Santa Clara Valley
Water District

1,4-Dioxane

and other

S O L V E N T   S T A B I L I Z E R S

W H I T E   P A P E R

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Introduction

Industrial solvents used in degreasing, electronics, metal finishing, fabric cleaning, and many other applications are commonly formulated with additives to enhance their performance. These additives, known as *solvent stabilizers*, serve to prevent solvent breakdown and to inhibit reactions that may degrade solvent properties. Many solvent stabilizer compounds are present at volumetrically inconsequential proportions to be considered significant for solvent release site investigation and cleanup. One ether stabilizer, 1,4-dioxane, has been included with 1,1,1-trichloroethane (TCA, also called methyl chloroform) in mixtures at 2 to 8% by volume, and has proven to be a contaminant of concern at solvent release sites. Other solvent stabilizer compounds may also be problematic. The industrial applications in which solvents are used, such as cold vapor degreasing, tend to increase the proportion of some stabilizers in condensate relative to the host solvent. Once these waste residuals are spilled, leaked, or dumped to the subsurface, 1,4-dioxane tends to be refractory to the biotransformation of TCA, resulting in further increases in the relative proportion of stabilizers.

Solvent stabilizer compounds have thus far received relatively little attention from regulatory caseworkers and remedial project managers at solvent release sites. 1,4-dioxane was not detectable at low concentrations in a standard laboratory scan for chlorinated solvents, and Maximum Contaminant Levels have not been established for this compound. This may explain why solvent stabilizer compounds are not routinely analyzed in groundwater at solvent release sites, or included in the cleanup objectives of regulatory orders. It is only within the past few years that improvements to laboratory methods for 1,4-dioxane have made it possible to obtain reliable detections at concentrations comparable to other volatile organic compounds. Familiarity with solvent stabilizer compounds can aide in site investigation, remedial design, forensic investigations, and water supply management.

California's regulatory guidance for 1,4-dioxane is a Department of Health Services Drinking Water Action Level (3 ug/L). 1,4-dioxane is listed as a Class II-B probable human carcinogen, and is known to damage the kidneys. 1,3-dioxolane, an alternative stabilizer for TCA, has similar physical and chemical properties to 1,4-dioxane (see Section 2.1, below); however, it is not listed as a US EPA Clean Water Act Priority Pollutant.

1,4-dioxane is not significantly removed by conventional pump and treat technologies (air stripping and carbon adsorption), and is generally resistant to biodegradation. Advanced oxidation processes, the primary available treatment technology successful in removing 1,4-dioxane from groundwater, is expensive and energy-intensive.

This report summarizes information obtained on solvent stabilizers from an extensive literature review, and presents the nature and use of solvent stabilizers, how they behave in the subsurface, a description of laboratory analytical techniques, a summary of toxicological information for solvent stabilizer compounds, and a survey of the effectiveness and costs of available treatment technologies. Calculations of expected migration rates are contrasted with case study examples. Implications for solvent release site remediation, forensic investigations, and groundwater basin management are also discussed.

1.0 SOLVENT STABILIZERS

Chlorinated solvents sold for use in metal cleaning, degreasing, electronics, and textile cleaning applications require solvent stabilizer compounds to ensure proper performance in the intended application. Without these compounds, solvents tend to break down in the presence of light, heat and oxygen, or react with acids and metal salts.

1.1 Purpose of Solvent Stabilizers

Addition of solvent stabilizers is necessary to supply solvents with acid acceptors, metal inhibitors, and antioxidants.

During the degreasing process, both solvents and oils can decompose and produce strong acids. These acids, usually hydrochloric acid, can corrode the parts being cleaned and the cleaning equipment itself. Acid acceptors react with and chemically neutralize trace amounts of hydrochloric acid formed during degreasing operations. Acid acceptor compounds are either neutral (epoxides) or slightly basic (amines), and react with hydrochloric acid, forming an alcohol in the process (Archer, 1984). If left unneutralized, hydrochloric acid can cause solvent degradation.

Metal inhibitors deactivate metal surfaces and complex any metal salts that might form. Metal stabilizers are Lewis bases that inhibit solvent degradation reactions in the presence of a metal and its chloride (e.g. aluminum and aluminum chloride). The inhibitor either reacts with the active aluminum site, forming an insoluble deposit, or complexes with aluminum chloride, preventing degradation of the solvent.

Antioxidants reduce the solvent's potential to form oxidation products (Archer, 1984). Antioxidants suppress the free radical chain decomposition reaction of unsaturated solvents by forming stable resonance hybrids and slowing the propagation step of auto-oxidation (Joshi et al, 1989).

1.2 Solvent Compositions and Stabilizer Packages

TCE and TCA require both metal inhibitor and acid acceptors, while TCE also requires an antioxidant (Archer 1996). Perchloroethylene (PCE) is relatively stable and requires only minor amounts of acid inhibitors for degreasing operations, but no metal inhibitors (Keil, 1978). Methylene chloride (MC) is also quite stable, requiring less than 0.1% acid inhibitors by volume.

Producers of chlorinated solvents emphasize the stability of their products in their marketing literature. For example: "NEU-TRI™ solvent [a TCE formulation] is highly stabilized for vapor degreasing. Its unique combination of stabilizers makes it especially effective for long-term use. The stabilizer system prevents the build-up of acid in the degreaser and also protects against metal corrosion and reaction in the solvent." (Dow Chemicals, 2001).

Composition of 1,1,1-Trichloroethane
Uninhibited (unstabilized) TCA may react with aluminum to produce aluminum chloride, 2,2,3,3-tetrachlorobutane, 1,1-dichloroethylene; and hydrogen chloride. Adequate metal inhibitors can prevent TCA-aluminum reactivity and allow the solvent to be used in aluminum metal-cleaning applications (Archer, 1979).

The solvent stabilizer packages added to commercially available TCA vary with grade and producer. Actual compositions are difficult to obtain because the formulas are proprietary. Viewing Material Safety Data Sheets (see Table 1.1), a general sense can be obtained for the variation of solvent composition and the inclusion of stabilizer compounds in the formulation. Several producers of TCA now use 1,3-

dioxolane instead of 1,4-dioxane, and some (Great Western Chemical) advertise their product as "Dioxane Free". Many current applications of TCA list 1,3-dioxolane as the stabilizer present at the greatest weight fraction, for example 3% in a cleaning solvent, 3% in "electrical grade silicon bulk", 2-3% in a tire-cleaning solvent, and 3% in a brake-cleaning solvent (Cornell University, 2001 a,b,c,d; Alonso, 2001)

One producer, Occidental Chemical, lists TCE as present in its formulation of TCA, but no weight fraction is specified. All of the MSDS referenced in Table 1.1 were obtained from the Internet in 2001; older formulations may have used different proportions, and discussions with solvent producers provide an anecdotal basis for greater amounts of these additives in past decades (Mertens, 2000; HSIA, 2000). The multitude of synonyms and trade names for the chemicals added to solvents as stabilizers and inhibitors can lead to confusion for non-chemists. Table 1.2 summarizes synonyms of the more common solvent stabilizers.

Table 1.1 Composition of 1,1,1-Trichoroethane from Material Safety Data Sheets

Compound	Fischer	Vulcan	J.T.Baker	PPG	UnoCal Chem	Occ. Chem.	GW Chem.
TCA	95%	>95%	96-100%	95 %	96-98%	96 –97.5%	95%
Nitromethane						0.2 –0.5%	
1,2-butylene oxide		<0.5%	< 0.5%				
1,4-dioxane	~5%		< 3%	+	0-4%	2 – 2.7%	0%
sec-butanol				<2%			1 – 2%
1,3-dioxolane		<3%		<2%			2%

("+" indicates present but weight fraction not specified. From web search for MSDS sheets for currently available formulations; does not reflect compositions of solvents used in past decades)

Table 1.2   Synonyms for Common Solvent Stabilizers

1,4-DIOXANE	*1,3-DIOXOLANE*	*1,2-BUTYLENE OXIDE*	*TETRAHYDRO FURAN*	*EPICHLOROHYDRIN*
DX 1,4-Diethylene-dioxide diethylene oxide *p*-dioxane tetrahydro-1,4-dioxan Dioxyethylene-ether Glycolethylene ether	1,3-dioxolan Glycolformal 1,3-dioxole dioxolane Glycol methylene ether dihydroethylene glycol formal formal glycol	1,2-Epoxybutane EBU Propyl Oxirane Epoxybutane 2-Ethyloxirane **DIMETHYL AMINE** DMA N-methyl-methanamine	THF 1,4-epoxybutane furanidine Cyclotetra-methylene oxide tetramethylene oxide hydrofuran oxacyclopentane Oxolane *NITROMETHANE* NMT Nitrocarbol	Chloromethyloxirane glycidyl chloride chloropropylene oxide Glycerol epichlorohydrin 1,2-epoxy-3-chloropropane 3-chloro-1,2-epoxypropane (chloromethyl)-ethylene oxide gamma-chloropropylene oxide 1-chloro-2,3-epoxypropane 2,3-epoxypropyl chloride

Composition of Trichloroethylene

TCE composition also varies with grade, producer, and intended application, but generally stabilizers comprise less than 1% of TCE. Stabilizers in TCE formulations include a long list of specialty compounds, most of which are not reflected on Material Safety Data Sheets due to the small quantities of additives and the proprietary nature of commercial solvent formulations. Table 1.3 presents a compilation of individual stabilizer compounds added to TCE as listed in the cited references.

Table 1.3 Additives to Trichloroethylene at Concentrations Totaling Less than 1%

Epichlorohydrin	1,2-epoxybutene	2,2,4-trimethylpentene-1
[1,4-dioxane]**	Propanol	Thymol
1,3-dioxolane	diethyl amine	amyl alcohol
Triethylamine	Isoeuganol	Diethanolamine
pentanol-2-triethanolamine	n-methylpyrrole	Isocyanates
styrene oxide	cyclohexene oxide	Diisopropylamine
p-tert-butylphenol	n-ethyl pyrrole	ethyl acetate
Diisobutylene	Thiazoles	Alkoxyaldehyde hydrazones
Pyridine	p-tert-amylphenol	5,5-dimethyl-2-hexene
1,2-propylene oxide	tetrahydrofuran	glycidyl acetate
Tetrahydropyran	Trioxane	n-methylmorpholine
2-methoxyphenol	borate esters	pentene oxide
Morpholine	Aniline	3-methoxy-1,2-epoxy propane
Isocyanates	Butadiene oxide	2-methyl-1,2-epoxypropanol
2,3-epoxy 1-propenol	o-cresol	Nitropropanes
Epoxy cyclopentanol	Stearates	(2-pyrryl)-trimethylsilane
methyl ethyl ketone		
n-methylpyrrole		

Sources: Kircher, 1957, Hardie, 1964, Mertens, 1993, Archer, 1996, Vonder Haar et al, 1994, Joshi et al, 1989, US EPA, 1984. **Primary evidence for the presence of 1,4-dioxane in TCE could not be found by the author or Doherty, 2001, although numerous articles list it as an additive to TCE. Officials at DOW Chemical assert that 1,4-dioxane was not a constituent of TCE (Mertens, 2001). Kircher, 1957, lists "normal ethers and inner ethers" as stabilizers of TCE, but does not explicitly list 1,4-dioxane.

Jackson and Dwarakanath (1999) presented many of these compounds classed by chemical type and purpose, as shown in Table 1.4:

Table 1.4 – TCE Additives classed by chemical type and purpose

Chemical Type	Examples	Purpose
Aliphatic amines	Triethylamine, diisopropyl-amine	Free radical scavengers
Heterocyclic nitrogen compounds	Pyridine, pyrrole, alkyl pyrroles	Antioxidants
Substituted phenols	2-methoxyphenol, cresol	Antioxidants
Oxygenated organics	1,4-dioxane, acetone, butylene oxide, propylene oxide, tetrahydrofuran, epichlorohydrin	Acid acceptors**

(after Jackson and Dwarakanath, 1999) **Jackson and Dwarakanath identify 1,4-dioxane as an acid acceptor, while Joshi et al, 1989, identify it as an aluminum stabilizer in TCA which is not needed in TCE.

Stabilizers are continually depleted during normal degreasing operations. Dow Chemical markets Maxistab™ (packaged stabilizer concentrates) for use with TCE and PCE in vapor degreasing applications. These products are said to boost performance and extend the use of the solvent. A vapor degreasing test kit for monitoring the solvent to determine when new stabilizers are required is also available (DOW Chemical 2001).

Presence of stabilizers in TCE cannot be readily discerned from current MSDS sheets, as the quantities added, often in the parts per million range, do not meet the threshold for listing. Table 1.5 summarizes a review of currently available MSDS Sheets for TCE.

Table 1.5 Composition of Trichoroethylene from Material Safety Data Sheets

Compound	ChemCentral/Kansas	Fisher	New Hermes Neu-TRI (DOW)	Baxter
Trichloroethylene	99.4%	100%	>99%	99%
1,2-butylene oxide (epoxybutane)	0.5%		<1%	1%

<u>Methylene Chloride</u>
Methylene chloride (DCM, also called dichloromethane) is preferred for low-temperature applications, to clean electronic parts with temperature sensitive components. It is generally distributed as 99.9% MC, with stabilizer additives commonly in the parts per million range. Cyclohexane, cyclohexene, amylene, and other olefins and hydrocarbons may be included with DCM to inhibit reactions with metals.

Methylene Chloride is a stable compound when pure and free of moisture, and will not corrode common metals such as mild or galvanized steel, copper, tin, nickel or lead. In contact with free phase moisture, however, DCM may slowly hydrolyze to form acidic by-products that will corrode these metals. The rate of the corrosion process is self-accelerating. Pure DCM absorbs atmospheric moisture slowly but will eventually become saturated.

DCM is less reactive to light metals such as aluminum, magnesium, and their alloys, than many other chlorinated solvents. These metals are naturally insulated from corrosion by the presence of an oxide film. Contact with well-stabilized DCM will not normally produce an adverse reaction. However, if the oxide layer is broken, for example by the metal surface becoming scratched, and the fresh, active metal surface comes into contact with DCM which is unstabilized, or has depleted or inadequate stabilization, a Friedal-Craft reaction can be initiated. Once started, the reaction will proceed rapidly, and in some cases explosively, with the evolution of heat and large quantities of hydrochloric acid (Chlor-chem, 2001).

<u>Percholorethylene</u>
Perchloroethylene (PCE, also called tetrachloroethylene) does not require a metal inhibitor, but may require acid acceptors for degreasing applications. In the presence of light and air, PCE slowly autooxidizes to trichloroacetyl chloride. Stabilizers, such as amines or phenols, inhibit the decomposition process to extend solvent life and protect equipment and materials. Cyclohexene oxide and butoxymethyloxirane are also listed as inhibitors in PCE (Joshi et al, 1989). Compared to other chlorinated ethanes and ethenes, PCE is relatively stable, and generally requires only small amounts of stabilizers (Keil, 1978).

## 1.3   Relative Proportions of Stabilizers in Vapor Degreasing Waste Residuals

<u>Vapor Degreasing</u>
A vapor degreaser is an enclosed chamber with a solvent reservoir and a heat source to boil the solvent, and a cooling surface to condense the vapor in the upper section. A schematic of a vapor degreasing system is shown in Figure 1.1. Metal objects from which grease will be removed are hung in the air-free zone of solvent vapor. The hot vapor condenses onto the cool parts dissolving oils and greases and providing a continuous rinse in clean solvent (ASTM, 1989; Murphy, 2000).

In vapor degreasing systems, stabilizers partition between the vapor phase and boiling liquid phase according to their boiling points. 1,4-dioxane boils at 101° C while TCA boils at 74°C (see Table 2.1). Systems designed to handle heavy loads of oil and grease are designed to distill the solvent for ongoing purification. In such vapor degreasers, additives such as 1,4-dioxane tend to be concentrated in sludges known as still bottoms. In vapor degreasing systems used by the aerospace industry, still bottoms generated by typical in-process distillation is composed of 70% to 80% solvent and 20 to 30% oil, grease, and solids with traces of water. In electronics industry manufacturing using CFC-113, still bottom compositions of 85 - 95% CFC113 with oil and flux comprising 5 to 15% (Jackson, 1999; Evanoff, 1990). Solvents are also reclaimed using activated carbon; however, this technique selectively sorbs some additives, requiring their reintroduction after reclamation.

Figure 1.1 Typical Vapor Degreaser Configuration
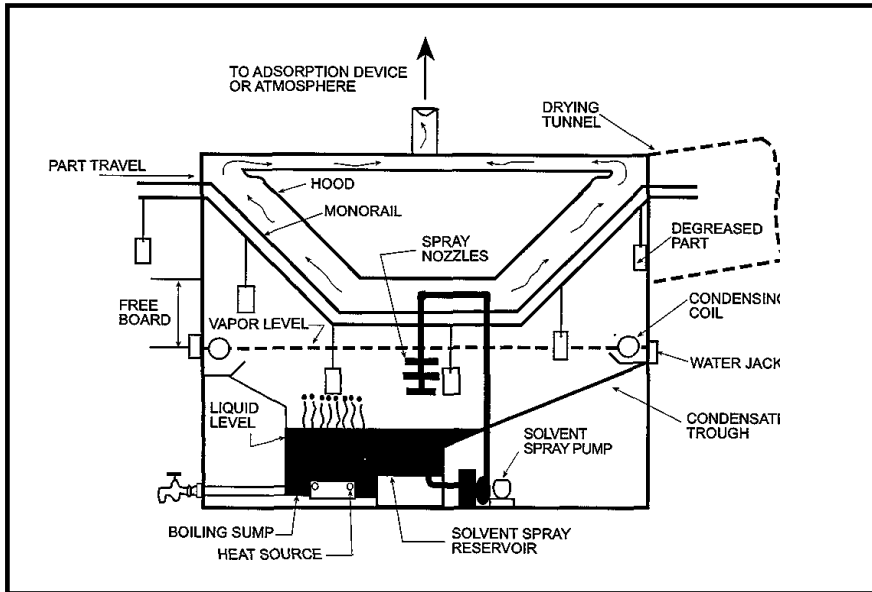
A study on the effects of distillation on solvent stabilizers and inhibitors for different solvents found that distillation significantly concentrates several stabilizers in still bottoms. Tables 1.6a, 1.6b, and 1.6c, below, profile results of this study (Joshi, et al, 1989). For all three solvents studied, stabilizers were retained in still bottoms in excess of 35% of their concentrations in the feed spent solvent. Used TCA showed a 68% increase in the weight fraction of 1,4-dioxane. This study also found that usage in vapor degreasers not equipped with in-process distillation units caused concentrations of several inhibitors and stabilizers to decrease with duration of use.

