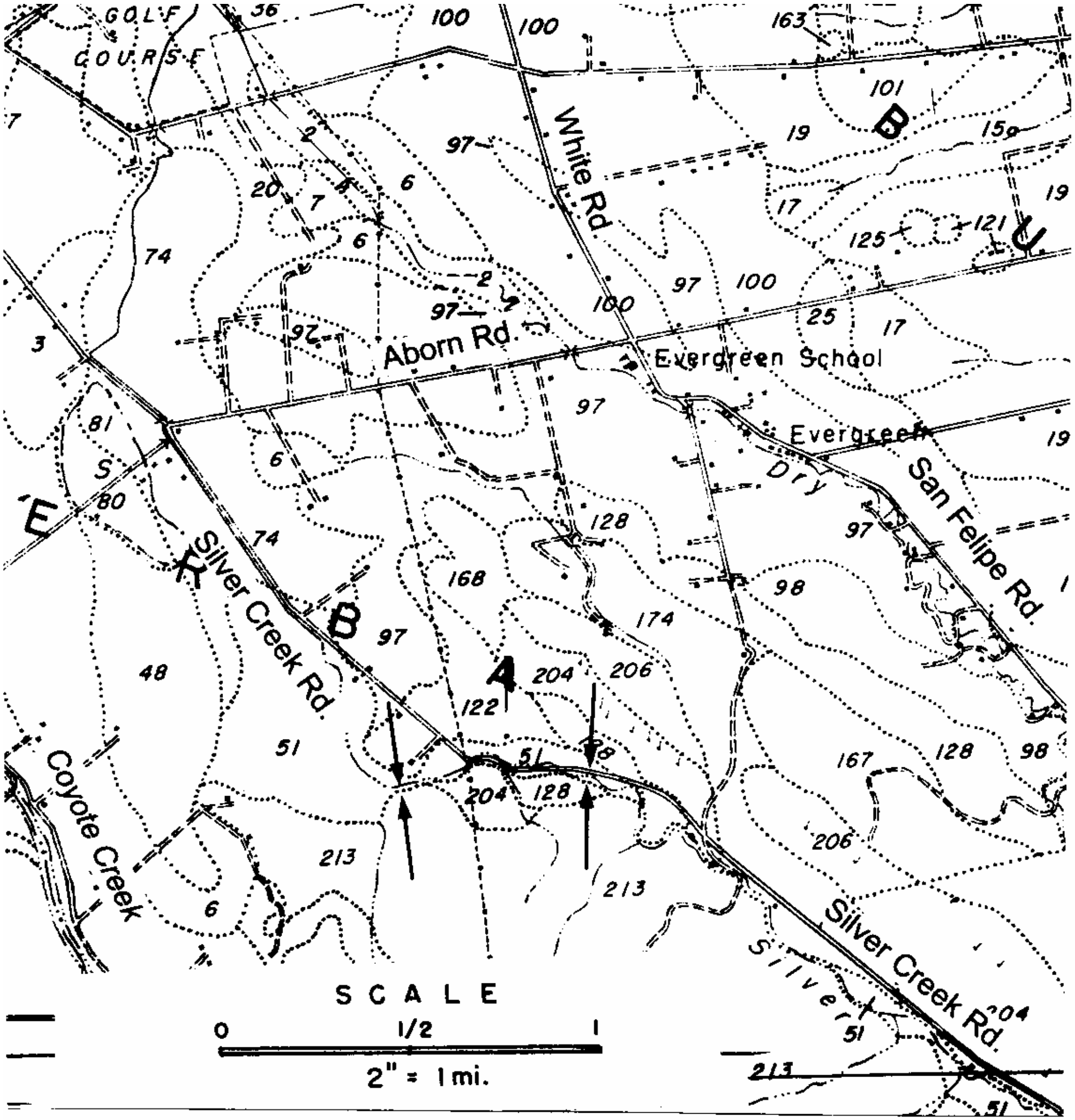


Figure 3. The soil map by Weir and Storie, 1947 provides information on soil texture and surface drainage along the segment of Upper Silver Creek, shown between the pairs of double arrows on the map.

