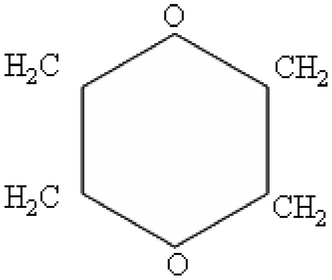
1,4-Dioxane –

A Primer for Air Force Remedial Program Managers and Risk Assessors



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A PRIMER FOR AIR FORCE REMEDIAL PROGRAM MANAGERS AND RISK ASSESSORS

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- Discussing the basis for heightened regulatory and public interest in the chemical;
- Providing background on how it was and is used in DoD operations, and the types of activities that may have led to environmental releases;
- Describing considerations in the choice and application of analytical methodologies to detect its presence in environmental samples;
- Understanding potential implications associated with its presence in site-specific risk assessments; and
- Evaluating, designing, and implementing cost-effective remedial technology options to manage the potential risks to human health and the environment that may be posed by exposure to 1,4-dioxane.

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Glossary of Acronyms

1,1,1-TCA	1,1,1-Trichloroethane
ACGIH	American Council on Governmental Industrial Hygienists
AF	Air Force
AFCEE	Air Force Center for Engineering and the Environment
AFIOH	Air Force Institute of Occupational Health
AFRIMS	Air Force Restoration Information Management System
AOP	Advanced Oxidation Processes
ASC	Aeronautical Systems Center
ATSDR	Agency for Toxic Substances and Disease Registry
BD/DR	Building Demolition/Debris Removal
CAA	Clean Air Act
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFC	Chlorofluorocarbons
CNS	Central Nervous System
DoD	Department of Defense
EPA	Environmental Protection Agency
ERA	Environmental Restoration Account
ERPIMS	Environmental Resources Program Information Management System
FBR	Fluidized Bed Reactor
FDA	Food and Drug Administration
FS	Feasibility Study
GC/MS	Gas Chromatography/Mass Spectrometry
gpm	Gallons per Minute
HAP	Hazardous Air Pollutant
HPV	High Production Volume
IARC	International Agency for Research on Cancer
IRIS	Integrated Risk Information System
IRP	Installation Restoration Program
MAJCOM	Major Command
MCL	Maximum Contaminant Level
MMRP	Military Munitions Response Program
MNA	Monitored Natural Attenuation
MRL	Minimal Risk Level
MTBE	Methyl Tert-Butyl Ether
NCEA	National Center for Environmental Assessment
NELAP	National Environmental Laboratory Accreditation Program
NIOSH	National Institute of Occupational Safety and Health
O&M	Operations and Maintenance
ODS	Ozone Depleting Substance
ORD	Office of Research and Development
OSHA	Occupational Safety and Health Administration

OSRTI	Office of Superfund Remediation and Technology Innovation
PA	Preliminary Assessment
PBPK	Physiologically Based Pharmacokinetic
PCE	Perchloroethylene
ppb	Parts Per Billion
ppm	Parts Per Million
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act
RfC	Reference Concentration
RfD	Reference Dose
RI	Remedial Investigation
ROD	Record of Decision
RPM	Remedial Program Manager
SAP	Sampling and Analysis Plan
SERDP	Strategic Environmental Research and Development Program
SI	Site Inspection
SIM	Selective Ion Monitoring
SMZ	Surfactant Modified Zeolites
SVOC	Semi Volatile Compound
TCE	Trichloroethylene
THF	Tetrahydrofuran
TRI	Toxic Release Inventory
UV	Ultraviolet
VOC	Volatile Organic Compound
ZVI	Zero Valent Iron