Table 1.6a *Stabilizer Concentrations of Reclaimed Trichloroethylene*

(Joshi et al, 1989)	Inhibitor Concentration (weight fraction)			
Sample	Butylene Oxide (x10^3)	Epichlorohydrin (x10^3)	Ethyl Acetate (x10^4)	Methyl Pyrrole (x10^4)
New TCE	1.64	1.66	3.46	1.59
Spent TCE	0.685	1.69	2.85	2.18
TCE Distillate	0.718	1.61	2.58	1.66
Carbon Adsorbed TCE	0.44	1.31	2.65	0.90

Table 1.6b *Stabilizer Concentrations of Reclaimed Perchloroethylene*

(Joshi et al, 1989)	Inhibitor Concentration (weight fraction)	
Sample	Cyclohexene Oxide (x10^3)	Butoxymethyl Oxirane (x10^3)
New PCE	1.06	4.26
Used PCE	0.988	7.45
PCE Distillate	0.968	5.42
Carbon Adsorbed PCE	0.091	5.40

Table 1.6c *Stabilizer Concentrations of Reclaimed 1,1,1-Trichloroethane*

| (Joshi et al, 1989)	Inhibitor Concentration (weight fraction)		
Sample	n-methoxy-methanamine (x10^4)	Formaldehyde dimethyl-hydrazone (x10^3)	1,4-Dioxane (x10^3)
New TCA	8.92	5.78	17.2
Used TCA	4.14	6.16	29.0
TCA Distillate	4.60	7.22	19.6
Carbon Adsorbed TCA	1.30	3.37	23.4

Guidance for operation of vapor degreasers often calls for adding additional solvent to restore solvent performance, thus further concentrating stabilizers in the still bottoms with each addition of new solvent. Waste solvent released to soil and groundwater from improperly disposed still bottoms may therefore have a substantially higher fraction of stabilizers than was originally formulated, particularly in the case of 1,4-dioxane and TCA.

Because vapor-degreasing processes consume solvent stabilizers and inhibitors or concentrate stabilizers in still bottoms, operators may also add stabilizers back into the solvent to ensure the solvent performs as intended. Stabilizer packages such as DOW Chemical's MaxiSTAB are marketed for this purpose. The need to reintroduce stabilizers into spent solvents has bearing for cleanup investigations at solvent recycling facilities, where solvent stabilizer compounds may have been stored in pure form to refortify spent solvents.

As the use of TCA has been phased out due to laws and taxes intended to reduce ozone depletion, alternative solvents have become available. Alternative vapor degreasing formulations, for example EnSolv Vapor Degreasing & Cleaning Solvent, use n-propyl bromide as an alternative solvent, but also use 3% 1,3-dioxolane as a stabilizer (Ensolv, 1996).

1.4   Chemistry of Solvent Stabilizers

1,4-Dioxane is a cyclic ether, and is also known by the synonyms *p*-dioxane, diethylene ether, diethylene dioxide, and glycol ethylene ether. It is a dimer of ethylene oxide. Dioxane is a Lewis base because the oxygen molecules in 1,4-dioxane have electrons available for sharing (a base is a proton acceptor; a

1,4-dioxane

Lewis base is an electron pair donor). The molecular structure of 1,4-dioxane is shown at left. Its two oxygen atoms make it hydrophilic and infinitely soluble in water. Dioxane has no dipole moment owing to the symmetrical position its two oxygen atoms in the chair conformation; in two different boat conformations, 1,4-dioxane has dipole moments of 1.4 and 2.4 (Ledger and Suppan, 1967). Dioxane boils at 101 °C (Windholz et al, 1983).
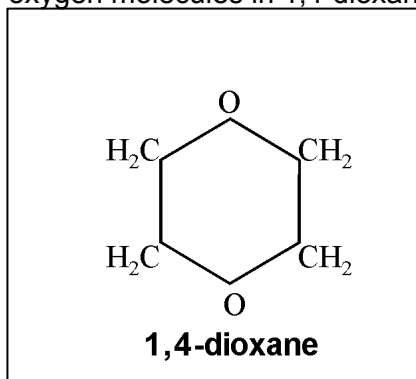
1,4-Dioxane is made from diethylene glycol by heating and distilling glycol with dehydration catalysts such as sulfuric acid. It can also be manufactured by treatment of bis(2-chloroethyl)ether with alkali, or by dimerization of ethylene oxide (IARC, 1972).
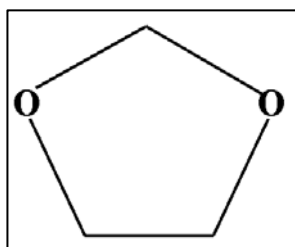
1,3-dioxolane is a stable reaction product of ethylene glycol and formaldehyde. It is a volatile liquid, miscible with water in all proportions. 1,3-dioxolane has a melting point of –95°C, and a boiling point of 78°C. 1,3-dioxolane is also known by the synonyms dioxolane; glycol methylene ether; 1,3-dioxacyclopentane;

glycolformal; 1,3-dioxoledioxolane; dihydroethylene glycol formal; and formal glycol.

1.5   Other Uses of Solvent Stabilizer Compounds in Manufacturing

Approximately 90% of the 1985 1,4-dioxane production in the United States was used as a stabilizer for chlorinated solvents, particularly, TCA (US EPA 1995). Knowledge of other industries using 1,4-dioxane in pure form, or producing 1,4-dioxane as a by-product of manufacturing, may aide in site investigation and forensic geochemical investigations for source apportionment.

1,4-dioxane is used in numerous industrial processes and is included with a variety of consumer and commercial products. Table 1.7 summarizes common applications of 1,4-dioxane. 1,4-dioxane may also occur as a by-product of some manufacturing processes, and as a contaminant in some products.

Table 1.7 Additional Industrial and Commercial Uses of Dioxane

Solvent in paper manufacturing	as a wetting & dispersing agent in textile process
Paints, lacquer, and varnish remover	In microscopy
Stain and printing compositions	as a purifying agent in pharmaceuticals
In liquid scintillation counters	In resins, oils, waxes, and cements
In deodorants, shampoos & cosmetics	In fumigants
Impregnating cellular acetate	as an additive in aircraft deicing fluid formulations
'inert' ingredients of pesticides	as an additive in antifreeze
As a by-product formed during esterification of polyester	

(Sources: Montgomery, 1996; Beernaert et al, 1987; Mackison et al, 1981; US EPA, 1979; ILO, 1979; NCI/DCE, 1985);

Polyethoxyleated surfactants used in detergents may contain dioxane formed during the polymerization of ethylene oxide. (Black et al, 1983; Abe, 1996, US EPA, 1999b). 1,4-dioxane is a contaminant in some surfactant compounds used in herbicides, such as polyoxyethyleneamine in the isopropylamine salt of glyphosate, an ingredient in the most common herbicides (common trade names Roundup, Pondmaster; Rattler; Rodeo) (Briggs et al, 1992; Brooks, et al, 1973). 1,4-dioxane and epichlorohydrin are listed as contaminants of toxicological concern among inert ingredients of pesticides (US EPA, 1989).

Cosmetics containing ethoxylated surfactants may be contaminated by 1,4 dioxane (Scalia et al, 1992). In shampoo manufacturing, 1,4-dioxane is introduced into the product via the use of ethoxylated fatty alcohol sulfates as cleansing agents. During the process of alcohol ethoxylation, ethylene oxide can dimerize to form 1,4-dioxane, which is subsequently carried through the shampoo manufacturing process[1]. A variety of commercially available cosmetics, including shampoos, liquid soaps, sun creams, moisturizing lotions, after-shave balms, baby lotions, day creams, and hair lotions, were analyzed for 1,4-dioxane; 56% of the total products investigated contained 1,4-dioxane with levels ranging from 3.4 to 108.4 mg/kg (Italia and Nunes, 1991). 1,4-dioxane is commonly found in treated wastewater effluent and landfill leachate (see Section 2.6, below). Many producers have begun vacuum stripping procedures in their manufacture of the fatty alcohol sulfates to limit contamination of their products by 1,4-dioxane.

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[1] For those curious to know whether their sundries may contain 1,4-dioxane, the following is a list of some of the commonly used ethoxylated ingredients in shampoos and other cosmetic products: Sodium laureth sulfate; Ammonium laureth sulfate; Triethanolamine laureth sulfate; Cocamide; Cocamide DEA; ingredients with TEA, MEA, DEA, MIPA, PEG; Polysorbates; Triethanolamine; Sodium C14-16 Olefin Sulfate (Sulphonate); Disodium Oleomido Sulfosuccinate; Cocamidopropyl Betaine; Ammonium Cocoyl Isethionate; Ammonium Lauryl Sulphate; Sodium C12-15 Pareth Sulfonate; Disodium Cocoamphodiacetate. Presence of these ingredients does not equate to presence of 1,4-dioxane, it only establishes an increased likelihood of its presence if vacuum removal of 1,4-dioxane is not employed during manufacturing. Direct testing is the only valid means of verification, and probably is not warranted. 1,4-dioxane has a comparatively low dermal toxicity to laboratory animals (see Section 4.3).

1,4-dioxane is a by-product in the production of polyethylene teraphthalate (PET) plastic, and substantial soil and groundwater contamination has occurred at some PET manufacturing facilities and waste sites in North Carolina (Zenker, 2001).   1,4-dioxane is used to impregnate cellular acetate membranes in the production of filters used in reverse osmosis and in laboratory and groundwater sampling filters. The Gelman Sciences facility in Scio, Michigan, which manufactures groundwater sampling filters familiar to groundwater professionals, is the site of one of the nation's largest releases of 1,4-dioxane in groundwater, where the municipal water supply has been impacted (Michigan Department of Environmental Quality, 2001).

1,3-dioxolane
1,3-dioxolane is primarily used for the production of polyacetals and other polymers (rigid plastics). Only 5% is used for other purposes, including stabilizers for halogenated organic solvents (Dioxolane Manufacturers Consortium, 2000).

1.6   History of Solvent and Solvent Stabilizer Production and Use

The following discussion highlights which solvents were preferred for common industrial applications in the past four decades, and accordingly, which stabilizers may have been released from past mishandling of solvent wastes.

TCE was the preferred solvent used in many industrial applications throughout the fifties and sixties. In the late 1960s, TCE came under increasing scrutiny for occupational exposure because it was identified as an animal carcinogen. As a result, many firms switched to TCA. During the late 1980s and early 1990s, many firms using Freon-113 as a solvent converted to TCA as it is a less potent ozone depleter. Because of the current production ban on TCA, some firms are now converting back to TCE.

1,4-dioxane has been produced in commercial quantities by relatively few American manufacturers (Table 1.8). In 1990, between 10.5 and 18.3 million pounds of dioxane were produced in the United States. Approximately 90% of the 1985 1,4-dioxane production was used as a stabilizer for chlorinated solvents, particularly TCA.

Table 1.8   Major American Producers of 1,4-dioxane

Manufacturer	Headquarters Location	Production Location
Ferro Corporation	Cleveland, Ohio	Baton Rouge, Louisiana
CPS Chemical Company Inc.	Old Bridge, New Jersey	New Jersey
Dow Chemical USA	Midland, Michigan	Freeport, Texas

(Source: Stanford Research Institute, 1989)

Table 1.9   Production Data for 1,4-dioxane, Pounds per Year

1973	1974	1975	1976	1977	1982
1,620,485	1,762,775	1,258,150	1,485,683	1,222,467	6,750,000

(Source, United States International Trade Commission, 1994)

The date that a manufacturer began synthesizing a chlorinated solvent is frequently used as evidence regarding when it was available at a facility. This approach assumes that potential suppliers and/or products containing chlorinated solvents are known. Table 1.10 identifies manufacturers of four chlorinated solvents in the United States from 1908 to 2000 (Morrison, 2001, after Doherty, 2000).

Table 1.10   Period of Solvent Production by Manufacturer

MANUFACTURER	TCE	TCA	MANUFACTURER	TCE	TCA
Carbide & Carbon Chemicals	1922-1935	-	Pittsburgh Plate Glass/ PPG Industries	1956-2000	-
Diamond Alkali/ Diamond Shamrock	-	-	PPG Industries	-	1962-2000
Dow Chemical	1921-2000	1936-1994	R&H Industries	1925-1972	-
DuPont Company	-	-	Vulcan materials	-	1970-2000
Ethyl Corporation	1967-1982	1964-1976	Westvaco Chlorine	1933-1949	-
Hooker Chemical/ Occidental Chemical	1956-1980	-	Diamond Shamrock	1969-1977	-
Hooker-Detrex/Detrex Chemical	1947-1972	-	Niagara Alkali	1949-1955	-

(adapted from Morrison, 2001. First compiled by Richard Doherty, and presented on the Internet by Robert Morrison)

1.7   History of Solvent Waste Disposal Practices

Historical handling, storage, and disposal practices for chlorinated solvents and their wastes have resulted in widespread soil and groundwater contamination by solvents. In the Silicon Valley, where accelerated demand for semiconductors and printed circuit boards lead to rapid expansion of the electronics industry in the 1970s, the large quantities of solvents needed for wafer fabrication and parts cleaning.   Public safety agencies required that these solvents and solvent wastes be stored in underground tanks. Many of these tanks and associated piping leaked, resulting in numerous instances of soil and groundwater contamination.

Among the oldest citations of solvent contamination of groundwater, the following text is an excerpt from a description of TCE contamination of groundwater in England published in the Analyst, in March of 1949 by F. Kyne and T. McLachlan (cited in Morrison, 2001).

> *Cases of contamination of wells by trichloroethylene have come to our notice. In the first, the well was situated beside a factory that used large quantities of trichloroethylene as a solvent. During a fire at the factory a tank of the liquid burst and the ground was saturated with the solvent. After more than four years the water in the well still had an odour of trichloroethylene and the well had to be abandoned. The well was sunk in gravel only about 20 feet from a river and one might have expected that the movement of water through the gravel would have removed the contaminant.*

> *In the other case, the well was situated 150 to 200 yards from a pit in an open field where waste trichloroethylene had been dumped. It was in valley gravel and in the direct line of flow towards the river. The water in it had a slight odour of trichloroethylene and was said to cause stomach disorders, giddiness, etc. The amount of trichloroethylene in the water was found to be 18 parts per million when estimated by . . . a modification of the Fujiwara pyridine-sodium hydroxide reaction. From these two cases it is evident that contamination by compounds of this nature is likely to be very persistent and there is some evidence of toxicity at very low concentrations.*

Users of chlorinated solvents were routinely advised to dispose of waste solvents by pouring onto the ground or into trenches for evaporation or burning. As we now know, these practices resulted in significant soil and groundwater contamination by still bottoms. The following industry guidance, cited in Pankow and Cherry, 1996, is notable:

Routine disposal practices Vapor Degreasing Sludge that Contains Chlorinated Solvents (1964):

Any procedure for disposal depends on local, state and federal regulations. In the absence of any clearly defined ordinances, the sludge is usually poured on dry ground well away from buildings, and the solvents are allowed to evaporate. If the sludge is free flowing, it is placed in shallow open containers and allowed to evaporate before the solids are dumped on the ground. [American Society of Metals, Metals Handbook: Heat Treating, 8th Edition, Volume 2. Metals Park, Ohio]

Chlorinated Solvent Disposal (1972):

Waste mixtures should not be discharged into drains or sewers where there is a danger that the vapor may be ignited. In cases such as these, the waste should be removed to a safe location (away from inhabited areas, highways, buildings, or combustible structures) and poured onto dry sand, earth, or ashes, then cautiously ignited. Burning of chlorinated hydrocarbon wastes should be done only when permitted by controlling authorities and then under constant supervision. In other instances, the chlorinated hydrocarbon waste may be placed in an isolated area as before and simply allow the liquid to evaporate. [Chemical Hazards Bulletin, American Insurance Association, C-86, March 1972. New York, NY. Pg. 42]

At electronics manufacturing, metals fabrication, and other industrial solvent release sites in the 1960's, 1970's and 1980's, improper disposal of still bottoms was often the cause of solvent contamination. Given the evidence for elevated concentrations of solvent stabilizers in still bottoms, stabilizers are likely to be present at these sites at elevated concentrations.

2.0   ENVIRONMENTAL OCCURRENCE AND SUBSURFACE BEHAVIOR OF SOLVENT STABILIZER COMPOUNDS

Like many commonly used industrial chemicals, 1,4-dioxane is widespread in the atmosphere and hydrosphere. This section examines the properties of 1,4-dioxane and other solvent stabilizers that dictate its behavior in the atmosphere, surface water, and groundwater, presents calculations of expected migration rates of 1,4-dioxane in groundwater, and cites laboratory and field studies of 1,4-dioxane's propensity to move relatively unimpeded through the subsurface.

2.1   Physico-Chemical Properties of Solvent Stabilizers

Ethers, which include 1,4-dioxane and 1,3-dioxolane, have been classified as generally resistant to hydrolysis (Lyman et al, 1982). 1,4-Dioxane has a moderate vapor pressure at 25 °C (37 mm Hg). Volatilization from dry soil may be significant. The linear partitioning coefficient between soil organic matter, or humic substances, and dissolved phase 1,4-dioxane (K_{OC}) is 1.23. As this value is low compared to most compounds, 1,4-dioxane is not expected to significantly sorb to suspended sediments or soil organic matter (Lyman, et al, 1982, Kenaga, 1980).   1,4-dioxane exhibited a negligible biochemical oxygen demand in two activated sludge experiments and the compound has been classified as relatively non-degradable. It is expected, therefore, that 1,4-dioxane will not biodegrade extensively in the aquatic environment (Lyman, et al, 1982).

Table 2.1 summarizes key physico-chemical properties governing fate and transport processes for common solvent stabilizer compounds and the solvents to which they're added.