Soil Map units adjacent to Upper Silver Creek in the area under consideration are:

51 = Edenvale adobe clay, surface drainage good
122 = Milpitas loam B to BB***, surface drainage fair
128 = Milpitas loam (moderately eroded) C to D. surface drainage fair
204 = Montara stony clay, climax clay, DD, surface drainage excellent
213 = Montara stony clay, CC to DD, surface drainage excellent

Edenvale Adobe Clay (51) falls in the A4 grouping of "heavy textured soils having moderately dense subsoils". This soil grouping is clay and silty clay and where associated with stream terraces are less well drained. Through the Silver Creek segment under consideration this soil is found on stream terraces west of the creek and a little to the east of the creek.

The Milpitas Clay Loam (122 and 128) is just east of the Edenvale Adobe Clay along the east side of Silver Creek in the area under consideration. The D9 soil grouping is "medium-textured soils having dense clay subsoils" that result in low permeability. The Milpitas Loam has subsoil with massive clay pans normally of very heavy clay texture. Milpitas soils have good surface drainage, but the dense subsoils restrict subsurface drainage. This is consistent with field observations of ponded water on the surface of these soils.

The Montara Stony Clay (204 and 213) is "heavy textured soils less than two feet in depth on hilly topography" and "stony soils, less than two feet in depth on rolling to hilly topography". These soils dominate the Edenvale Hills west of the creek and are consistent with field observations of soil, serpentenite, and calcareous marine sedimentary rocks exposed on the uphill (west) side of the pathway along the creek.

Generalized data from a soils map provides information about the rate of infiltration from the creek into the groundwater, as well as the likelihood of rapid groundwater movement.

FIELD EVALUATION

The objective of this excursion was to evaluate whether the location is in the unconfined groundwater area or not and the potential impact on groundwater quality of allowing recycled water to flow down Upper Silver Creek from the recycled Water Tank. In order to accomplish this objective it is necessary to observe the bed and banks of the stream to evaluate the location and amount of sand and gravel available for the stream to recharge the groundwater. In addition it is appropriate to evaluate the general geologic and topographic conditions.

On January 13, 2005 Seena Hoose, Chris Gurr, and Henry Barrientos conducted a reconnaissance field excursion along the Upper Silver Creek footpath from the end of Silver Creek Road upstream to the Recycled Water Tank Facility (fig. 4). This was followed by driving, with two stops, from the footpath bridge downstream as far as the beginning of the concrete lined channel section of the creek.

The portion of the reach upstream of the footbridge is either immediately adjacent to the bedrock hillside or has very clay rich banks and it appears the creek bottom is also clay rich. Both of these conditions also exist along the reach downstream from the footbridge at the end of Silver Creek Road to the concrete lined channel.

The portion of the creek between the upstream bridge and the approximate location of the swale downstream of the recycled water tank has sand and some gravel in the bedload and includes some sandy zones (beds) in the creek banks.

Just north of the recycled water tank, a swale was observed coming off the hillside at an oblique angle toward the creek. The swale had boggy places or pond in the bottom. The swale exhibits the characteristics of a fault trace and could be a potential fault that has not been identified on readily available geologic maps. Fault investigations were performed by Kleinfelder Inc. for the Silver Creek Golf and Country Club development in the City of San Jose. These maps are currently not available at the District.

DISCUSSION

Previous investigations (Kao and Hoose) identified several faults crossing the Evergreen Area that appear to create very small groundwater micro-basins in the area. Thus, the reach upstream of the swale (probable fault) will most likely recharge a limited area of groundwater.

Faults are typically either a pathway for groundwater flow or a barrier to groundwater flow. The INSAR data indicates that the Silver Creek fault is a barrier to groundwater flow. The Silver Creek is really a complex series of fault strands and probably has moved the permeable stream channel and alluvial fan deposits up against more fine grained, clay rich, flood basin, lake, marsh, or bay mud deposits. This effectively shuts off the pathways for groundwater movement across the fault zone.