Introduction

The chemical 1,4-dioxane has gained increased visibility as an emerging contaminant at a number of locations across the United States. Produced in large quantities throughout the 1970's, 1980's, and into the early 1990's it was used as a stabilizer to prevent degradation of chlorinated industrial solvents, primarily 1,1,1-trichloroethane (or 1,1,1-TCA, sometimes referred to as methyl chloroform). 1,1,1-TCA itself is a common chemical contaminant found at many hazardous waste sites across the country. While historical use of 1,4-dioxane was as a solvent stabilizer, the compound is also used in a wide range of industrial products, is present as a byproduct in many common consumer products, and is a natural component of some food items. Although its use in commercial products spans decades, 1,4-dioxane is considered an emerging contaminant because of characteristics such as: heightened public and regulatory interest due to a perceived or real threat to human health and the environment; a lack of or revisions to published health standards; and advances in analytical detection methodologies that have allowed it to be detected at lower concentrations than before.[1]

Heightened interest in the potential human health and environmental impacts of 1,4-dioxane can be traced back to 1997 when analytical advances allowed for its detection at low microgram/liter (commonly reported as parts per billion [ppb]) concentrations. Classified as a Group B "probable human carcinogen" by the United States Environmental Protection Agency (EPA), the toxicological studies used to derive exposure risk values for 1,4-dioxane are being re-evaluated by EPA. Risk values such as cancer slope factors and oral reference doses (RfDs) serve as the scientific basis for regulatory standards such as drinking water maximum contaminant levels (MCLs) and groundwater and soil cleanup levels. At this time, 1,4-dioxane is not one of the EPA's priority pollutants and does not have an MCL for drinking water. The EPA re-evaluation of the 1,4-dioxane toxicological database includes the assessment of new or previously unavailable data, may be used to support the development of a revised cancer slope factor, and could lead to the formal establishment of an oral RfD for 1,4-dioxane. In the absence of final risk factors, federal drinking water and cleanup levels for 1,4-dioxane have not yet been promulgated, leading a number of states to establish state-specific, risk-based levels which in themselves vary widely.

These characteristics, coupled with unique chemical and physical properties of the compound, suggest that 1,4-dioxane, primarily as a past component of a 1,1,1-TCA solvent host, may present risk assessment and risk management challenges for Air Force remedial program managers (RPMs). Pending completion of EPA's re-evaluation of its risks, 1,4-dioxane is expected to remain a fairly visible environmental issue, and depending on the outcome of the re-evaluation, may gain even greater visibility than before. Accordingly, RPMs are expected to be asked by regulators about past use of 1,4-dioxane, to define the nature of its potential risk to human health and the environment at their facilities, and as necessary evaluate and implement appropriate remedial actions to manage associated risks. Such requests may be particularly problematic in that as 1,4-dioxane was used primarily in conjunction with 1,1,1-TCA solvent application, these additional requests for information may occur well after site characterization and remedial design for 1,1,1-TCA or other previously identified chemical contaminants has occurred or have been completed.

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[1] DoD Materials of Evolving Regulatory Interest Team, *What is an Emerging Contaminant?*

This assessment of 1,4-dioxane is intended to assist Air Force and other DoD RPMs, risk assessors, and policy makers in the following ways:

- Understand the basis for heightened regulatory and public interest in 1,4-dioxane;
- Understand how the chemical was and is used in Air Force operations, and the types of activities that may have led to environmental releases;
- Plan for and use appropriate analytical methodologies as needed to detect the presence of the chemical in environmental samples;
- Consider the implications of its presence in site-specific risk assessments; and
- Evaluate, design, and implement cost-effective remedial technology options as appropriate to manage the potential risks to human health and the environment that may be posed by exposure to 1,4-dioxane.

Overview of 1,4-Dioxane Use and Production

1,4-dioxane was widely used in the past as a stabilizing agent to prevent the degradation of chlorinated solvents, particularly 1,1,1-TCA; EPA has estimated that 90% of the 1,4-dioxane production in the 1980s was for use as a stabilizer.[2] Previous studies have used analyses of material data safety sheets to conclude that typical 1,4-dioxane concentrations in 1,1,1-TCA ranged from 2-5% by volume, with evidence of concentrations as high as 8%.[3] This apparent strength of association between 1,4-dioxane and 1,1,1-TCA appears to be supported by its detection at known 1,1,1-TCA solvent release sites,[4,5] and by similar evidence indicating its link to 1,1,1-TCA's abiotic degradation product 1,1-dichloroethane (1,1-DCE).[6,7]