Table 2.1   Properties of Common Solvent Stabilizers and Host Solvents

Property	1,4-dioxane	1,3-dioxolane	1,1,1-trichloro-ethane	Tetrahydro Furan	1,2-butylene oxide	Trichloro-ethylene
CAS RN (a)	123-91-1	646-06-0	71-55-6	109-99-9	106-88-7	79-01-6
Molecular weight	88.10 [4]	74.09	133.4	72.11	72.12	131.39
Molecular Form	$C_4H_8O_2$	$C_3H_6O_2$	$C_2H_3Cl_3$	C_4H_8O	C_4H_8O	C_2HCl_3
H$_2$O Solubility mg/L @ 20°C	Miscible	Miscible	1,360	Miscible	82,400	1,100
Boiling Pt. °C at 760 mm Hg	101.1 °C	78°C	74.1	66°C	63°C	87°C
Vapor Pressure Mm Hg @ 20° C	37 mm Hg @ 25° C	70 mm Hg @ 20°C	96 mm Hg @20 °C	114 mm Hg @ 15°C	140 mm Hg @20°C	55 mm Hg @ 20°C
Vapor Density	3.03 [6]	2.6	5.45	2.5	2.2	5.37
Henry's Const. atm-m3/mol	3×10^{-6}	2.4×10^{-5}	1.5×10^{-2}	7.06×10^{-5}	$\sim 1.6 \times 10^{-4}$	9.9×10^{-3}
Log K_{OW}	0.43	- 0.37	2.49	0.46	0.26	2.6
Log K_{OC}	0.54	1.18	2.85	1.37		2.6
Specific Gravity	1.03 @ 20°C	1.06 @ 20°C	1.34 @ 20°C	0.8892	0.84@17°C	1.46 @ 20°C

Sources: Montgomery, 1996; Mackay et al, 1996; Verschueren, 1983; Lyman, et al, 1982; Hansch et al, 1995; Sax, 1984.

The hydrophilic nature of 1,4-dioxane, 1,3-dioxolane, tetrahydrofuran, and 1,2-butylene oxide makes these compounds miscible or highly soluble, in either case significantly more soluble than TCA and TCE. The mobility of a compound in the subsurface is directly proportional to its solubility. Hydrophilic compounds are only weakly retarded by sorption during transport. Retardation of chlorinated organics is expected to be directly proportional to the octanol-water partition coefficient (K_{OW}), such that these stabilizers will migrate much more quickly than their host solvents (Jackson and Dwarakanath, 1999).

2.2   Susceptibility to Microbial Degradation

1,4-dioxane is not typically degraded by indigenous soil microorganisms under ambient conditions (Fincher et al, 1962; Howard, 1990). Under enhanced conditions, or where selected strains of bacteria capable of degrading 1,4-dioxane are cultured, microbial degradation has been documented to be viable in engineered bioreactors (see Section 5.3 for discussion). Like MtBE, which was at first thought to be highly resistant to microbial degradation, there is promise for the use of microbial degradation in the cleanup of 1,4-dioxane from extracted groundwater.

2.3   Simulated Migration of Solvent Stabilizers Using BIOCHLOR

To determine expected relative rates of migration of 1,4-dioxane, 1,3-dioxolane, and TCA in groundwater, transport and biotransformation of TCA, and transport of 1,4-dioxane and 1,3-dioxolane without biodegradation were modeled. The objective of the modeling was to anticipate relative rates of migration at release sites, and the relative distances within which regulatory thresholds would be exceeded for the stabilizers, TCA, and the biotransformation products of TCA, 1,1-dichloroethane and chloroethane. At actual solvent release sites, 1,4-dioxane has been found to migrate considerably farther in groundwater than TCA or its breakdown products (see Section 2.5). The model selected to estimate relative rates of migration was US EPA's BIOCHLOR.

BIOCHLOR is a spreadsheet template developed for the USEPA that executes an analytical solute transport model for a saturated, anaerobic, porous medium that may include any or all of the following processes: one-dimensional advection, dispersion in up to three dimensions, instantaneous sorption, and biotransformation (Aziz et al, 2000). The model is used as a tool to predict the spatial distribution of the concentration of chlorinated ethenes or ethanes in porous media. The advection-dispersion equation contains terms that account for various transport processes and can be adjusted or eliminated individually. A source of contamination is defined by width and thickness measured as the distance from the top of the water table downward. The duration of the source is defined (denoted as the simulation time). The source may be of constant concentration or undergo first order decay.

The results of this modeling exercise do not necessarily represent true behavior of a mixture of these compounds as would be expected in the field. Among other basic limitations, running BIOCHLOR separately for the chlorinated ethanes, 1,4-dioxane, and 1,3-dioxolane ignores any competitive sorption that may occur, thereby possibly underestimating the spatial extent of an actual plume. Competitive sorption is likely to occur between DCA, chloroethane, dioxane, and dioxolane, since they have similar linear organic carbon partitioning coefficients (K_{OC}). TCA, however, has an order of magnitude larger K_{OC} and therefore would experience relatively less competition. The model does not account for aquifer heterogeneities such as channels or other preferential pathways. Use of BIOCHLOR in this application is not intended to simulate dioxane migration absolutely. It is used to simulate relative mobility and persistence of 1,4-dioxane and 1,3-dioxolane in contrast to the host solvent TCA.

Hydraulic and soil properties of an aquifer studied at the Cape Canaveral Air Station, Florida, included as a preloaded case study in BIOCHLOR, were used to model transport of TCA, 1,4-dioxane, and 1,3-dioxolane (Table 2.2). With the exception of redefining source dimensions (50 feet wide by 5 feet in thickness), dispersivities, simulation time, and domain length, all other parameters were left as the defaults of the Cape Canaveral case study for TCA simulations. Table 2.3 summarizes the transport parameters for each compound. The model imposes first order decay of TCA and its two degradation products, DCA and chloroethane, terminating in sequential fashion with ethane. Sorption is modeled according to K_{OC} values. In cases of multiple contaminants, the median K_{OC} was arbitrarily used. No biotransformation was assumed for 1,4-dioxane and 1,3-dioxolane.

Table 2.2 Hydraulic parameters for modeled domain.

| Seepage velocity	111.7 ft/y	α_X	26.9
Conductivity	0.018 cm/s	α_Y	2.69
$\alpha_X, \alpha_Y, \alpha_Z$ = dispersivities (ft)		α_Z	0

Table 2.3–Regulatory levels and transport properties of modeled compounds.

	TCA	DCA	Chloroethane	1,4-dioxane	1,3-dioxolane
Regulatory level ug/L	200	5	16	3	-
K_{OC} **(L/kg)**	426	130	125	-	15.1
R	7.13	2.87[*]	2.8	1.1	1.22
Degradation, λ (yr^{-1})	2.0	1.0	0.7	0	0

[*]R-value used in model for all chlorinated ethanes.

Dispersion is a term inclusive of physical processes that cause a plume to shear. Fixed values for dispersivities in the mean flow and horizontally orthogonal directions were used in all model runs. The BIOCHLOR model was run several times using different source durations with an initial aqueous concentration of 100 mg/L TCA (zero initial concentrations of degradation products). Separate trials were performed each for 1,4-dioxane at initial concentrations of 3 and 15 mg/L and 1,3-dioxolane at 3 mg/L.

The 3 mg/L scenario represents virgin TCA released to groundwater, while the 15 mg/L scenario is intended to represent the release of still bottoms enriched with respect to 1,4-dioxane due to partitioning in the vapor degreasing process. Modeling 1,3-dioxolane at 3 mg/L was done to estimate behavior of currently available formulations of TCA in the subsurface; the two stabilizers are not expected to both be present in high proportions in TCA. 1,3-dioxolane was not modeled higher than 3 mg/L because enrichment of still bottoms with 1,3-dioxolane is not expected to any significant degree due to its boiling point being within a few degrees of the boiling point for TCA.
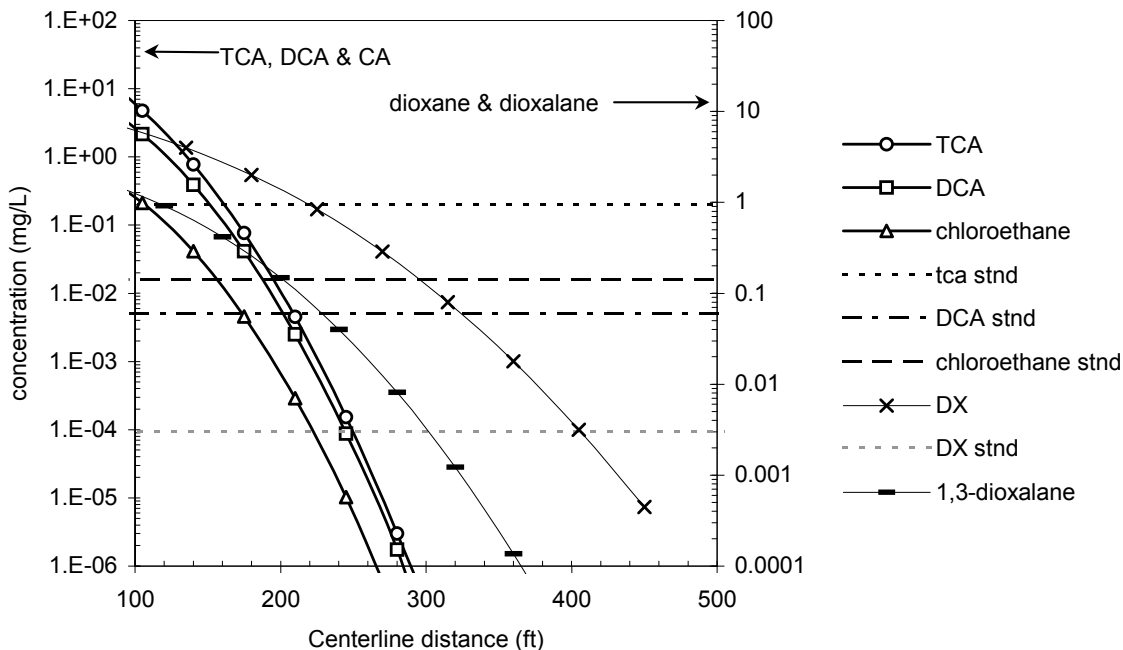
Figure 2.1   *BIOCHLOR*-modeled transport of chlorinated ethanes, 1,4-dioxane (DX), and 1,3-dioxolane; 1-year continuous source release; source concentrations: 100 mg/L TCA, 15 mg/L 1,4-dioxane, and 3 mg/L 1,3-dioxolane. ("stnd" = regulatory threshold)
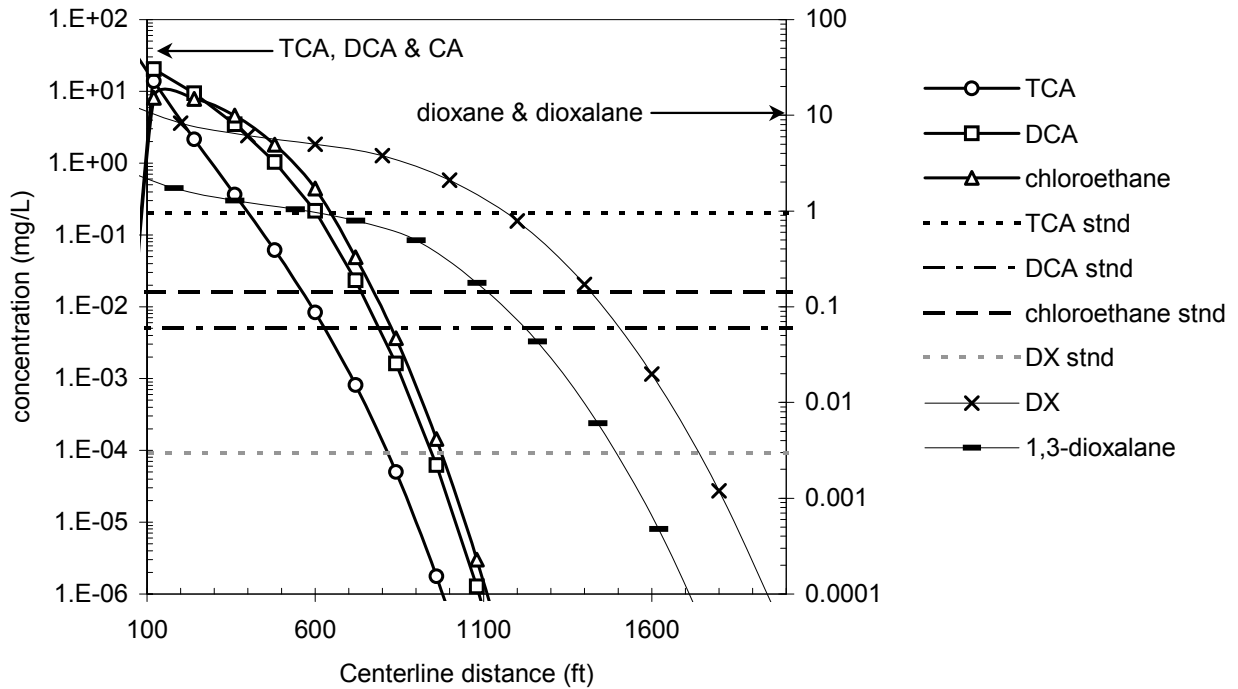
Figure 2.2–*BIOCHLOR*-modeled transport of chlorinated ethanes, 1,4-dixoane (DX), and 1,3-dioxolane; 10-year continuous source release; source concentrations: 100 mg/L TCA, 15 mg/L 1,4-dioxane, and 3 mg/L 1,3- dioxolane.

Figure 2.3–*BIOCHLOR*-modeled distance along plume centerline at which contaminant concentration exceeds regulatory levels (source TCA concentration 100 mg/L).

BIOCHLOR does not account for movement of solvents in the subsurface as dense non-aqueous phase liquids; only dissolved phase movement is considered. The initial concentration modeled, 100 mg/L, is less than 10% of the overall solubility of TCA.

Figure 2.1 illustrates the distribution of the various compounds along the centerline of the plume. 1,4-dioxane and 1,3-dioxolane persist over larger 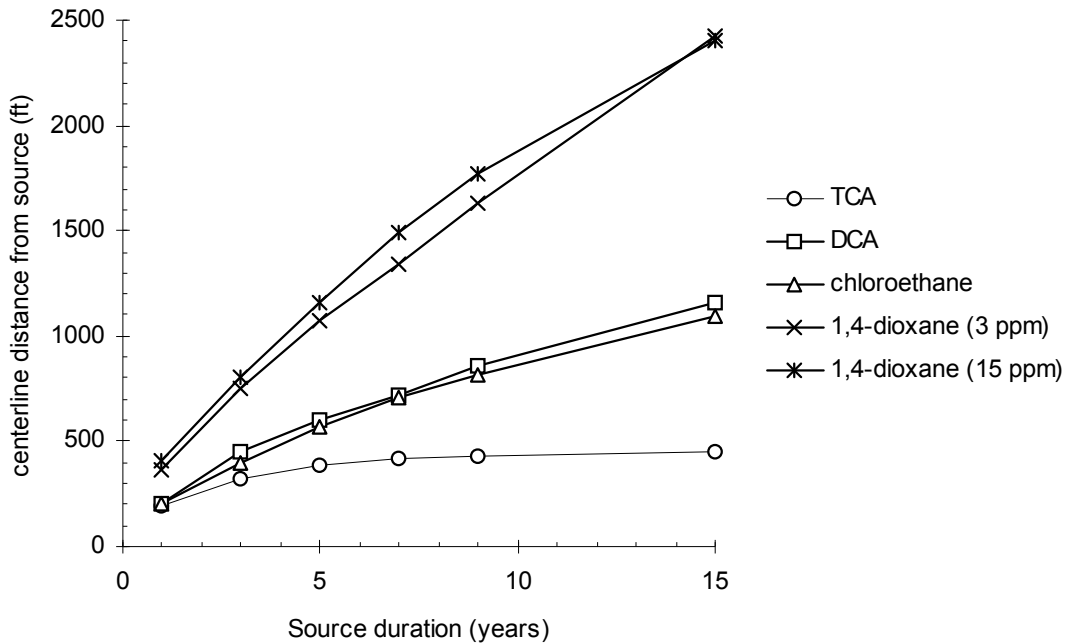distances from the source than the chlorinated ethanes due to lower sorption, incorporated in a lower retardation factor (R), and lack of biochemical degradation. Figure 2.2 illustrates similar results for a 10-year source duration. Differing by only a lower estimate of R (1.1 compared to 1.22), an initial concentration of 3 mg/L 1,4-dioxane would appear parallel and slightly higher than the curves for 1,3-dioxolane (Figures 2.1 and 2.2). Figure 2.3 illustrates the distance from the source at which the contaminant concentration reaches the regulatory level (see Table 2.3) as a function of the source lifetime.

2.4   Migration Experiments and Studies

Three studies have been conducted on the migration of 1,4-dioxane in soil and groundwater, by laboratory column studies and analysis of field observed plume behaviors. 1,4-dioxane passes through saturated and unsaturated soils relatively quickly due to its high solubility and low affinity for sorption to soil organic matter.

An adsorption coefficient (K_D) for 1,4-dioxane was estimated based on laboratory diffusion tests in a saturated and undisturbed clayey soil (Barone, et al, 1992). A K_D value of 0.17 mL/g was estimated for 1,4-dioxane, based on a measured diffusion coefficient of 4 x10^{-6} cm^2/s in a clayey soil with grain sizes of clay (45%), silt (43%), sand (10%), and gravel (2%), and mineralogy of the sub-gravel grains as calcite/dolomite (34%), quartz and feldspars (15%), illite (25%), chlorite (24%), and smectite, (2%). Soil organic carbon content was 0.58%, and the cation exchange capacity of this soil was 10 milliequivalents per 100 grams dry weight. In contrast, the same study produced an estimated adsorption coefficient for toluene of 26 mL/g (Barone et al, 1992). Estimated breakthrough times for vertical transport in a clay soil were also given, with 1,4-dioxane advancing more than five meters in 100 years, while toluene advanced less than one meter in the same time frame. The inference made in this study is that given a leachate containing 1,4-dioxane in sufficient amounts, enough 1,4-dioxane could pass through a one-meter thick clay landfill liner in five years to contaminate underlying groundwater to concentrations in excess of drinking water action levels.