The exact location of the Silver Creek fault strands where they leave the ridges to cross the valley floor is only generally known. Thus, there is some uncertainty about a series of fault strands west of the segment of Upper Silver Creek under consideration to provide a barrier to groundwater flow into the main sub-basin. If the swale is formed by a fault strand, then recharge from the creek will reach a micro-basin to the south and east of that particular fault strand. If the swale is simply a topographic feature and not a fault strand, then the recharge from the creek will reach a downstream micro-basin and would rely on those portions of the Silver Creek fault which are only generally located to prevent groundwater migration into the main sub-basin. This second situation has a greater degree of uncertainty than the one where the swale is known to be a fault trace.

The soil map shows heavy clay with low permeability in the subsoil along most of the segment of Silver Creek under consideration. This indicates that not much recycled water will recharge from the creek to the groundwater. The field observations coincide with the soil map information.

FINDINGS

- The segment of Upper Silver Creek being considered for stream augmentation is in the unconfined area of the groundwater sub-basin, as shown on fig. 2.

- It appears that discharge of recycled water into Upper Silver Creek adjacent to the Recycled Water tank will recharge along a short upstream portion of the reach and will enter a groundwater area of limited extent. The reconnaissance information together with office review and previous work appears to indicate that a direct groundwater connection to the main portion of the Santa Clara Valley sub-basin is unlikely.

RECOMMENDATIONS

- Chris Gurr indicated that they were planning to install two wells to monitor the impact of the recycled water on the groundwater, if any. He asked for my suggestions which follow. Monitoring wells should be installed on the north side of the creek. The first well should be located close to the discharge point into the creek and screened in the first permeable material just below the creek bed elevation. A second well should be located somewhat further downstream, further to the west of the creek, and screened at a greater depth. The exact locations and screen intervals should be determined at a later date and will depend on site specific conditions.

- Abandoned, lost, or unused wells should be located and properly destroyed within 2000 ft of the creek.

- Creek and groundwater samples should be collected and analyzed as baseline data before the project begins. There should be a minimum of 4 to 8 samples collected at different times and different flow conditions.

- Obtain copies of the various Silver Creek fault investigations done for developments. These are needed for future work in the Evergreen area by the District.

- Prior to beginning the project, the groundwater data collected by the City of San Jose at sites using recycled water should be provided to the District. The District should analyze this data for potential impacts to groundwater from the use of recycled water.

Seena N. Hoose, Engineering Geologist, E.G. 1492
Professional Geologist, P.G. 4355

List of Figures

B. The segment of Upper Silver Creek under consideration on an air photo base map.
2. A regional map showing the confined area and the unconfined area, the reach under consideration, faults, and planned recycled water users.
3. Soil map showing the reach under consideration and the soil types present along the creek.
4. A contour map showing the parking place, footpath, recycled water tank, bridges, concrete lined channel, swale and hypothetical fault.

References

California Department of Conservation, Division of Mines and Geology, 1982, Official Maps of Alquist-Priolo Earthquake Fault Zones of California, Central Coast Region, San Jose East Quadrangle, Scale 1:24,000.

Dibblee, Thomas W. Jr., 1972, Preliminary geologic map of the San Jose East quadrangle, Santa Clara County, California: U. S. Geological Survey Open-File Map No. 72-92.

Hoose, S., and Kao, C., 2002, Evergreen Area Groundwater Movement and Relationship to Main Basin; Memorandum Report to Behzad Ahmadi, February 16, 2002, 9 pages, 4 figures.

Ikehara, Marti E., Galloway, Devin L., Fielding, Eric J., Burgmann, Roland, Lewis, A. Scott, Ahmadi, Behzad, 1999, INSAR imagery reveals seasonal and longer-term land-surface elevation changes influenced by ground-water levels and fault alignment in Santa Clara Valley, California: U.S. Geological Survey cooperative study.

Kao, C., and Hoose, S., 2002, Irrigation of Recycled Water in Evergreen and Potential to Impact Groundwater Quality on Santa Clara County, Santa Clara Valley Water District Report May 2002, 7 pages, 2 figures.

Weir, W. W., and Storie, R.E., 1947, Soils of Santa Clara County, California: University of California, College of Agriculture, Agricultural Experiment Station, Berkeley, California, 62 pages, sheets 15, 10, and 11.

Geologic information on file at the City of San Jose Building Department but not readily available for this evaluation.