- EPA estimates 90% of 1,4-dioxane produced was for use as a stabilizer for chlorinated solvents, particularly 1,1,1-TCA.
- 1,4-dioxane is currently used in a range of commercial products, including aircraft de-icing and automotive cooling fluids.
- Synonyms include dioxane, diethylene dioxide, 1,4-diethylene oxide, diethylene ether, and glycolethylene ether
- Soil or groundwater known to be contaminated with 1,1,1-TCA or its degradation product 1,1-DCE, may serve as a surrogate to aid in the identification of potential locations of 1,4-dioxane releases.

While its primary past use was as a stabilizer for 1,1,1-TCA solvent, 1,4-dioxane is still used in a variety of commercial applications including as an ingredient in aircraft de-icing and automotive cooling fluids; paints, lacquers, varnishes, inks, and dyes; as a solvent for fats, oils, waxes, and natural and synthetic resins; and as a wetting and dispersing agent in textile processing. It is also used in laboratory environments as a fluid for scintillation counter samples, for the purification of drugs and preparation of tissue sections for histology, and as a solvent in spectroscopic and photometric measurements, and as a surfactant or emulsifier in cosmetic products such as shampoos, detergents, bath preparations, and other consumer products.[8] 1,4-dioxane has also reportedly been found in manufactured food additives and is a natural component in shrimp, chicken, and tomatoes.[9]

To assist Air Force personnel in better understanding how 1,4-dioxane was used and how environmental releases may have occurred from past use and disposal of its host solvent, a brief overview of important aspects of 1,4-dioxane use and production is provided below. Because of the strength of information indicating its primary use was as a stabilizer for 1,1,1-TCA, the overview explores important aspects of this relationship.

The Use of Chlorinated Solvents for Cleaning and Degreasing Purposes

In the early part of the 20th century chlorinated solvents such as trichloroethylene (TCE) and perchloroethylene (PCE) became widely used as replacements for the flammable and toxic

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[2] 1,4-Dioxane Fact Sheet: Support Document, EPA OPPT, EPA-749-F-95-010a, February 1995.

[3] Draft Solvent Stabilizers White Paper, Santa Clara Valley Water District, T. Mohr, June 2001.

[4] Ibid.

[5] 1,4-Dioxane – Widespread Presence and Prevalence in Shallow Groundwater?, Reddig and Lucas, Integrated Scientific Solutions, Inc.

[6] Sampling for 1,4-Dioxane at Ft Lewis, USACE/HTRW, 17 September 2004.

[7] 1,4-Dioxane & Other Solvent Stabilizer Compounds in the Environment, Groundwater Resource Association's 1,4-Dioxane Conference Profiles, The National Challenge of Emerging and Unregulated Contaminants, December 2003.

[8] Toxicological Profile for 1,4-Dioxane, U.S. Department of Health and Human Services, Public Health Service, ATSDR, July 2006.

[9] Memorandum from George Alexeef, California Office of Environmental Health Hazard Assessment to David Spath, California Department of Health Services, March 1998.

petroleum distillates that had historically been used for cleaning and degreasing purposes. TCE became the solvent of choice for vapor degreasing in the 1930s and remained the preferred solvent in many industrial applications throughout the 1940s, 1950s, and 1960s. The trend toward significant use of 1,1,1-TCA as a solvent did not begin until the 1950s with its introduction as an alternative cold cleaning solvent due to the development of effective stabilizer formulations.[10] TCE's widespread use as a solvent came under increasing scrutiny in the late 1960s because of toxicological evidence suggesting it was carcinogenic and because of regulatory initiatives to limit volatile solvent emissions from industrial facilities. As a consequence many industrial operations switched from TCE solvent to 1,1,1-TCA in the 1970s because of its strong cleaning properties, its low flammability, its low relative toxicity, and absence of a carcinogenic link. As can be expected, the demand for 1,1,1-TCA for primary use in solvent cleaning applications increased significantly.