Another laboratory column experiment using cores of sandy aquifer material contrasted measured retardation factors of several volatile organic compounds to field derived retardation factors estimated from plume lengths at the Gloucester Landfill site in Ontario, Canada. Retardation factors were measured at different groundwater velocities and over different test durations. The measured retardation factors, listed in Table 2.4, compared well with field derived estimates based on plume lengths and purge tests. Dioxane and tetrahydrofuran were found to have the lowest retardation factors (Priddle and Jackson, 1991).

While the different methods for deriving retardation factors in Priddle and Jackson's study yield somewhat different results, strong evidence is provided for the propensity of dioxane and tetrahydrofuran to migrate much further than chlorinated solvents with which they are commonly released to aquifers. The failure of the Schwartzenbach and Westall equation[2] to accurately predict retardation factors is attributed to it being derived from empirical relationships of compounds with much higher octanol-water coefficients (K_{OW}).

At the Seymour Superfund site in Indiana, field sampled distribution of 1,4-dioxane, tetrahydrofuran, benzene, and chloroethane were compared to model-predicted transport distances. The model, a combination of USGS MODFLOW and the SWIFT code, accounted only for retardation and dispersion.

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[2] see notes, Table 2.4

Table 2.4   Comparison of Retardation Factors in Column Tests and Field Derived Estimates for 1,4-dioxane, Tetrahydrofuran and other VOCs (Priddle and Jackson, 1991)

Compound	1) Plume Length	2) Purge Well	3) Correlation Equation	4) S & W equation	5) Column Center of Mass	6) Column C_{max}
1,4-dioxane	1.6	1.4	1.6	1.0	1.1	1.2
Tetrahydrofuran	2.2	2.2	2.5	1.0	-	-
Diethyl ether	3.3	3.0	3.4	1.1	1.7	1.6
1,2-DCA	7.6	.nm	5.7	1.2	7.2	4 – 5
Trichloromethane	.nm	.nm	9.3	1.3	7.5	4 – 5
Benzene	8.8	.nm	10.0	1.4	14.3	6 – 8
1,1-DCE	.nm	.nm	11.0	1.5	10.7	6 – 7

Notes: Retardation Factor = $R_f = 1 + p_b \cdot K_D /n = V_W/V_C$ where p_b is bulk density [M/L^3], K_D is contaminant distribution coefficient [L^3/M], n is the dimensionless porosity of the aquifer material, V_W is velocity of water, and V_C is velocity of contaminant. 1) R_f interpreted from length of organic compound plume vs. length of chloride plume. .nm = not mapped or measured. 2) Purge well evaluation test, cited in Whiffin and Bahr, 1985. 3) Correlation equation $\log(R_f -1) = 0.5 \cdot \log KOW$ - 0.065, from field data (Patterson et al, 1985). 4) Schwarzenbach and Westall equation: $R_f = 1 + p_b \cdot KD/n$ where $KD = 3.2 \cdot f_{OC} \cdot K_{OW} \cdot 0.72$ (Schwartzenbach and Westall, 1981) 5) Column Tests comparing center of mass of organic compound to center of mass of iodide. 6) Column test comparing C/CMAX = 0.5 organic vs. C/CMAX = 0.5 of iodide.

Travel distance for 1,4-dioxane was accurately predicted, but failure to account for biochemical reactions resulted in an overestimated travel distance for the other compounds. 1,4-Dioxane was found to travel 2.5 times further than tetrahydrofuran. These two compounds have nearly identical retardation factors and solubilities, but tetrahydrofuran is slightly biodegradable whereas 1,4-dioxane is not amenable to biodegradation (Nyer et al, 1991).

Calculated and laboratory measured migration rates for 1,4-dioxane in the subsurface suggest this compound should move rapidly in groundwater, well ahead of a plume of chlorinated solvents. The following sections profile examples of measured 1,4-dioxane plumes.

2.5   Occurrence and Distribution of 1,4-dioxane at Solvent Release Sites
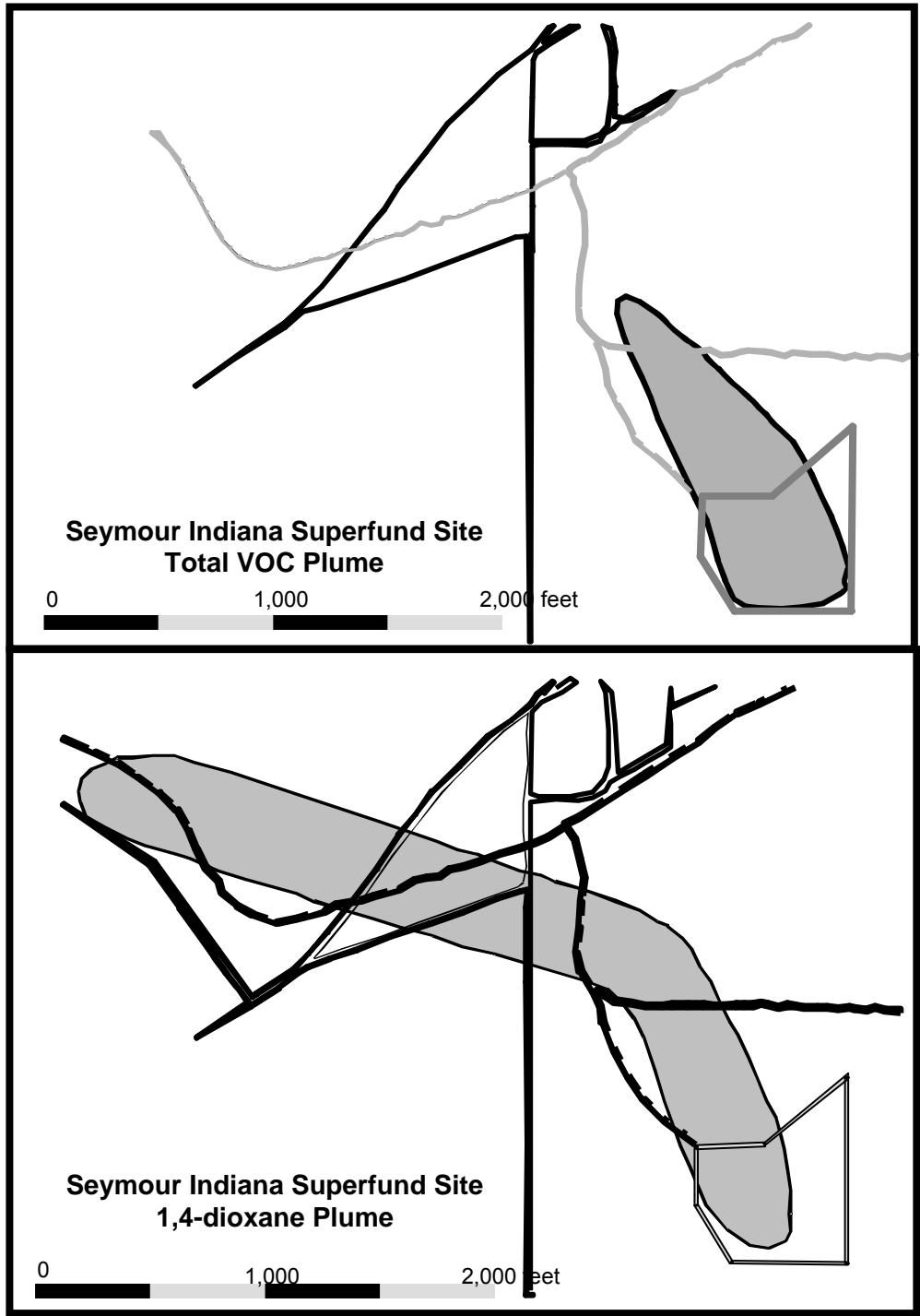
Data from contaminant release sites at which the occurrence and distribution of 1,4-dioxane has been characterized were collected with the goal of compiling a reference set for 1,4-dioxane plume behavior. Because there have been relatively few published studies, sources are primarily regulatory compliance reports obtained from those firms and agencies willing or able to share their work.   While the resulting compilation is ad hoc in nature, useful attributes of 1,4-dioxane behavior in the subsurface can nonetheless be discerned.

Seymour, Indiana Superfund Site
A solvent recovery and recycling plant in Seymour Indiana went bankrupt after nine years of operation, abandoning 50,000 drums and 98 large tanks, all filled with organic chemicals, many of which were found to be leaking. This case is documented in detail in Fetter, 1994 (see page 494). Shallow groundwater flow was estimated to be 400 feet per year. In the space of six years, between 1984 and 1990, the plume of dioxane contaminated groundwater advanced approximately 2,000 feet, for a total length of approximately 3,500 feet. Data from July of 1999 provided by the remedial project manager for this site indicate that remedial efforts have been successful in capturing the plume of 1,4-dioxane at the Seymour Site (Feldman, 2000).   Figure 2.4 presents the migration distances from sources at the Seymour site for total volatile organic compounds reported on a routine scan for halogenated VOCs, for tetrahydrofuran, and for 1,4-dioxane.

Fetter notes: "as it turned out, one of the tentatively identified compounds was more mobile and less subject to natural biodegradation than any of the compounds on the target organic list. The reported extent of this compound, 1,4-dioxane, a cyclical ether . . . and another mobile compound, tetrahydrofuran, had spread much farther than expected." Roy and Griffin, 1985, list 1,4-dioxane first, and tetrahydrofuran fourth, in a comprehensive list ranking the mobility of more than 100 organic compounds.

Figure 2.4

Seymour Indiana Superfund Site
Total VOC Plume

0   1,000   2,000 feet

Seymour Indiana Superfund Site
1,4-dioxane Plume

0   1,000   2,000 feet

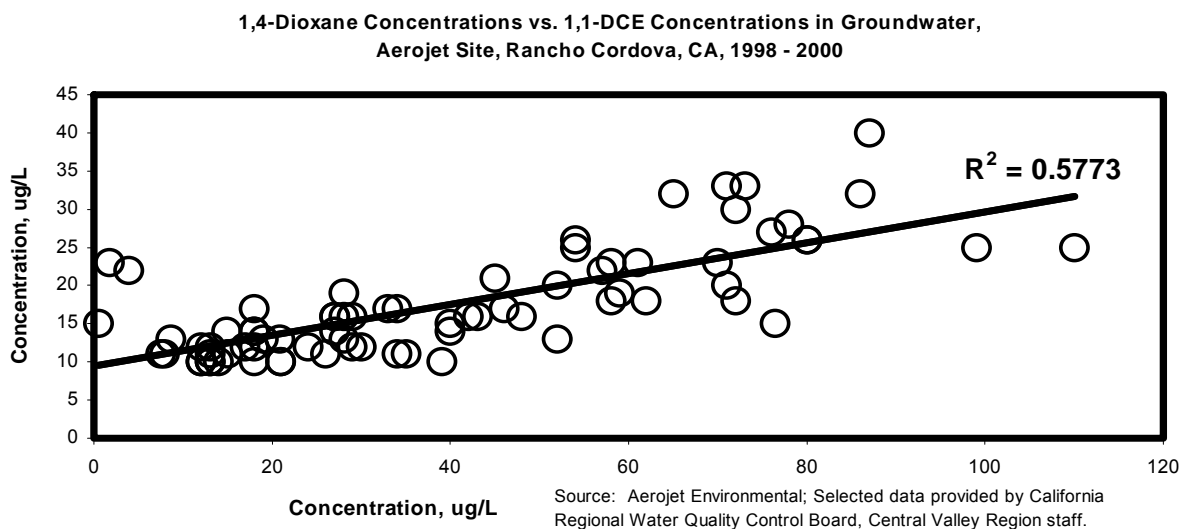San Gabriel Basin, California Superfund Sites– Baldwin Park Operable Unit
Several dozen sources have combined to form a plume extending eight miles in the San Gabriel Basin. 1,4-dioxane has been found to occur at many locations within the plume, but has not been found to extend significantly beyond the plume. One of the sources in this set of commingled plumes was a solvent recycler.   Contamination by 1,4-dioxane has impacted some supply wells, requiring well-head treatment. In El Monte, California, the average ratio of 1,4-dioxane to the sum of TCA, and its daughter products DCA and DCE is 76% (Bowman, et al, 2001).

The City of Industry installed a high-volume air stripper to treat a suite of volatile organic compounds including TCE, TCA and PCE.   After discovery of 1,4-dioxane and other contaminants at nearby contamination sites, influent flow was tested for 1,4-dioxane. Influent 1,4-dioxane concentrations measured at this air stripper were 610 ug/L, while effluent concentrations were 430 ug/L. The ratio of dioxane to the sum of TCA and DCA was 50% (Bowman, et al, 2001).

Rancho Cordova, California: Liquid Rocket Fuel Production Facility
1,4-dioxane has been detected during investigations for rocket fuel components at the Aerojet facility in Rancho Cordova, northern California, where it is believed to be associated with chlorinated solvents. A cursory review of available data for 74 analyses in which 1,4-dioxane was detected showed a moderate degree of correlation between 1,4-dioxane and 1,1-dichloroethylene (DCE), as shown in Figure 2.5. DCE is the abiotic transformation product of TCA. This should not be considered a rigorous analysis of data available from this site as non-detects were not included in the evaluation, and samples from the same wells on different dates were not weighted differently. No TCA detections are reported at this site; the solvent present in groundwater at highest concentrations is TCE.

Figure 2.5 Correlation of 1,4-dioxane to 1,1,Dichloroethylene at Rancho Cordova Aerojet Site

1,4-Dioxane Concentrations vs. 1,1-DCE Concentrations in Groundwater, Aerojet Site, Rancho Cordova, CA, 1998 - 2000

$R^2 = 0.5773$

Concentration, ug/L (y-axis)
Concentration, ug/L (x-axis)

Source: Aerojet Environmental; Selected data provided by California Regional Water Quality Control Board, Central Valley Region staff.

Solvent Recycling Facility, Silicon Valley, California
A solvent recycling facility in Silicon Valley, California, had completed design and installation of plume capture and treatment systems to remove chlorinated solvents from a high concentration release when 1,4-dioxane and tetrahydrofuran were reported in 1998. Because concentrations reached a maximum of 340,000 ug/L, additional investigation was performed, and tetrahydrofuran and 1,4-dioxane were determined to have migrated considerably further than the VOCs. Figure 2.6 shows the relative migration of VOCs, tetrahydrofuran, and 1,4-dioxane (Safety Kleen, 2000).

Figures 2.6   Solvent Recycling Facility, Silicon Valley, California

1,000,000

0   50

TOTAL VOCs, ug/L

1

10

1000

0   500

Tetrahydrofuran Conc., ug/L

10

100

1,000

10,000

100,000

1,4-Dioxane Concentrations, ug/L   0   500
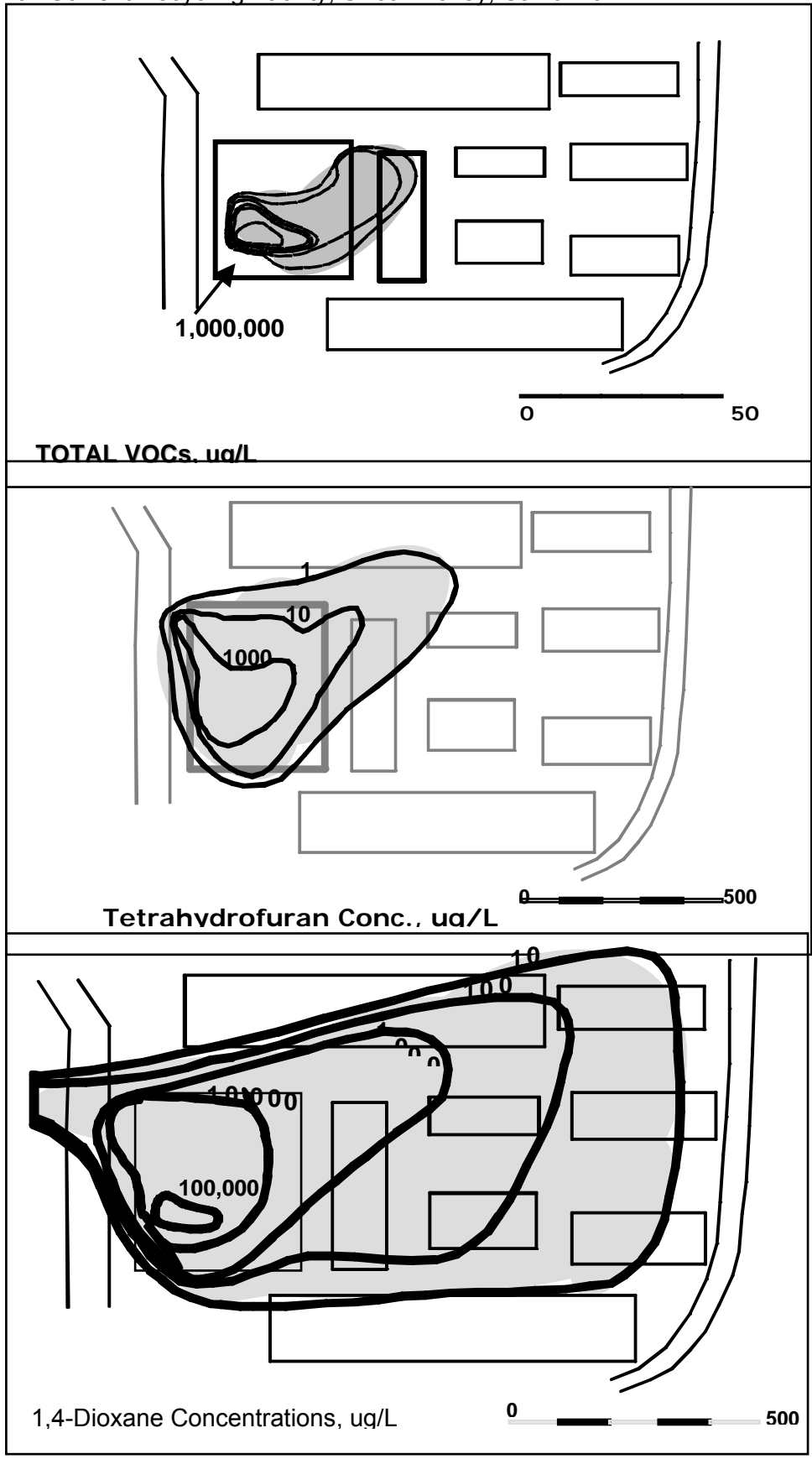
Hayward California, Aluminum Extrusion Facility

An aluminum products facility in Hayward, California at which TCA was used in a jet stream to wash aluminum product, released solvents and fuels to groundwater. Past practices allowed TCA to be released to the subsurface, forming a plume in which peak TCA concentrations were 16,000 ug/L. In 2000, 1,4-dioxane was analyzed in groundwater samples at the request of the Alameda County Water District hydrogeologist, and found to be present in an area of distribution greater than the host solvent, with peak concentrations at 94 ug/L (Trenholme, 2001).