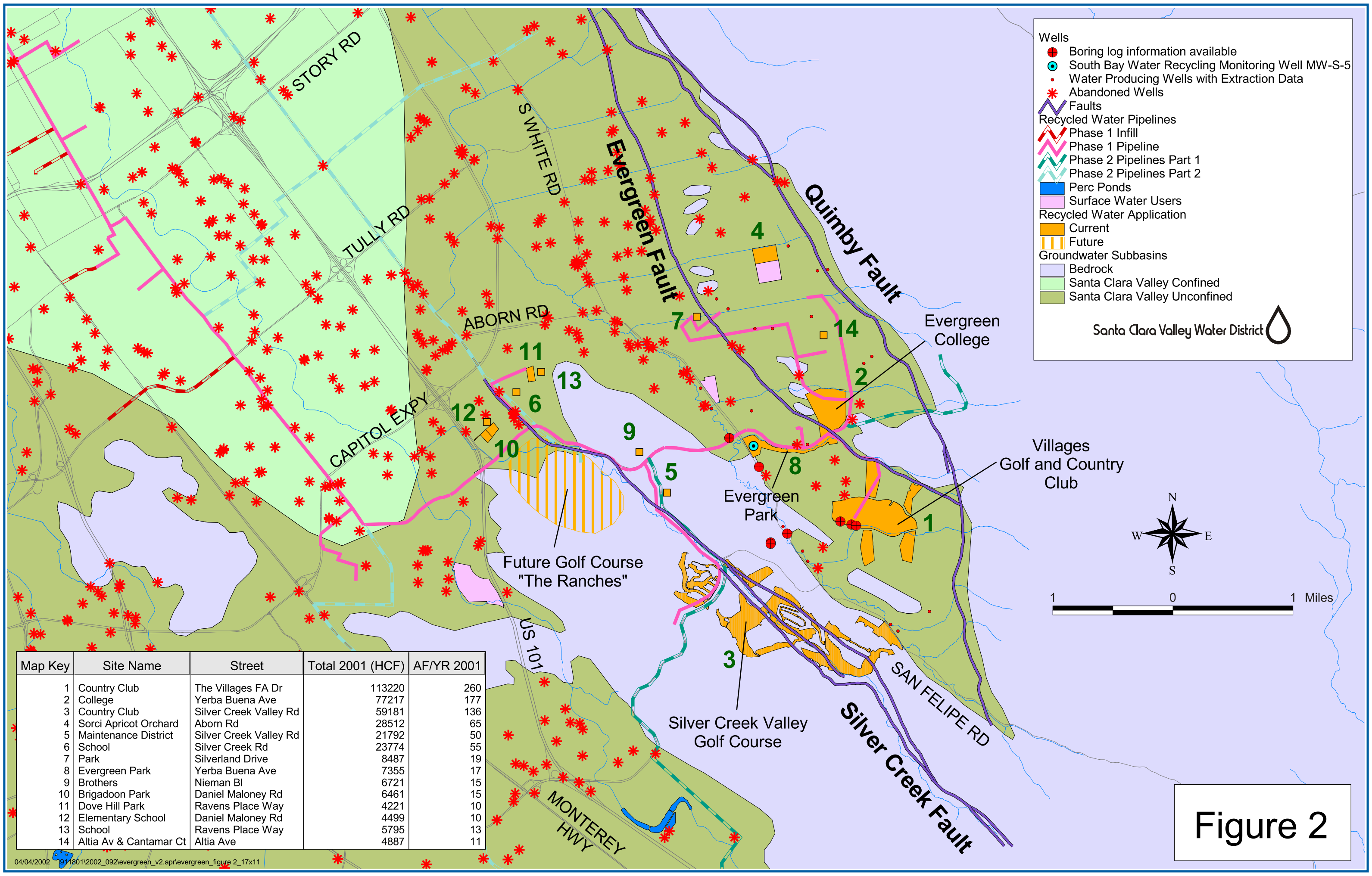
Alquist-Priolo Fault Hazard Investigations submitted to the City of San Jose for the Silver Creek Golf and Country Club development.