Chlorinated Solvents and the Need for Stabilizers

Over the years the use of chlorinated solvents in industrial cleaning and degreasing processes led to the understanding that chemical stabilizers are often required to prevent solvent degradation and adverse reactions with light, heat, air, and water that may result in corrosion of treated materials and cleaning equipment. There are three general categories of solvent stabilizers: antioxidants, metal inhibitors, and acid acceptors.

> <u>Antioxidants</u> - Antioxidants prevent solvents from oxidizing, or reacting with oxygen in air. The degree that a solvent can undergo oxidation depends on its chemical structure, light exposure, and, if used in a vapor degreaser, its boiling point.
>
> <u>Metal Inhibitors</u> - Metals inhibitors are Lewis bases that inhibit and prevent corrosive solvent degradation reactions with metals by forming an insoluble reaction layer on the metal, or by preventing the solvent/metal reaction itself.
>
> <u>Acid Acceptors</u> - Acid acceptors neutralize the acids that are formed when solvents react with water during cleaning/degreasing operations. In the case of chlorinated solvents hydrogen chloride is produced and reacts with water to form hydrochloric acid. Acid acceptors react with the hydrochloric acid to form comparatively benign alcohol.[11]

Where as TCE requires the use of all three types of stabilizers, and PCE is relatively stable and requires only very small amounts of acid acceptors, 1,1,1-TCA requires the use of a metal inhibitor and an acid acceptor to maximize its effectiveness as a cleaning and degreasing agent. 1,4-dioxane provides both of these types of stabilizer protection.[12,13] This information further supports the notion of a strong relationship between the two chemicals.

Exploring the Link Between 1,1,1-TCA and 1,4-Dioxane

To explore reports which link the vast majority of the 1,4-dioxane produced domestically to its former use as a stabilizer for 1,1,1-TCA, production data for both chemicals were collected and analyzed. Annual production data for 1,4-dioxane beginning in the 1970s was previously reported in regulatory systems in very specific quantities. However, because EPA's Inventory

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[10] A History of the Production and Use of Carbon Tetrachloride, Tetrachloroethylene, Trichloroethylene, and 1,1,1-Trichloroethane in the United States, R. Doherty, Journal of Environmental Forensics, June 2000.

[11] Stabilizing Halogenated Solvents Thwarts Undesirable Reactions, Precision Cleaning – the Magazine of Critical Cleaning Technology, R. DeGroot, February 1998.

[12] Draft Solvent Stabilizers White Paper, Prepublication Copy, Santa Clara Valley Water District, T. Mohr, June 2001.

[13] 1,4-Dioxane – Widespread Presence and Prevalence in Shallow Groundwater?, Reddig and Lucas, Integrated Scientific Solutions, Inc.

Update Reporting regulation provides production information as an aggregated production range due to Agency procedures to protect confidential business information, recent data is not as specific and is provided instead as aggregated production ranges. Available domestic 1,4-dioxane production information is provided in Table 1.

Table 1. Domestic 1,4-Dioxane Production Trends

Production Year	Production Quantity (M lbs)	Data Source
1973	1.62	U.S. International Trade Commission
1974	1.76	U.S. International Trade Commission
1975	1.26	U.S. International Trade Commission
1976	1.49	U.S. International Trade Commission
1977	12	EPA 1,4-Dioxane Chemical Fact Sheet
1982	15	EPA 1,4-Dioxane Chemical Fact Sheet
1986	10-50	EPA Inventory Update Reporting
1990	10-50	EPA Inventory Update Reporting
1994	1-10	EPA Inventory Update Reporting
1998	1-10	EPA Inventory Update Reporting
2002	1-10	EPA Inventory Update Reporting

1,4-dioxane production data for calendar year 2006 is being compiled by the EPA and is not available at this time. Personnel in EPA's High Production Volume (HPV) Challenge program confirm, however, that 1,4-dioxane remains on the agency's HPV chemical list, indicating that production totals are expected to exceed the program's 1 million pound threshold. As of 2007, only two domestic producers of 1,4-dioxane remain.[14]