Ratios of 1,4-dioxane to the sum of 1,1-dichloroethane, 1,1-dichloroethene, and TCA on five wells at this site ranged from 5% to 94%. Ratios decreased with distance from the source, counter to the expected trend. With increasing distance, biotransformation is expected to decrease TCA concentrations, resulting in a higher 1,4-dioxane to TCA ratio. Fuel constituents released near the source of the solvents may have resulted in cometabolism of solvents, or multiple sources may result in a more complicated pattern.

Figure 2.7 shows the relative distribution of solvent and stabilizers at this site. Figure 2.8 presents a bar chart contrasting 1,4-dioxane to host solvent concentrations. Solvent concentration is taken as the sum of TCA, the microbially mediated degradation product 1,1-dichloroethane, and the abiotic degradation product 1,1-dichloroethene. This example shows that 1,4-dioxane may occur in all ratios with respect to TCA and its degradation products.

Figure 2.7   Occurrence of 1,4-dioxane at TCA Release Site, Hayward, CA

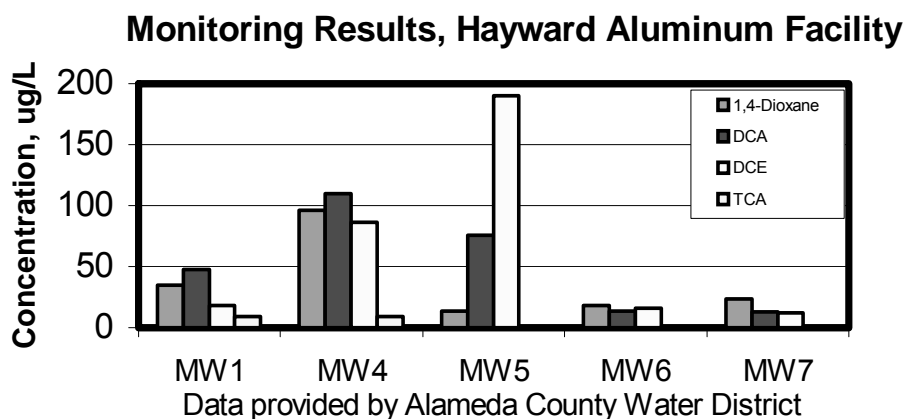## Monitoring Results, Hayward Aluminum Facility
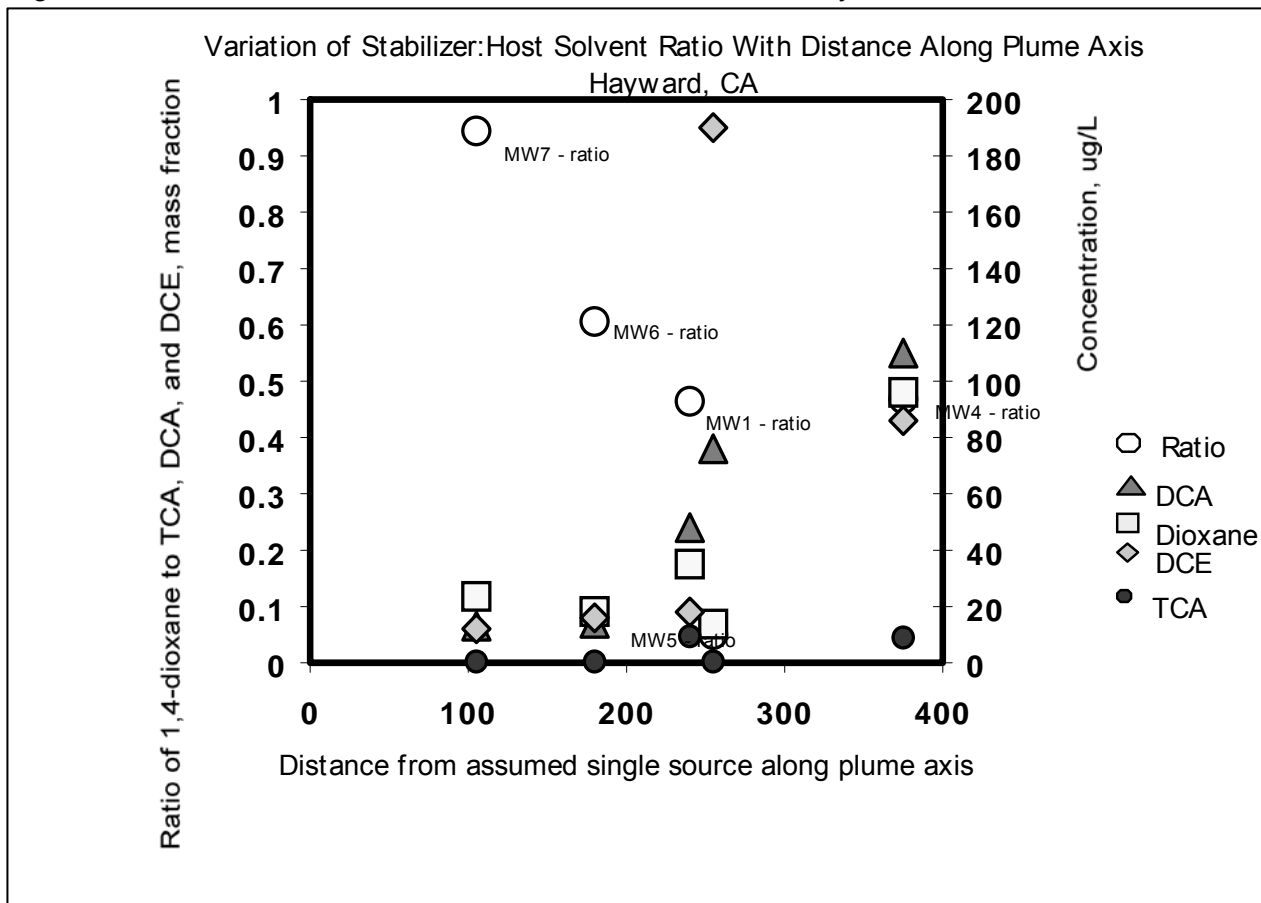
Figure 2.8   Sampling Results from TCA Release Site

Fullerton, California - Defense Industry Site
At the Hughes/Raytheon site in Fullerton, California, shallow groundwater sampled from a well
completed in a perched aquifer downgradient of the stills that caused the solvents release was found to
contain 1,4-dioxane at up to 133 ug/L, which is about 11% of the total chlorinated solvents detected in
this well, and about 12% of the sum of TCA and daughter product concentrations. 1,4-dioxane has not
been found in nine other wells sampled, and the extent of 1,4-dioxane in groundwater at this site has not
yet been delineated (DTSC, 2001).

Stockton, California Metal Fabricator
At the Kearney-KPF site in Stockton, California, where TCA was used in manufacture of flagpoles and
other metal products, 1,4-dioxane has been detected at up to 220 ug/L. At this site, air stripper effluent is
reinjected into the aquifer. Because air stripping is ineffective at removing 1,4-dioxane, a nearby water
supply well has been impacted, with 1,4-dioxane detected at 2 ug/L (Mello, 2001).

Orange County Groundwater Monitoring for 1,4-Dioxane
Efforts by the Orange County Water District to contain the threat of groundwater contaminated with
chlorinated solvents in their forebay region were frustrated by the discovery of 1,4-dioxane in
groundwater at concentrations up to 17 ug/L. A feasibility study for the removal of VOCs using air
stripping and liquid phase granular activated carbon had already been completed in 2000 when the
dioxane was discovered, but these methods are known to be ineffective in removing 1,4-dioxane. They
are now completing a second feasibility study to consider advanced oxidation techniques (Orange
County Water District, 2001).

Gloucester Landfill, Ontario, Canada
This landfill received and incinerated solvents in trenches from a nearby government laboratory for an
11-year period. Average linear groundwater flow velocity is estimated at 60 feet per year in a semi-
confined glacial outwash aquifer consisting of feldspar (50%), quartz (20%), minor fractions of mica,
calcite, dolomite, and hornblende, and an organic carbon content averaging 0.06%. The zone of highest
concentration of 1,4-dioxane was observed to move 80 feet in six years and remained essentially
unchanged. The plume of 1,4-dioxane identified at this facility, while not definitively associated with TCA
as a source at this site, leads the plume of TCA by nearly 500 feet (Jackson and Dwarakanath, 1999).

1,4-dioxane migrated about 660 feet overall within 8 years of the cessation of solvent incineration at this landfill, or within 20 years of the introduction of laboratory solvents to the subsurface at this site. 1,4-dioxane migration at this location was therefore a minimum of 35 feet per year. Concentrations ranged from 250 ug/L to 2000 ug/L (Lesage et al, 1990; Jackson and Dwarakanath, 1999).

Duke University Landfill, Durham, North Carolina
At the Duke Forrest Landfill at Duke University in Durham, North Carolina, 1,4-dioxane concentrations have been routinely measured in the 1,000 ug/L range, with peak concentrations before source removal at 2,800 ug/L. Researchers at Duke University determined that a mean retardation factor of 1.2 was suitable for estimating 1,4-dioxane migration following a series of soil column tests using site soils (Liu, et al, 2000).

Other Landfills – Occurrence in Leachate
1,4-dioxane was found in Operating Industries Landfill leachate (Monterey Park, Los Angeles area) at concentrations up to 19 mg/L. (US EPA, 1998b). In leachate samples from three hazardous waste landfills in Japan, 1,4-dioxane concentrations ranged from 20.7 to 1,370 mg/mL (Yasuhara, 1995). 1,4-dioxane is described as occurring in low abundance in leachate from an Oklahoma municipal landfill taking only residential waste and no industrial wastes (Eganhouse et al, 2001).

Printed Circuit Board Manufacturing Facility, Tampa Florida
A printed circuit board plant in Tampa, Florida, used degreaser tanks for preparing printed circuit boards. Leaks from the tanks steadily released solvent and still bottoms including TCE and TCA. Remedial investigations and treatment system design by previous investigators did not initially target or account for 1,4-dioxane, nor did regulatory orders require it. Initial 1,4-dioxane concentrations in extracted groundwater are less than 20 ug/L, however treated effluent in Florida may not exceed 5 ug/L, the Florida drinking water standard. Because discharge from the treatment system is to the sanitary sewer, water agency officials have expressed concern over the discharge of 1,4-dioxane, which could end up in reclaimed water used to recharge groundwater (Alonso, 2001).

2.6   Impacted Supply Wells

Domestic and municipal water supply wells have been impacted by 1,4-dioxane in numerous instances from solvent releases and other sources, including the following examples:

- In the San Gabriel Basin, California, the La Puente Valley Water District's water supply wells were shut down in 1998 due to perchlorate, NDMA, and 1,4-dioxane contamination migrating from the Baldwin Park Operable Unit Superfund Site (CRWQCB-LAR, 1998).
- A Massachusetts drinking water well contained 1,4-dioxane at 2100 ppb (Burmaster, 1982).
- 1,4-Dioxane was detected in 37% of the samples of well water collected near a solid waste landfill located 60 miles southwest of Wilmington, Delaware (Dewalle, et al, 1981).
- In Ann Arbor, Michigan, use of two municipal supply wells was halted in April 2001 pending further investigation when 1,4-dioxane was detected at 1 and 2 ug/L (Ann Arbor, 2001). The contamination is believed to originate from the Gelman Sciences site, which has also impacted domestic supply wells, initially discovered in 1989 (Michigan DEQ, 2000). Many households have been connected to the municipal water supply because 1,4-dioxane in their domestic wells exceeded the State of Michigan's generic residential limit (first 3 ug/L, then 77 ug/L, and revised again to 85 ug/L). Fifty supply wells in Washtenaw County are monitored quarterly for 1,4-dioxane, with 13 of these wells showing presence of 1,4-dioxane from 1 to 24 ug/L.
- In Stockton, CA, 1,4-dioxane was detected in a water supply well at 2 ug/L downgradient of a solvent release site at a metal fabricating facility. To treat solvent contaminated groundwater, extraction wells were installed and discharge was treated using packed tower air strippers, with effluent

reinjected into the ground. Because 1,4-dioxane is not effectively removed by conventional air-stripping, water bearing at least 20 ug/L 1,4-dioxane was reinjected (Mello, 2001).

- The California Department of Health Services tested 116 drinking water sources statewide for 1,4-dioxane between 1984 and November of 2000, and found no detectable concentrations of 1,4-dioxane (DHS, 2001). However, laboratory techniques have only recently allowed detection limits to approach the California DHS drinking water action level. Orange County Water District is in the process of installing and testing monitoring wells near solvent plumes for 1,4-dioxane (Herndon, 2001).

2.7   Distribution and Fate of 1,4-dioxane in Water and Air

1,4-dioxane is short-lived in the atmosphere, but persists in surface and groundwater, and is relatively immune to biodegradation. It is not significantly bioconcentrated in the food chain.

As discussed in Section 5.1 and 5.7, the hydrophilic nature of 1,4-dioxane and 1,3-dioxolane, coupled with their very low Henry's Law constants and octanol-water partition coefficients, cause these compounds to pass through groundwater and municipal wastewater treatment facilities without significant concentration reduction. The following sections examine the fate of these two compounds when released to surface water and the atmosphere.

A 1999 study by Dr. Akemi Abe at the Kanagawa Environmental Research Center in Japan profiled the distribution of 1,4-dioxane in relation to sources in the water environment in Kanagawa Prefecture, Japan (Abe, 1999). The study found that 1,4-dioxane was widely distributed in both surface and groundwater, with detections in nearly all samples with the exception of a few spring water samples. Presence of 1,4-dioxane was closely correlated to the presence of TCA, with a correlation coefficient of 0.872 for 27 samples, and ratios ranging from 0.08 to 5.89% by volume.

2.7.1   Aquatic Fate

1,4-dioxane
1,4-dioxane is not expected to hydrolyze significantly (Lyman, et al, 1982).   Volatilization data for 1,4-dioxane were not found in a literature search; since 1,4-dioxane is infinitely soluble in water, a volatilization half-life cannot be estimated. 1,4-dioxane has a moderate vapor pressure at 25 °C (37 mm Hg); therefore, volatilization is possible (Lange, 1967; Lyman et al, 1982).   The low estimated Henry's Law Constant (3×10^{-6} atm-m^3/mol) suggests transfer of dioxane from water to air is negligible (Montgomery, 1996). 1,4-Dioxane is photo-oxidized by aqueous hydroxyl radicals with a half-life of 336 days at *p*H 7 (Anbar et al, 1967).

With an estimated K_{OC} of 1.23, 1,4-dioxane is not expected to significantly adsorb on suspended sediments. 1,4-Dioxane exhibited a negligible biological oxygen demand in two activated sludge experiments and the compound has been classified as relatively non-biodegradable (Lyman et al, 1982; Mills and Stack, 1954; Alexander, 1973; Heukelekian and Rand, 1955; Fincher and Payne, 1962; Lyman et al, 1982).

1,4-dioxane should volatilize from dry soil based on its moderate vapor pressure (37 mm Hg at 25° C, Verschueren, 1983). No bioconcentration data for 1,4-dioxane were available. The log octanol/water partition coefficient (K_{OW}) of 1,4-dioxane is -0.27.   This very low K_{OW} suggests that 1,4-dioxane will not bioconcentrate significantly in aquatic organisms (Hansch and Leo, 1985).

1,3-dioxolane
Based on an experimental octanol-water partition coefficient (log K_{OW}) of -0.37 and a linear regression relating K_{OC} to K_{OW}, the K_{OC} for 1,3-dioxolane can be estimated to be 15, indicating high mobility in soil. Leaching to groundwater can be expected (Hansch et al, 1985; Lyman et al, 1982; Swann et al 1983). An experimental vapor pressure of 79 mm Hg at 20 °C suggests that volatilization from dry soil surfaces may be important (Riddick, et al, 1986).

Based on an experimental Henry's Law constant for 1,3-dioxolane of 2.4 x 10^{-5} atm-m^3/mole at 25° C (Hine and Mookerjee, 1975), volatilization from water and soil is classified as not rapid but possibly significant (Lyman et al, 1982).

If released to water, hydrolysis, aquatic oxidation with photochemically produced hydroxyl radicals, sorption to sediment and bioconcentration in aquatic organisms are not expected to be environmentally important removal processes of 1,3-dioxolane (US EPA, 1987). The bioconcentration factor for 1,3-dioxolane is estimated to be 0.3 (US EPA, 1987).   1,3-dioxolane has been tested for water stability at pH 4, 7 and 9, and is estimated to be stable in the aquatic environment under typical environmental conditions for over one year, neglecting volatilization (Dioxolane Manufacturers Consortium, 2000).

Volatilization half-lives of 34 hrs and 15 days have been estimated for a model river (one meter deep) and a model environmental pond, respectively (Lyman et al, 1982; US EPA, 1987).

Its complete water solubility suggests that 1,3-dioxolane may be susceptible to significant transport in aquatic environments. Aquatic oxidation with photochemically produced hydroxyl radicals is not likely to be an important fate process based on a half-life of 200 days for 1,3-dioxolane in water under continuous sunlight, with the aquatic oxidation rate experimentally determined to be 4.0X10^9 L/mol-s (pH not stated) (Buxton, et al, 1988).

2.7.2 Atmospheric Fate

1,4-dioxane
The half-life of the reaction of 1,4-dioxane with photochemically produced hydroxyl radicals in the atmosphere was estimated to be 6.69 to 9.6 hr (Brown et al, 1975; US EPA, 1986). Experimental results of sunlight-irradiated mixtures of 1,4-dioxane/NO suggest similar half-lives (Dilling, et al, 1976). The products of the reaction of ethers with hydroxyl radicals are likely to be aldehydes and ketones (Graedel, et al, 1986).