Alquist-Priolo Fault Hazard Investigations submitted to the City of San Jose for the recycled water tank and associated facilities.

Alquist-Priolo Fault Hazard Investigations submitted to the City of San Jose for the new housing development accessed by a bridge across Upper Silver Creek at the beginning of the concrete lined channel.

Location of files associated with this report.

Text File and path: G://Seena/Memo_Silver Creek Recycle h2o.msw.doc
Figure 2 File and Path: G\\Seena\Silver Creek-05\figure2_rev1.pdf (an adobe file)
Figure 3 scanned and included in the text as an object
Figure 4 File and Path: G:\\Seena\Silver Creek -05\Silver_Creek_Airphoto.mxd (an Arc Map file, see the layout)



Map Key	Site Name	Street	Total 2001 (HCF)	AF/YR 2001
1	Country Club	The Villages FA Dr	113220	260
2	College	Yerba Buena Ave	77217	177
3	Country Club	Silver Creek Valley Rd	59181	136
4	Sorci Apricot Orchard	Aborn Rd	28512	65
5	Maintenance District	Silver Creek Valley Rd	21792	50
6	School	Silver Creek Rd	23774	55
7	Park	Silverland Drive	8487	19
8	Evergreen Park	Yerba Buena Ave	7355	17
9	Brothers	Nieman Bl	6721	15
10	Brigadoon Park	Daniel Maloney Rd	6461	15
11	Dove Hill Park	Ravens Place Way	4221	10
12	Elementary School	Daniel Maloney Rd	4499	10
13	School	Ravens Place Way	5795	13
14	Altia Av & Cantamar Ct	Altia Ave	4887	11