Air samples at three urban sites in New Jersey were collected from July 6-August 16, 1981. The geometric mean 1,4-dioxane concentrations ranged from 0.01-0.02 ppb. Fifty-one percent of the samples were positive for 1,4-dioxane (Harkov, et al, 1984). Dioxane is also found in indoor air samples. 1,4-Dioxane is among the organic compounds emitted from building materials (California Department of Health Services, 1996).

1,3-dioxolane
Based on a measured vapor pressure of 79 mm Hg at 20° C (Riddick et al, 1986), 1,3-dioxolane is expected to exist almost entirely in the vapor phase in the ambient atmosphere (Eisenreich et al, 1981). Vapor-phase 1,3-dioxolane is expected to degrade by reaction with photochemically produced hydroxyl radicals. The rate constant for the vapor-phase reaction of 1,3-dioxolane with photochemically produced hydroxyl radicals can be estimated to be 14.6 x 10^{-12} cm^3/molecule-sec at 25° C, which corresponds to an atmospheric half-life of about 1.1 days at an atmospheric concentration of 5 x 10^5 hydroxyl radicals per cm^3 (Atkinson 1988). Based on its complete water solubility, removal of 1,3-dioxolane from air via wet deposition may occur (Riddick, et al, 1986).

3.0   LABORATORY ANALYSIS OF SOLVENT STABILIZER COMPOUNDS

Commercial laboratories commonly analyze for 1,4-dioxane in water by three methods: EPA 524.2 for drinking water, and EPA 8260 and 8270 for groundwater and hazardous waste (Mackenzie, 2001).   Use of EPA 8260 without modifications typically leads to detection limits in the range of 100 to 150 ug/L due to the water solubility of dioxane, i.e., purging efficiency is poor.

A modification to EPA 8260 has allowed lower detection limits. A salt, sodium sulfate, is added to samples to enhance the purge efficiency of 1,4-dioxane. A heated sparge is also used to further improve the sensitivity of the method. Combined with optimized scan parameters on the GCMS system, sensitivity was greatly improved, allowing detection limits of 2.0 ug/L. However, these low detection limits are not consistently achievable, leaving doubt as to the reliability of this approach (West Coast Analytical Services, 2001).

Determination of 1,4-dioxane in water at low detection levels is most often accomplished using modified EPA 8270 with liquid-liquid extraction and isotope dilution by capillary column gas chromatography-mass spectrometry (GC-MS). This GC-MS method is optimized for a single analyte, 1,4-dioxane, and is not appropriate as a multi-residue procedure due to the scan range, chromatographic conditions, and tuning requirements specified. The method is described as follows:

> A one-liter sample is dechlorinated by addition of sodium sulfite. An internal standard, 1,4-dioxane-d_8 , is added and the sample is transferred to a continuous liquid-liquid extractor. The sample is extracted with methylene chloride for several hours, often overnight, and the extract is concentrated under a stream of nitrogen to a one-mL final volume. 1,4-dioxane and the deuterated internal standard are separated, identified, and determined by GC-MS, using a system equipped with a fused silica capillary column. Compounds are identified by retention time and selected ions relative to authentic standards and a user generated mass spectrum library. Reference spectra, retention times, and response factors are determined under conditions used in the analysis of sample extracts. The concentration of 1,4-dioxane is measured by relating the MS response of its quantitation ion to the response of the deuterated internal standard quantitation ion. Deuterated dioxane and pure dioxane standards are available from Aldrich Chemical in St. Louis, Missouri (Draper et al, 2000).

The California Department of Health Services' Sanitation and Radiation Laboratory Branch in Berkeley conducted an evaluation of available analytical techniques for reliable determination of 1,4-dioxane in drinking water. This investigation determined that conventional purge and trap is strictly limited by 1,4-dioxane's poor purge efficiency with detection limits about 100 times higher than for more efficiently purged volatile organic compounds. Liquid-liquid extraction techniques can achieve reliable reporting limits of 0.2 ug/L. Methane chemical ionization MS-MS offers detection limits three orders of magnitude lower than for electron ionization MS ion trap methods, making it possible to analyze for dioxane in the part per trillion range. Analytical precision is improved by the use of isotope-labeled standards (1,4-dioxane-d_8), which also results in significantly improved accuracy, approaching 100%. Isotope dilution is also possible using non-selective gas chromatographic detectors because of the high resolving power of capillary GC columns that separate deuterium labeled compounds from their native analogues (Draper, 2000).

West Coast Analytical Services reports that replicate analysis of samples spiked with 3 ug/L analyzed by the Modified EPA 8270 Isotope Dilution, Extraction and GCMS yielded a Relative Standard Difference of only 5%, i.e. a three standard deviation detection limit of 0.5 ug/L (West Coast Analytical Services, 2001).

Matrix Environmental Group of Ann Arbor, Michigan, has contributed to the development of a GC/MS technique, Method 1624 (Holodnick, 2001). This method is applicable to the analysis of 1,4-dioxane in water in the range of 1-200ug/L. The practical quantitation limit is 1 ppb (ug/L). Reproducibility as Relative Percent Difference is typically less than 10%.

Analysis by Method 1624 is performed by heated purge and trap technology preparing the sample in the presence of a salt and a deuterated form of 1,4-dioxane. Detection is achieved via an Ion Trap Detector. Qualitative identification is made by comparing resultant mass spectra and GC retention time against the same for the standard reference material. Quantitation is achieved by relating the MS response for the selected ion produced by 1,4-Dioxane with the MS response for the selected ion of the internal standard (Holodnick, 2001).

An ad hoc survey of a few analytical laboratories for the methods, detection limits, reporting limits, and sample requirements is summarized in Table 3.1 below.

Table 3.1 Comparison of Commercial Laboratory Services for Analysis of 1,4-dioxane

Laboratory	Method	MDL	PQL	Sample Volume	Pres.
E.S. Babcock & Sons (1)	EPA 524.2	20 ug/L	30 ug/L	2 x 40 mL	HCl
E.S. Babcock & Sons	EPA 8260	20 ug/L	30 ug/L	2 x 40 mL	HCl
E.S. Babcock & Sons	EPA 8270	0.06 ug/L	0.2 ug/L	1 Liter	None
Matrix Environmental Group, Inc. (2)	EPA 1624	-	1 ug/L RPD<10%	2 x 40 mL	HCl
WCAS (3)	EPA 8270	0.23 ug/L	0.5 ug/L	1 Liter	None

1) Riverside, CA 909-653-3351; 2) Ann Arbor, Michigan, 734-665-4610; 3) West Coast Analytical Services, Santa Fe Springs, CA, 562-948-2225

Current prices for analysis of 1,4-dioxane range from $90 - $120 for EPA 8260, $180 to $275 for modified EPA 8270, and $120 - $150 for EPA 1624 (surveyed Spring 2001, including additional commercial laboratories not listed here).

To verify the accuracy of the laboratory performing the analysis, third-party whole-volume standards are available to submit double-blind samples of 1,4-dioxane. This may be important for new projects as most labs do not routinely analyze for 1,4-dioxane, and accuracy and precision should be verified. Environmental Resources Associates of Colorado, among others, provides whole volume custom standards (3-40 mL VOAs for EPA 8260 and 2-1 L bottles for EPA 8270); both for less than $300 plus express shipping (ERA, 2001).

4.0 TOXICOLOGY OF 1,4-DIOXANE AND APPLICABLE REGULATORY STANDARDS

Availability of ample toxicological data is critical to the determination of the degree to which 1,4-dioxane, 1,3-dioxolane and other solvent stabilizers pose a threat to drinking water quality. Because regulatory standards for 1,4-dioxane do not yet include a Federal Maximum Contaminant Level, state government environmental officials and scientists have used various federal advisory levels or performed their own risk assessments to establish state advisory levels. The result has been a spectrum of professional opinion among toxicologists in different states, and also within states. For example, California uses a drinking water advisory level of 3 ug/L for 1,4-dioxane, while published and peer reviewed journal articles recommend a standard on the order of 1,200 ug/L using physiology-based models. The flexible nature of California's advisory level make these two determinations more similar than it first appears, yet regulatory agencies have employed strict cleanup standards at solvent release and other industrial waste sites closer to 3 ug/L due to the finding that 1,4-dioxane is listed as a probable human carcinogen. The following sections summarize regulatory standards, and salient information from the toxicology literature for 1,4-dioxane summarizing studies of its carcinogenicity and toxicity. The determination of site cleanup standards for 1,4-dioxane from health risk assessments is also discussed.

4.1 Drinking Water Standards

<table>
<tr><td colspan="4">WATER QUALITY CRITERIA and GUIDELINES
FOR PROTECTION OF HUMAN HEALTH FROM SOLVENT STABILIZER COMPOUNDS
(compiled in March 2001)</td></tr>
<tr><td colspan="4">1,4-DIOXANE</td></tr>
<tr><td>Jurisdiction</td><td>Guideline</td><td>Application</td><td>Reference</td></tr>
<tr><td>Massachusetts</td><td>50 µg/L</td><td>Guideline</td><td>Anastas 1988</td></tr>
<tr><td>Florida</td><td>5 ug/L</td><td>Drinking water standard</td><td>US EPA 1993</td></tr>
<tr><td>Maine</td><td>70 ug/L</td><td>Drinking water standard</td><td>US EPA 1993</td></tr>
<tr><td>Michigan</td><td>85 ug/L</td><td>Drinking water standard</td><td>Michigan DEQ, 2001</td></tr>
<tr><td>California</td><td>3 ug/L</td><td>Drinking water action level</td><td>Cal-EPA DHS, 2001</td></tr>
<tr><td>North Carolina</td><td>7 ug/L</td><td>Drinking water action level</td><td>US EPA 2001</td></tr>
<tr><td colspan="4">EPICHLOROHYDRIN</td></tr>
<tr><td>Jurisdiction</td><td>Guideline</td><td>Application</td><td>Reference</td></tr>
<tr><td>California</td><td>4.5 ug/L</td><td>Prop 65 Regulatory Level; No significant risk level for carcinogens</td><td>CDWR 1997</td></tr>
<tr><td>United States</td><td>Zero</td><td>MCLG – maximum contaminant goal for carcinogens is zero</td><td>CFR 40(1)141.50</td></tr>
<tr><td colspan="4">TETRAHYDROFURAN</td></tr>
<tr><td>Jurisdiction</td><td>Guideline</td><td>Application</td><td>Reference</td></tr>
<tr><td>New York</td><td>50 µg/L</td><td>Guidance value</td><td>NYSDEC 1998</td></tr>
<tr><td>Massachusetts</td><td>1300 µg/L</td><td>Guideline</td><td>Anastas 1998</td></tr>
<tr><td>Michigan</td><td>230 µg/L</td><td>Drinking water standard</td><td>US EPA 1993</td></tr>
<tr><td>New Hampshire</td><td>156 µg/L</td><td>Drinking water standard</td><td>US EPA 1993</td></tr>
<tr><td>Wisconsin</td><td>50 µg/L</td><td>Drinking water standard</td><td>US EPA 1993</td></tr>
<tr><td colspan="4">1,3-Dioxolane – none found</td></tr>
</table>

The California Action Level is not a regulated limit for which testing must be performed. The California Department of Health Services (DHS) explains its Action Levels as follows:

> *If a contaminant exceeds its Action Level in drinking water, the (DHS) recommends that the utility inform its customers and consumers as soon as is feasible about the presence of the contaminant, and its potential for adverse health effects. If the concentration of a contaminant for which no MCL has been established and for which the Action Level is*

based on cancer risk is detected at concentrations 100 times the Action Level, DHS recommends the well be taken out of service.

Action Levels for contaminants considered carcinogens [including 1,4-dioxane], correspond to a theoretical lifetime risk of up to one excess case of cancer in a population of 1,000,000 people—the 10^{-6} de minimis risk level. (In that population, approximately 250,000-300,000 cases of cancer would be anticipated to occur naturally.) A level 100 times greater corresponds to a theoretical lifetime risk of up to one excess case of cancer in 10,000 people (i.e., 10^{-4} risk), the upper value of the 10^{-6} to 10^{-4} risk range typically allowed by regulatory agencies. If the action level for a carcinogen is a concentration corresponding to a risk greater than 10^{-6}, the recommendation for source removal remains at the 10^{-4} level.

The risk calculation used to determine DHS Action Levels follows the conventional 70 kg body weight model, 2 liters per day consumption, with the carcinogen slope factor (CSF) for 1,4-dioxane as 0.011 mg/kg/day, resulting in the health-based limit at the 10^{-6} risk level as 0.003 mg/L. A reference dose (RfD) and a maximum contaminant level (MCL) has not been established for 1,4-dioxane.

4.2   Human health data

Little data is available for human exposure to 1,4-dioxane. One account of acute exposure includes reports of five cases of fatal poisoning in men working in a textile factory who inhaled excessive amounts of 1,4-dioxane. Symptoms were irritation of the upper respiratory passages, coughing, irritation of eyes, drowsiness, vertigo, headache, anorexia, stomach pains, nausea, vomiting, uremia, coma, and death. Autopsy revealed congestion & edema of lungs and brain, and marked injury of liver and kidney. Death was attributable to kidney injury. Blood counts showed no abnormalities other than considerable leukocytosis. Exposure levels for these cases are unknown and investigators consider it debatable whether this was an instance of chronic or acute exposure (Clayton, et al, 1982).

1,4-dioxane & beta-hydroxyethoxyacetic acid (HEAA – a metabolite of 1,4-dioxane) were found in urine of plant personnel exposed to time-weighted average concentrations of 1.6 ppm dioxane for 7.5 hours. Average concentrations of dioxane HEAA in urine were 3.5 and 414 micro-moles/L, respectively (Young, et al, 1976).

No adequate epidemiological data were available to assess the carcinogenicity of 1,4 dioxane to humans. (Anonymous, 1990).

A physiologically based pharmacokinetic model (PBPK model) was developed for a lactating woman to estimate the amount of chemical that a nursing infant ingests for a given nursing schedule and maternal occupational exposure. Human blood/air and milk/air partition coefficients (PCs) were determined for 1,4-dioxane and 18 other VOCs. Milk/blood PC values were above 3 for carbon tetrachloride, TCA, perchloroethylene (PCE), and 1,4-dioxane. In a simulated exposure of a lactating woman to a threshold limit value concentration of an individual chemical, only PCE and 1,4-dioxane exceeded the U.S. Environmental Protection Agency non-cancer drinking water ingestion rates for children. Very little data exists on the pharmacokinetics of lactational transfer of volatile organics. (Fisher et al, 1997).

IARC and the National Toxicology Program (NTP) stated that variability in the mutagenicity test results with TCE might be due to the presence of various stabilizers used in TCE which are mutagens (e.g. epoxybutane, epichlorohydrin).

4.2.1   Occupational Exposure

Most occupational exposure limits are for the inhalation pathway. Exposure limits for breathing vapors of 1,4-dioxane has bearing on water quality as it may limit the concentration that can be distributed in water

systems. Volatile organic compounds may be inhaled while showering, dishwashing, or other household uses of water.

The National Occupational Hazard Survey estimates that 334,000 workers are potentially exposed to 1,4-dioxane, 100,000 of whom are exposed as a result of dioxane contamination of TCA. OSHA estimates that 466,000 workers are potentially exposed (Sittig, 1985).

The Permissible Exposure Limit (PEL) for 1,4-dioxane is 100 ppm as an 8-hour Time Weighted Average (TWA 360 mg/m^3 – skin designation) (Code of Federal Regulations, 1998). The PEL was raised from the 1989 OSHA PEL TWA of 25 ppm (90 mg/m^3), skin designation, although the lower PEL is still enforced in some states (NIOSH, 1997). The Threshold Limit Value for 1,4-dioxane is 25 ppm as an 8-hour Time Weighted Average (TWA), skin, (ACGIH, 1998)

The National Institute of Occupational Safety and Health (NIOSH) recommends that dioxane be regulated as a potential human carcinogen (NIOSH, 1997). NIOSH usually recommends that occupational exposures to carcinogens be limited to the lowest feasible concentration. The NIOSH Recommended Exposure Limit for a thirty minute period lists a ceiling value of 1 ppm (3.6 mg/m^3).

1,3-dioxolane
Human exposure is thought to be limited to production workers involved in the manufacture of 1,3-dioxolane, the production of polyacetals (plastics), or the use of dioxolane as a chemical intermediate. Industrial hygiene monitoring of production and polyacetal manufacturing areas at a major production facility indicated that worker exposure levels are low. Over several years, of monitoring, data from 91 measurements of air concentrations showed an average level of 0.29 ppm and values ranged from 0 to 1.6 ppm.

4.3   Animal Laboratory Studies

The following summaries of toxicity and carcinogenicity studies will be of greatest interest to toxicologists and other scientists engaged in health risk assessments.

4.3.1   Toxicity

- dogs given dioxane orally over a period of 9 days died after a total consumption of about 3 g/kg, with severe liver & kidney damage (ACGIH, 1986)
- kidney and liver injury occurs in rabbits and guinea pigs after repeated dermal application (Doull et al, 1980).

Various studies with 1,4-dioxane identified:
- oral LD50 of 5.66 g/kg in mice
- oral LD50 of 5.17 g/kg in rats
- oral LD50 of 3.90 g/kg in guinea pigs
- inhalation LC50 for rats was estimated to be 14,250 ppm
- dermal LD50 for rabbits of 7.6 g/kg
- 1,4-Dioxane is absorbed through skin, causing kidney and liver injury in rabbits and guinea pigs following repeated topical application of 20 and 10 drops of 80% dioxane/day for 14 weeks. (Shell Oil, 1980).

4.3.2 Carcinogenicity

The International Agency for Research on Cancer classifies 1,4-dioxane as a probable human carcinogen ('B2'). The basis provided for this classification of carcinogenicity is 1) evidence in humans: inadequate; 2) evidence in animals: sufficient; 3) evidence for activity in short-term tests: inadequate (IARC, 1976). The animal evidence cited is the induction of nasal cavity and liver carcinomas in multiple strains of rats, liver carcinomas in mice, and gall bladder carcinomas in guinea pigs (US EPA, 2000c).

Willhite et al (1999) note the limitations of the quantitative risk assessment techniques employed to derive preliminary drinking water standards. Animal studies note a non-linear nature of exposure to 1,4-dioxane, with toxic and tumorogenic effects occurring only after saturation of the uptake and elimination systems for the animals studied. The US EPA linearized multi-stage procedure relies on body surface area procedures that do not work well for interspecies scaling of dose. Willhite et al (1999) advocate a physiological based pharmacokinetic (PBPK) model, and Reitz et al (1990) used a PBPK model to determine that a more appropriate drinking water standard may be on the order of 1.2 mg/L rather than 0.003 mg/L, the current California Action Level.

The following summaries highlight key studies on the carcinogenicity of 1,4-dioxane in laboratory animal tests[3].

Goldsworthy et al (1991) summarizes several studies as follows (summaries of individual studies follow):

> *Several long-term studies with 1,4-dioxane have shown it to induce liver tumors in mice, and nasal and liver tumors in rats when administered in amounts from 0.5 to 1.8% in the drinking water (Argus et al. 1965; Kociba et al. 1974; National Cancer Institute, 1978). In order to examine potential mechanisms of action, chemically-induced DNA repair (as an indicator of DNA reactivity) and cell proliferation (as an indicator of promotional activity) were examined in nasal turbinate epithelial cells and hepatocytes of male Fischer-344 rats treated with dioxane. Neither dioxane nor 1,4-dioxane-2-one, one of the proposed metabolites, exhibited activity in the in vitro primary rat hepatocyte DNA repair assay, even from cells that had been isolated from animals given either 1 or 2% dioxane in the drinking water for 1 week to induce enzymes that might be responsible for producing genotoxic metabolites. No activity was seen in the in-vivo hepatocyte DNA repair assay in animals given a single dose of up to 1000 mg/kg dioxane or up to 2% dioxane in the drinking water for 1 week. Treatment of rats with 1.0% dioxane in the drinking water for 5 days yielded no increase in liver/body weight nor induction of palmitoyl CoA oxidase, indicating that dioxane does not fit into the class of peroxisomal proliferating carcinogens. The percentage of cells in DNA synthesis phase (S-phase) was determined by administration of 3H-thymidine and subsequent quantitative histoautoradiography. The hepatic labeling index (LI) did not increase at either 24 or 48 h following a single dose of 1000 mg/kg dioxane. The LI did increase approximately two-fold in animals given dioxane in the drinking water for 2 weeks. No DNA repair was seen in either nasoturbinate or maxilloturbinate nasal epithelial cells isolated from animals treated with 1% dioxane in the drinking water for 8 days followed by a single dose of up to 1000 mg/kg dioxane by gavage 12 h before sacrifice. Reexamination of the nasal passages of male rats in archived material from the NTP bioassay (National Cancer Institute 1978), revealed that the primary site of tumor formation was the anterior third of the dorsal meatus. The location of these tumors supports the proposal that inhalation of dioxane-containing drinking water may account for the site specificity of these nasal lesions. In vivo studies showed no increase relative to controls in cell proliferation at the site of highest tumor formation in the nose in response to 1.0% dioxane in the drinking water for 2 weeks. Thus, repair-inducing DNA adduct formation, peroxisomal proliferation in the liver, and short-term induction of cell proliferation in the nose do not appear to be involved in tumor formation by dioxane. There may be a role of dioxane-induced cell proliferation in the formation of the liver tumors. However, the quantitative relationships between induced cell proliferation and tumorogenic potential have yet to be established. (Goldsworthy, et al, 1991).*

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[3] the toxicology information listed is selected verbatim from the sources, and presented for the convenience of those readers experienced in the development of Health Risk Assessments. The author is not a toxicologist and has not evaluated the quality or validity of the studies cited.

- *A bioassay of 1,4-dioxane for possible carcinogenicity was conducted by administering the test chemical in drinking water to Osborne Mendel rats and B6C3F1 mice at concentrations of either 0.5% or 1.0% (v/v) in drinking water. The rats were dosed for 110 weeks and the mice for 90 weeks. In rats, the incidence of squamous cell carcinomas of the nasal turbinates was statistically significant. In both male and female mice, the incidence of hepatocellular carcinomas was statistically significant (p < 0.001). 1,4-Dioxane induced hepatocellular adenomas in female Osborne Mendel rats. 1,4-Dioxane was carcinogenic in both sexes of rats, producing squamous cell carcinomas of the nasal turbinates, and in both sexes of B6C3F1 mice, producing hepatocellular carcinomas (NCI, 1978).*

- *Liver tumors, ranging from small neoplastic nodules to multifocal hepatocellular carcinomas in 6 of 26 male Wistar rats given 1% 1,4-dioxane in drinking water for 63 weeks (total dose 130 g). One rat developed a transitional-cell carcinoma of kidney pelvis, and one developed leukemia. There was also one lymphosarcoma in 9 control animals (Argus et al, 1965).*

- *60 male and 60 female Sherman rats given 0, 0.01, 0.1 or 1% 1,4-dioxane in drinking water for 716 days. At the highest level, 10 developed hepatocellular carcinomas, 2 developed cholangiomas, and 3 developed squamous-cell carcinomas of the nasal cavity. One rat receiving 1,4-dixoane at the 0.1% level developed hepatocellular carcinoma. No statistically significant increases in incidence of tumors were seen in rats given the two lower dose levels (Kociba et al, 1974). This study did not report the tumor incidences for male and female rats separately.*

- *4 groups of 28 to 32 male Sprague-Dawley rats were given 0.75, 1.0, 1.4 or 1.8% ... in drinking water for 13 months (total dose 104-256 g/rat). One rat receiving 0.75%; one receiving 1.0%; two receiving 1.4%; and two receiving 1.8% developed nasal cavity tumors. These were mainly squamous-cell carcinomas, with adenocarcinomas in 2 cases. Liver cell tumors developed in 3 rats receiving 1.4%, and subcutaneous fibroma developed in 12 rats receiving 1.8% 1,4-dioxane compared to one in thirty among control animals (Argus et al, 1973; Hogh-Ligeti et al, 1970).*

- *22 male guinea pigs received drinking-water containing 0.5 to 2% 1,4-dioxane over 23 months (total dose, 588-623 g/animal). Two animals had carcinomas of the gall bladder, and 3 had hepatomas. No liver tumors were reported in 10 untreated controls (Hogh-Ligeti and Argus, 1970).*

- *Rats given 1.0 or 0.1% 1,4-dioxane in drinking water for 4 to 24 months showed renal tubular and hepatocellular degeneration, necrosis and regeneration. Rats ingesting 1.0% had increased incidence of liver tumors and nasal carcinomas (Kociba, et al, 1975).*

- *1,4-dioxane induced liver neoplasms after chronic ingestion of cytotoxic dosages in rats. Treatment of rats with tumorigenic dose levels of 1,4-dioxane (1 g/kg/day) in drinking water for 11 weeks resulted in a 1.5 times increase in hepatic DNA synthesis. Cytotoxicity was not detected in rats dosed orally with non-tumorigenic levels of 1,4-dioxane (10 mg/kg/day). Alkylation of hepatic DNA and DNA repair was not detected in rats dosed orally with 1 g ^{14}C-1,4-dioxane/kg. 1,4-dioxane did not elicit a positive response in Ames bacterial mutagenicity or Williams hepatocyte DNA repair in vitro assay. The lack of genotoxic activity of 1,4-dioxane and its cytotoxicity at tumorigenic dose levels suggest a non-genetic mechanism of liver tumor induction in rats (Stott et al, 1981).*

The following discussion on the applicability of laboratory animal cancer bioassay data to the potency of 1,4-dioxane in humans reveals inherent limitations to the extrapolation methods employed in conventional risk assessments:

> *A cancer bioassay conducted in 1974 (Kociba et al.) indicated that rats given drinking water containing dioxane at a dose of 1184 mg increased incidence of liver tumors. Applying the linearized multistage extrapolation model to these data, the administered dose estimated to present a human cancer risk of 1 in 100,000 (10^{-5}) was 0.01 mg. This estimate assumed that humans were about 5.5 times more sensitive than rats on a mg/kg basis. However, this approach did not consider that the metabolism of dioxane is saturable at high doses. Based on experience with similar chemicals, it is known that the conventional risk extrapolation method may overestimate the most likely human cancer risk.*

In order to determine more accurately the likely human response following lifetime exposure to dioxane, a physiologically based pharmacokinetic (PB-PK) model was developed. The objective of this study was to establish a quantitative relationship between the administered dose of dioxane and the internal dose delivered to the target organ. Using this PB-PK model, and assuming that the best dose surrogate for estimating the liver tumor response was the time-weighted average lifetime liver dioxane concentration, the cancer risk for humans exposed to low doses of dioxane was estimated. The dose surrogate in humans most likely to be associated with a tumorigenic response of 1 in 100,000 is 280 micro-mol/L, equivalent to an administered dose of about 59 mg lower confidence limit on the dose surrogate at the same response level is 1.28 micro-mole/L, equivalent to an administered dose of 0.8 mg. Traditional approaches based on the administered doses in the rodent bioassay, if uncorrected for metabolic and physiological differences between rats and humans, will overestimate the human cancer risk of dioxane by as much as 80-fold. (Leung H-W, 1990).

1,3-dioxolane
Dioxolane demonstrates a low order of acute toxicity to mammals by the oral, inhalation, and dermal routes. Genotoxicity has been evaluated using multiple *in vitro* and *in vivo* experimental procedures covering both mutation and chromosome aberration. The weight of evidence indicates lack of significant genotoxic properties. Adverse reproductive effects are absent at dosage levels below maternally toxic doses. Dioxolane is not a specific developmental toxin. (Dioxolane Manufacturers Consortium, 2000).

4.3.3   Teratogenicity and Reproductive Effects

- *The teratogenic potential of the industrial solvent 1,4-dioxane was evaluated in rats. The compound was administered to pregnant Sprague Dawley rats on gestation days 6 to 15 by gavage in doses of 0, 0.25, 0.5, or 1.0 mL/kg/day. Food consumption and weight gain of the dam were followed. Rats were killed on gestation day 21. Females in the highest dose group had slightly lower weight gains compared to controls, both during treatment and later. Compared with controls, dioxane did not induce variations in the number of implantations, live fetuses, or resorptions, but the average weight of live fetuses from dams treated with 1 ml/kg/day was significantly less than controls. Mean fetal weight in this group was 3.6 g, compared to 3.8 g for controls. The frequency of major malformations remained within normal limits for all groups, and no deviations were found regarding minor anomalies and variants when compared with controls. However, with the highest dioxane dose, a significant retardation was found in the development of the sternum* (Giavini et al, 1985).

1,3-dioxolane
- *Tests provide evidence of genotoxic activity of dioxolane (Przybojewska B et al, 1984). Application of 1,3-Dioxolane to rats in drinking water resulted in decreased maternal body weights and increased number of stillborn pups, decreased survival of pups, and decreased numbers of pups* (Industrial BIO-TEST Labs, Inc., 1975).

  - *1,3-dioxolane was evaluated in Salmonella tester strains TA98, TA100, TA1535, TA1537 and TA1538 (Ames Test), both in the presence and absence of added metabolic activation. 1,3-Dioxolane did not produce a reproducible positive response in any tester strain with or without metabolic activation* (Goodyear, 1979).

4.4   Ecotoxicity of 1,4-dioxane and 1,3-dioxolane

- A report describing acute and chronic toxicity of 1,4-dioxane to fathead minnows, (*Pimephales promelas*), noted acute effects at concentrations of 10,000 mg/L; the highest no-observed-adverse-effect level was 6000 mg/L.
- An LC 50 was developed for bluegill sunfish (*Lepomis macrochirus*) as 10,000 ppm in a 96 hour static bioassay in fresh water at 23 °C (Verschueren ,1983).
- An LC 50 was developed for inland silverside fish (*Menidia beryllina*) as 6,700 ppm in a 96 hour static bioassay in synthetic seawater at 23 °C (Verschueren ,1983).

A calculated Log Bioconcentration Factor was determined to be -0.44. 1,4-Dioxane is not expected to bioconcentrate in fish and other aquatic organisms (Hansch et al, 1985; Howard 1990).

1,3-dioxolane
Dioxolane has been found to have a low order of toxicity to typical aquatic environmental species. A 96-hour LC_{50} static renewal study using bluegill with daily renewal of test solution to prevent loss due to volatilization recorded no mortality, with a resultant No Observed Effects Concentration of 95.4 mg/L (Dioxolane Manufacturers Consortium, 2000).

4.5   Site Cleanup Standards for 1,4-dioxane

Cleanup standards for 1,4-dioxane and other solvent stabilizers have not been widely established for solvent release sites. Where standards have been established, target concentrations vary by state and by site. If a contaminant is detected that does not have established Maximum Contaminant Levels or Maximum Contaminant Level Goals (e.g., 1,4-dioxane), EPA will evaluate available standards and information, such as California Department of Health Services drinking water action levels, to identify a relevant and appropriate standard for the contaminant (US EPA, 2000b).

Cleanup levels for the Gelman Sciences Site in Washtenaw County, Michigan, have been raised on two occasions following re-evaluation of toxicological data and performance of health risk assessments. When the contamination was first discovered in 1985, the generic residential cleanup criterion was 3 parts per billion (ppb) for groundwater and 60 ppb for soils. In June 1995, the State of Michigan amended the Natural Resources and Environmental Protection Act, and the generic residential cleanup criteria was increased to 77 ppb for groundwater and 1,500 ppb for soils. In June 2000, the Michigan Department of Environmental Quality adopted the US EPA methodology for calculating risk-based cleanup criteria, which resulted in the cleanup standards being raised to 85 ppb for groundwater, and 1,700 ppb for soils. The concentration of 1,4-dioxane in surface water considered by DEQ as safe for human contact and the environment is 2,800 ppb (Michigan DEQ, 2000).

A health risk assessment performed for 1,4-dioxane in groundwater by Blasland Bouck and Lee suggested that 38 ug/L would be an appropriate cleanup level for a Florida Gulf Coast shallow aquifer (Alonso, 2001).

The discharge limit for 1,4-dioxane in an NPDES permit for discharge of treated groundwater from various areas impacted by the release at Gelman Sciences was initially proposed at 60 ug/L. Although the residential cleanup criteria was raised to 77 ug/L, public comment was considered and allowable limits for 1,4-dioxane were reduced to 10 ppb as a monthly average with 30 ppb as a daily maximum. This permit was later contested by Gelman Sciences, asking for a daily maximum of 100 ug/L, and by local citizens, asking for the limit to be lowered to 3 ug/L.

In Spartanburg, South Carolina, the effluent limit set for 1,4-dioxane in a NPDES[4] permit for a polyester plant was 30 ug/L (McGrane, 1997).

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[4] National Pollution Discharge Elimination System

5.0 TREATABILITY OF 1,4-DIOXANE – TECHNOLOGIES AND ENERGY COSTS

The discovery of 1,4-dioxane at cleanup sites has often occurred well after site characterization and remedial design is complete, making implementation of effective remedial measures for 1,4-dioxane cumbersome. Possible presence of 1,4-dioxane has not been investigated at the majority of solvent release sites. This is due to the relatively recent development of the laboratory methods necessary to detect 1,4-dioxane at concentrations less than 100 ug/L, and the recent and increasing awareness that the halogenated solvents are not the only contaminant of concern at solvent release sites.

Conventional treatment systems have been ineffective at removing 1,4-dioxane to site cleanup levels or drinking water advisory limits in the case of well-head treatment. Advanced oxidation processes have proven effective at removal of 1,4-dioxane, and progress is being made at developing engineered bioreactors, phytoremediation, and other techniques for treatment of 1,4-dioxane. The monitored natural attenuation approach to solvent contamination is unlikely to achieve degradation of 1,4-dioxane or 1,3-dioxolane.

5.1 Ability of Conventional Pump and Treat Technologies to Remove 1,4-dioxane

Very low K_{OC} values and Henry's Law constant for 1,4-dioxane makes carbon adsorption and air stripping inefficient treatment processes for 1,4-dioxane. At a groundwater treatment facility in El Monte, California, a liquid granular activated carbon treatment system consisting of two 20,000-pound carbon vessels and treating 500 gallons per minute of solvent-contaminated groundwater was ineffective at reducing influent 1,4-dioxane concentrations at 14 ug/L to the treatment target of 3 ug/L (Bowman et al, 2001). In the City of Industry, California, 1,4-dioxane concentration in influent at an air stripper designed to remove 1.2 mg/L chlorinated solvents at 70 gallons per minute was measured at 610 ug/L, while 1,4-dioxane in effluent was measured at 430 ug/L (Bowman et al, 2001).

Because the most common conventional groundwater treatment technologies employed for treating contamination by chlorinated solvents are ineffective at removing 1,4-dioxane and other solvent stabilizer compounds, many existing treatment systems are likely to be discharging or reinjecting unmitigated amounts of 1,4-dioxane. In the San Gabriel Basin Baldwin Park Operable Unit, the following adjustments to treatment technologies were made following the discovery of the presence of 1,4-dioxane, and two rocket fuel contaminants:

GROUNDWATER TREATMENT TECHNOLOGIES AT BPOU, AZUZA, SAN GABRIEL VALLEY, CA	
Original Cleanup Plan	**Updated Cleanup Plan (after finding 1,4-dioxane)**
Use air stripping or carbon treatment to remove VOCs from the groundwater.	Use same technologies to remove VOCs. Also use UV oxidation to remove 1,4-dioxane.

Source: US EPA, 1999a.

Distillation is physically viable, but the relatively high boiling point (101°C) makes this approach uneconomical for most applications. Distillation is used to remove high concentrations of 1,4-dioxane from process wastewater effluent in the manufacture of polyester fiber (McGrane, 1997).

Chlorination of dioxane has been attempted, and found to optimally break down dioxane at 75°C and pH 5.2. Chlorination byproducts, however, are from 12 to 1,000 times more toxic than 1,4-dioxane (Woo et al, 1980). This raises questions as to whether 1,4-dioxane subjected to chlorination in drinking water supply wells and at municipal wastewater treatment plants may lead to distribution or discharge of toxic byproducts.

Conventional activated sludge and other common municipal wastewater treatment technologies have also proven ineffective at removing 1,4-dioxane (see Section 5.6, Lyman et al, 1982;Klecka and Gonsior, 1986; Abe, 1999). This has implications for the viability of the use of reclaimed municipal wastewater for groundwater recharge, which may contain 1,4-dioxane.