04/04/2002 911801\2002_092\evergreen_v2.apr\evergreen_figure 2_17x11

Figure 2

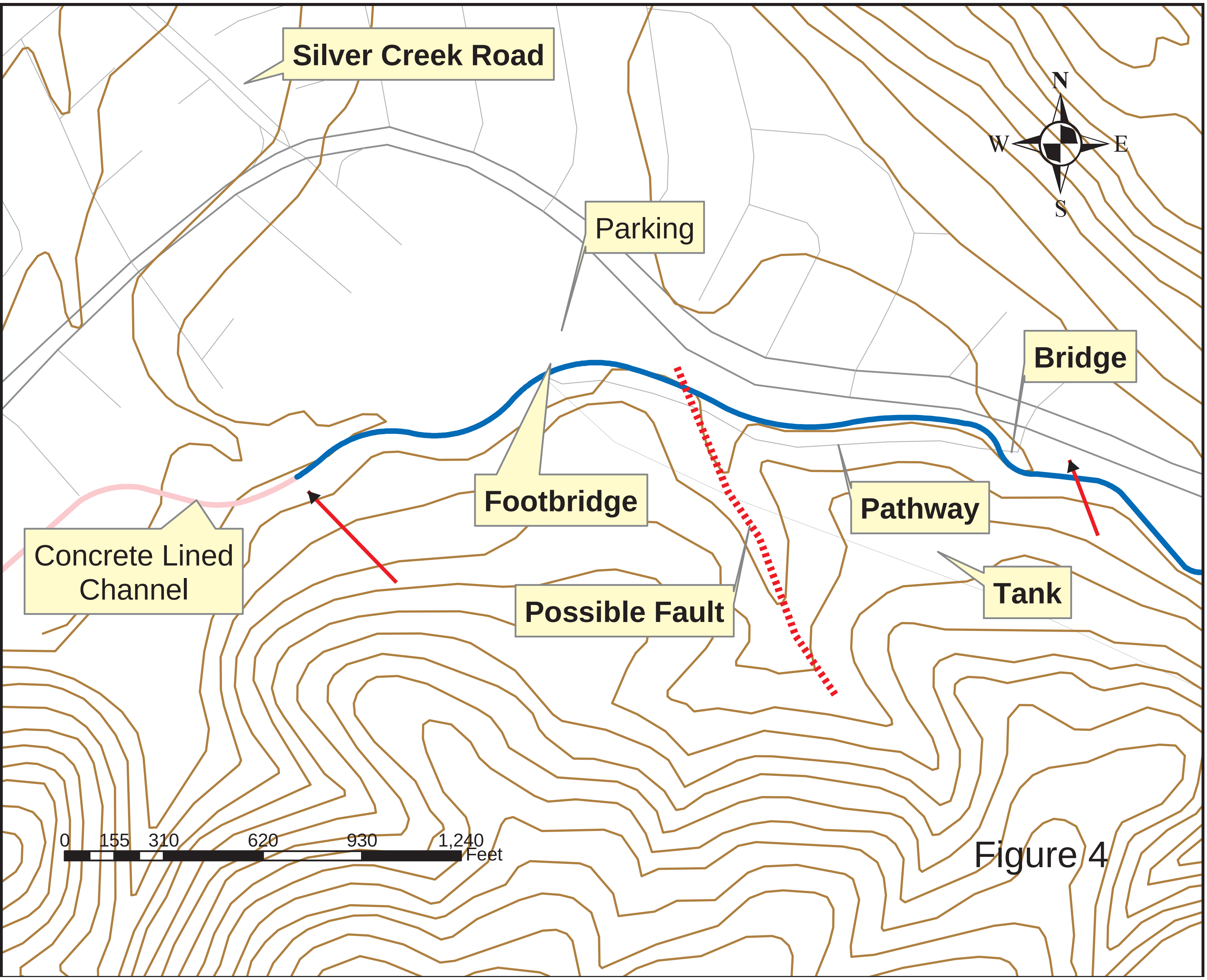

Silver Creek Road
N
W
E
S
Parking
Bridge
Footbridge
Pathway
Concrete Lined Channel
Tank
Possible Fault
0
155
310
620
930
1,240
Feet

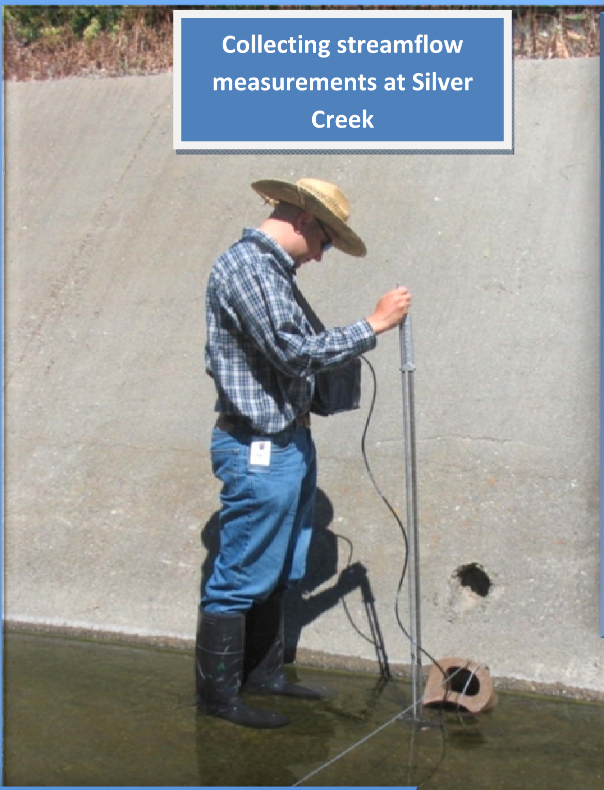
Figure 4

Appendix K

Project Photographs

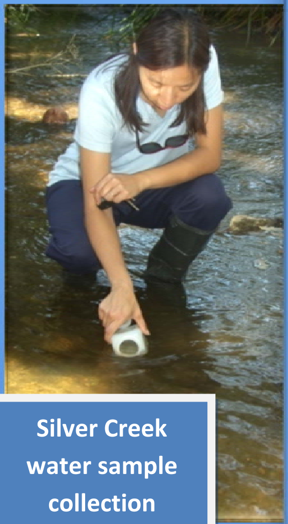
Water level measurements from push wells in stream

Equipment inventory at Silver Creek



Collecting streamflow measurements at Silver Creek

Taking temperature loggers out of streams



Silver Creek water sample collection

Demonstration of temperature loggers in streams

Demonstration of temperature loggers in push wells