5.2   Advanced Oxidation Processes

The remedial technology most commonly employed in the removal of 1,4-dioxane from groundwater ex-situ is advanced oxidation processes (AOP), often in combination with ultraviolet light. AOP processes include ultraviolet light with ozone, hydrogen peroxide with ultraviolet light, ozone and hydrogen peroxide in combination, and Fenton's Reagent (hydrogen peroxide and ferrous iron)**.**

Ultraviolet light causes release of hydroxyl radicals from hydrogen peroxide added to influent contaminated water. The hydroxyl radicals react with 1,4-dioxane to oxidize the molecule to harmless reaction products (water, carbon dioxide, and residual chloride). The decay of 1,4-dioxane by UV-oxidation in a laboratory study generated several intermediates identified and quantified as aldehydes (formaldehyde, acetaldehyde, and glyoxal), organic acids (formic, methoxyacetic, acetic, glycolic, glyoxylic, and oxalic acids) and the mono- and diformate esters of 1,2-ethanediol (ethylene glycol). (Stefan and Bolton, 1998).

In the presence of hydroxyl radicals produced by direct photolysis of hydrogen peroxide, 1,4-dioxane decays rapidly following first order kinetics with a rate constant of k = $(8.7\pm 0.4) \times 10^{-3} \, s^{-1}$ (much higher than that determined for the direct photolysis of dioxane, $(6.4 \pm 0.3) \times 10^{-5} \, s^{-1}$). Within the first five minutes of UV irradiation, almost 90% of the initial concentration of 1,4-dioxane was depleted, while four major primary reaction intermediates, 1,2-ethanediol mono and diformate esters, formic acid, and methoxyacetic acid were generated. These byproducts undergo further oxidative degradation initiated by hydroxyl radicals, leading to glycolic and acetic acids, and finally to oxalic acid as the end product. As these reactions progress, pH has been measured to drop from 5 to 3.25 within the first 12 minutes, then slowly to a minimum of 3.12 within 25 minutes, and gradually increases to 4.2 by the end of the 60-minute UV irradiation period (Stefan and Bolton, 1998).

Dioxane is characterized as a very weak absorber of ultraviolet light; direct photolysis is not expected. In experiments studying the decay products of dioxane in UV-oxidation, 1 mM 1,4-dioxane and 15mM hydrogen peroxide were exposed to UV light in the 200 to 400 nm wavelength range. Hydrogen peroxide absorbed 50% of the UV light entering the Rayox reactor while dioxane absorbed only 0.15% (Stefan and Bolton, 1998).

Stefan and Bolton (1998) found that for their particular configuration, the removal of dioxane itself requires 46 kWh/kg of carbon in the contaminant mass, however the removal of the residual total organic carbon follows zero order kinetics in two stages, requiring higher electrical energy input, about 1500 kWh/kg in the first five minutes, followed by 418 kWh/kg for the next twenty minutes.

Ozonation of many synthetic organic compounds has been shown to enhance their biodegradability. Ozone is a strongly selective oxidant. Advanced oxidation processes utilize hydroxyl radicals, which are much stronger oxidants, non-selective, and have reaction rate constants often 9 orders of magnitude greater than ozone for the same organic compounds (Fahataziz and Ross, 1977; McGrane, 1997).

An evaluation of the effectiveness of the oxidant combination of ozone and hydrogen peroxide found that biodegradation of 1,4-dioxane was enhanced following oxidation. Neither ozone nor hydrogen peroxide alone readily oxidized 1,4-dioxane. The optimum peroxide/ozone molar ratio lies within the range of 0.5 to 1.0 for most industrial wastewaters. Below this range, less than the stoichiometric amount of hydrogen peroxide is added, precluding efficient conversion of ozone to hydroxyl radicals. Above this

range, hydrogen peroxide may increase scavenging by hydroxyl radicals without increasing oxidation efficiency, or cause excessive residual hydrogen peroxide concentrations in effluent. Competition for oxidants during advanced oxidation was observed from bicarbonate alkalinity, which scavenges hydroxyl radicals, and also from other synthetic organic compounds, including 1,3-dioxolane. Anaerobic pretreatment of industrial wastewaters containing 1,4-dioxane may be effective at reducing the net chemical oxidant demand (Adams, et al, 1994; McGrane, 1997).

Safarzadeh, et al, (1997) compared visible-range UV photolysis of ferrioxalate in the presence of hydrogen peroxide for treatment efficiency of tank bottom waters including 1,4-dioxane, and found the UV/ferrioxalate/H_2O_2 process significantly more efficient than either the UV/H or UV/Fe(II)/H_2O_2 (UV-Fenton) processes, by a factor of 3 to 30.

Example Applications of Advanced Oxidation Processes for 1,4-Dioxane Removal from Groundwater

Applied Process Technologies Inc. (APT) has developed an advanced oxidation process proven effective at removal of 1,4-dioxane from high-volume flows containing elevated concentrations of chlorinated solvents, at line pressures without ultraviolet light. APT's HiPOx™ system meters hydrogen peroxide at about 7 ppm through an injection system, while introducing ozone at about 9%. The performance of this system has been studied at two groundwater treatment facilities in the San Gabriel Basin (southern California), and proven effective at removal or 1,4-dioxane and reduction of chlorinated solvents. Installation of HiPOx™ units ahead of conventional treatment systems such as liquid granular activated carbon will significantly extend the life of the carbon vessels by reducing influent concentrations of VOCs. The advanced oxidation process employed in APT's HiPOx™ units is *p*H dependent, therefore treatment of air stripper of carbon vessel treatment system effluent is not viable, because *p*H variations from acid addition or other scale control measures will impair system performance (Bowman, et al, 2001).

Calgon Carbon markets a medium-pressure peroxide UV oxidation system that does not use ozone, thereby avoiding formation of undesirable bromates. Capital costs for a system installed in La Puente, California were approximately $135,000, with operating costs estimated at $50/acre-foot in a normal power market for a 2,500 gpm drinking water treatment system with peroxide addition at 5 mg/L for removal of low concentration 1,4-dioxane and NDMA (nitrosodimethylamine, a contaminant of liquid rocket fuel).   In another Calgon installation, a 170 gpm system for 110 ug/L 1,4-dioxane and a treatment target of 2 ug/L cost $150,000 to install, and about 50 cents per 1,000 gallons to operate. Calgon markets the Rayox® reactor system to handle non-adsorbable, non-strippable organic compounds such as 1,4-dioxane, NDMA, PAH's, pentachlorophenol and other phenols. In another installation at a chemical manufacturing facility in Salisbury, North Carolina, three 90 kW Rayox reactors were installed to treat up to 615 gallons per minute of water contaminated with 1,4-dioxane up to 2.5 mg/L, reducing concentrations to less than 10 ug/L (99.96% destruction), at a cost of about 75 cents per thousand gallons. (Calgon Carbon, 2001, Drewery, 2001)

Hydrogeochem, of Tucson, Arizona, markets another variation of the UV-oxidation system for 1,4-dioxane treatment. Hydrogeochem has developed low pressure UV-oxidation systems for a site at which perchlorate, NDMA, and 1,4-dioxane are contaminants. They have also developed tools to optimize concentrations and flow rates to minimize energy costs. For a drinking water system in La Puente, CA (San Gabriel Basin Water Authority) operating at 600 gallons per minute, a system that reduced 1,4-dioxane from 8 ug/L to 2 ug/L is operated at a cost of 19 cents per 1,000 gallons, and cost $240,000 to install. Success of this technology is dependent on water clarity. UV light with a transmittance of 254 nanometers is used, and should have 90% penetration for optimal performance. Nitrate interferes with UV light transmittance, even in turbidity-free water (Kuhn, 2001).

A team of engineers from Blasland, Bouck, and Lee presented this account of their experience at successfully designing and operating a UV-oxidation treatment system for 1,4-dioxane (Alonso, 2001):

A printed circuit board plant in Tampa, Florida, used degreaser tanks for preparing printed circuit boards. Leaks from the tanks steadily released solvent and still bottoms including TCE and TCA. Remedial investigations and treatment system design by previous investigators did not initially look for or account for 1,4-dioxane, nor did regulatory orders require it. The solution to remove 1,4-dioxane was a system provided by Calgon Carbon Oxidation Technologies. Initial 1,4-dioxane concentrations in extracted groundwater are less than 20 ug/L, however treated effluent in Florida may not exceed 5 ug/L, the Florida drinking water standard. The system is designed with four 30 kW units in series. Capital cost was about $200,000, with life-cycle cost expected to be about $1.8 million. While capital costs are considered similar to conventional stripping and polishing systems, realized operating costs for UV-oxidation are considerably higher. The peroxide feed solution, a 50% mixture, costs $0.35 per pound. UV lamps are $3,000, and since they burn with a surface temperature of about 2000° F, they are short-lived and must be replaced three times per year. System controls require frequent inspection and adjustment, as slight variations in flow, mixture, or other interrelated parameters may cause treatment targets to be missed or lamps to overheat.

5.3   Potential for Biodegradation of 1,4-dioxane and 1,3-dioxolane

There has not yet been a peer-reviewed publish account of documented biodegradation of 1,4-dioxane under ambient in-situ conditions, and research completed to date suggests indigenous soil bacteria do not possess the metabolic ability to biodegrade ethers. Enhanced biodegradation in ex-situ engineered bioreactors, or by isolation, culturing, and introduction of specific microbe strains capable of metabolizing cyclic ethers in the presence of specific cometabolites and nutrients, remains promising.

Biodegradation of 1,4-dioxane and 1,3-dioxolane in-situ is not presently considered a viable remediation option. The ether bond is a highly stable linkage and not readily biodegraded under ambient conditions (Zenker et al, 2000). No data were located which suggest biodegradation is an important fate process of 1,3-dioxolane in soil or water under ambient conditions. The biochemical oxygen demand of 1,4-dioxane was found to be negligible after twenty days of observation, and no biodegradation of dioxane was observed in cultures of sewer microorganisms exposed for one year at 100 to 900 mg/L. Dioxane concentrations up to 300 mg/L had no adverse effect on the performance of activated sludge (Klecka and Gonsior, 1986).

Cultures of naturally occurring organisms have been reportedly isolated that are capable of biodegradation of 1,4-dioxane under controlled conditions (Adams, et al, 1994).
Using microorganisms acclimated to a mixed domestic and industrial wastewater with a dioxane concentration of 1,080 mg/L and a total organic carbon of 5,200 mg/L, 44% removal of dioxane was observed after 44 days (Roy et al, 1994). This microbial population was also shown to be capable of degrading pure 1,4-dioxane in the absence of other industrial wastes or organic matter. For initial concentrations of 150, 300, and 670 mg/L 1-4,dioxane, reductions of 100%, 67.5%, and 49.5% were obtained, respectively. The biodegradation of pure 1,4-dioxane in batch reactors appears to result in the formation of toxic byproducts, inhibiting biologic activity after a threshold reduction is obtained (Roy et al, 1994).

Mycobacterium vaccae reportedly catabolize 1,4-dioxane less than 50% when incubated at 30°C for 48 hours on a rotary shaker and using propane as a substrate. M. vaccae were not able to use dioxane as a sole source of carbon to support growth (Burback and Perry, 1993).

In soil microcosm studies of 1,4-dioxane and tetrahydrofuran, no biodegradation of either compound was exhibited when incubated under ambient conditions. When incubated at 35° C, however, complete biodegradation of both compounds occurred in soil previously exposed to 1,4-dioxane, and to which phosphorous and trace minerals were added. Biodegradation of 1,4-dioxane in these studies depended on elevated incubation temperatures and the presence of tetrahydrofuran (Zenker et al, 1999).

In pure culture, an actinomycete was found to degrade 1,4-dioxane at a rate of 0.33 mg of dioxane per minute per milligram of protein. The strain CB1190 was isolated from a dioxane contaminated sludge sample after first enriching the culture with yeast extract and tetrahydrofuran, and incubating the culture aerobically. Strain CB1190 was the first reported pure culture demonstrating sustained growth on 1,4-dioxane as a sole carbon and energy source. In three replicate samples, 60% of carbon from dioxane was converted to CO_2. No other organic byproducts or other intermediates accumulated in the medium, suggesting complete metabolism. CB1190 was tested on other ethers, with the fastest growth rate found for tetrahydrofuran, and no growth found on 1,3-dioxolane and MtBE. Direct enrichments of CB1190 were unsuccessful; early enrichments in the isolation process appeared to be cometabolizing 1,4-dioxane in the presence of tetrahydrofuran (Parales et al, 1994).

Biodegradation of 1,4-dioxane in a laboratory scale fluidized bed reactor was studied using the propane oxidizing bacterium ENV425 acclimated to methyl tert butyl ether (MtBE) (Vainberg, et al, 1999.) After 4 months of acclimation to MTBE, an influent concentration of 8 mg/L 1,4-dioxane was added, and following an additional month of operation, more than 60% of the influent concentration of 1,4-dioxane was removed during a 2 hour hydraulic residence in the reactor.

Research performed at Clemson University confirmed that microorganisms capable of metabolizing 1,4-dioxane under controlled aerobic wastewater treatment conditions could be cultured (Sock, 1993). McGrane (1997) confirmed bacteria could degrade 1,4-dioxane in the presence of tetrahydrofuran using an innoculum or return-activated sludge from four industrial waste treatment processes, all of which had been historically exposed to 1,4-dioxane, in a submerged attached growth air-lift reactor. Cultures of 1,4-dioxane degrading bacteria were developed that proved capable of degrading 1,4-dioxane in the absence of tetrahydrofuran, and eventually in the absence of residual organic carbon (McGrane, 1997).

5.4   Innovative In-Situ Treatment Technologies and 1,4-dioxane

Fenton's Reagent
Fenton's reagent has been used in the mineralization of 1,4-dioxane in process wastewater, however chemical costs and reaction time requirements limited the feasibility of this process (McGrane, 1997). No published work was found documenting in-situ use of Fenton's Reagent to eliminate 1,4-dioxane in groundwater.

Phytoremediation
Phytoremediation, the use of vegetation for remediating contaminated soil and groundwater, has been investigated for its suitability for removal of 1,4-dioxane in groundwater. Hybrid poplar cuttings (*Populus deltoides X nigra*, DN 34, Imperial Carolina) removed 23 mg/L 1,4-dioxane rapidly, at 54± 19% within 9 days. Phytoremediation was also determined to effectively remove 1,4-dioxane from soil, with only 18.8 ± 7.9% of the initially spiked concentration remaining after 15 days. In both hydroponic experiments for groundwater remediation and soil experiments, 76 to 83% of the dioxane taken up by poplars were transpired from leaf surfaces to the atmosphere, where it can be readily dispersed and photo-degraded. The poplar cuttings used in this study did not exhibit visible toxic effects when subjected to water contaminated with 1,4-dioxane. Phytoremediation is considered a relatively inexpensive treatment alternative, costing 10 to 50% of conventional treatment technologies such as soil excavation, and providing a more aesthetically pleasing appearance to the contaminated site (Aitchison et al, 2000).

Effectiveness of phytoremediation is limited to shallow groundwater settings where contamination is confined to a limited depth within the root zone of poplar trees. Long-term stabilization of contaminated soil for which excavation and stockpiling is otherwise required is another viable application for phytoremediation. For low-flow groundwater treatment regimens, above-ground hydroponic treatment systems may also be a viable solution for 1,4-dioxane removal.

5.5   Treatability of 1,4-dioxane and 1,3-dioxolane in POTWs

Dioxane is essentially immune to biodegradation by microorganisms under conditions normally present in conventional industrial and municipal biotreatment processes. No significant aerobic biodegradation was achieved by microorganisms acclimated to municipal wastewater, soils, or to other synthetic organic chemicals. Dioxane is also not amenable to biodegradation under anaerobic conditions (Adams, et al, 1994).

Treated effluent from a wastewater treatment plant serving several apartment complexes in Japan was found to contain an average of 0.25 mg/person/day. Sources of dioxane in households discharging to the treatment plant were presumed to be shampoos, and liquid dishwashing and laundry soaps, which contain from 0.2 to 0.56 mg/L dioxane (Abe, 1999).

1,4-Dioxane exhibited a negligible biological oxygen demand in two activated sludge experiments and the compound has been classified as relatively non-degradable (Lyman et al, 1982). Abe (1999) found that dioxane in domestic wastewater was not significantly removed at a treatment plant which used an activated sludge process, supporting the general understanding that dioxane is a recalcitrant compound, relatively immune to biodegradation under ambient conditions. The biochemical oxygen demand of dioxane was found to be negligible after twenty days of observation, and no biodegradation of dioxane was observed in cultures of sewer microorganisms exposed for one year at 100 to 900 mg/L (Klecka and Gonsior, 1986).

1,4-Dioxane was detected at 1 ug/L in effluents from the North Side and Calumet sewage treatment plants on the Lake Michigan basin (Konasewich, et al, 1978). 1,3-Dioxolane was qualitatively detected in 4 samples of final effluents taken from 3 publicly owned treatment works (POTWs) in Roselle, Danville, and Decatur, Illinois (Ellis et al, 1982).

Recycled wastewater used for groundwater recharge should be tested for 1,4-dioxane to ensure this practice isn't introducing a highly mobile and recalcitrant contaminant to the aquifer.

CONCLUSIONS AND RECOMMENDATIONS: IMPLICATIONS FOR SOLVENT CLEANUP SITES

Where solvents have been released from spills, leaks, and dumping, particularly at facilities whose operational use of TCA extends for decades and where groundwater contamination by TCA is extensive, the presence of 1,4-dioxane should be expected. Accordingly, site investigations and remedial designs that have failed to account for this contaminant are incomplete and should be revisited with at least sampling and analysis for 1,4-dioxane in treatment system influent and effluent, in the core of the plume, and at the sentinel wells beyond the leading edge of the plume.

The consequence of finding 1,4-dioxane in groundwater, treatment system effluent, recycled wastewater, or water supply wells is made somewhat ambiguous by the lack of a legal standard for human health and other beneficial uses of groundwater. Cleanup criteria are currently issued at restrictive levels, while some toxicologists believe that physiological based pharmaco-kinetic models support higher limits.

Much work remains to characterize the patterns of occurrence and migration of 1,4-dioxane and other stabilizers, to develop federal maximum contaminant levels, and to refine treatment technologies to effectively remove these contaminants from groundwater.

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