Demand for 1,1,1-TCA increased substantially during the early- and mid-1970s as a result of TCE's emerging environmental, safety and health concerns, and soared throughout the late-1970s and 1980s with production reaching approximately 803 million pounds in 1990.[15] EPA has estimated that by 1991, nearly 55% of the 1,1,1-TCA consumed in the United States was used for metal and electronics cleaning and degreasing purposes.[16] The widespread use of 1,1,1-TCA as the solvent of choice for cleaning and degreasing operations began to wane in the early 1990s due to other emerging environmental concerns. The primary drivers for this decline were the international determination under the Montreal Protocol on Substances that Deplete the Ozone Layer that 1,1,1-TCA was an ozone depleting substance (ODS), and Title VI of the 1990 Amendments to the Clean Air Act (CAA) which enacted regulations to control the releases of ODS materials.[17] The CAA not only addressed 1,1,1-TCA as an ODS, but also identified it as one of 189 hazardous air pollutants under Title III which resulted in more stringent regulation of degreasing operations in general to minimize the release of hazardous air pollutant emissions.

Concern over 1,1,1-TCA's ozone depletion potential also led to the chemical being subject to an incremental production phase-out under the CAA and international treaty.[18] Under the production phase-out schedule, the allowable production of 1,1,1-TCA was initially set at 50% of 1989 production by 1994, reduced to 30% by 1995, and with the exception of essential uses

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[14] Personal Communication, EPA High Production Volume Chemical Challenge Program.

[15] Locating and Estimating Air Emissions from Sources of Methyl Chloroform, USEPA, EPA-454/R-93-045, February 1994.

[16] Chemical Survey for Methyl Chloroform, Office of Pollution Prevention and Toxics, EPA, August 1994.

[17] Ozone Layer Depletion – Regulatory Programs, EPA Office of Air and Radiation.

[18] White Paper on 1,1,1-Trichloroethane, Halogenated Solvents Industry Alliance, February 1994.

only, near totally phased-out beginning in 1996.[19] Its identification as one of the 17 commonly used chemicals targeted for significant reduction under EPA's Toxic Release Inventory 33/50 Program also resulted in numerous pollution prevention initiatives which led to the identification of more environmentally benign alternatives to 1,1,1-TCA, and further hastened the reduction in its use for cleaning and degreasing purposes.

While pollution prevention efforts by DoD have successfully eliminated most uses of 1,1,1-TCA, the chemical is still used in limited quantities to produce small arms ammunition. Specifically, it is employed as an ingredient and thinning agent in the asphaltic compound used in case mouth waterproofing, a process by which a sealant is introduced between the bullet and the inside of the case mouth. Alternative water-based sealants are available and have been in use since the late 1990's.[20] Table 2 summarizes domestic 1,1,1-TCA production data.

Table 2. Domestic 1,1,1-TCA Production Trends

Production Year	Production Quantity (M lbs)	Data Source
1980	315	EPA Locating & Estimating Air Emissions from Sources of Methyl Chloroform
1985	590	EPA Locating & Estimating Air Emissions from Sources of Methyl Chloroform
1986	652	EPA Locating & Estimating Air Emissions from Sources of Methyl Chloroform
1987	694	EPA Locating & Estimating Air Emissions from Sources of Methyl Chloroform
1988	724	EPA Locating & Estimating Air Emissions from Sources of Methyl Chloroform
1989	783	EPA Locating & Estimating Air Emissions from Sources of Methyl Chloroform
1990	803	EPA Locating & Estimating Air Emissions from Sources of Methyl Chloroform
1991	649	EPA Locating & Estimating Air Emissions from Sources of Methyl Chloroform
1992	600	EPA Locating & Estimating Air Emissions from Sources of Methyl Chloroform
1994	100-500	EPA Inventory Update Reporting
1998	100-500	EPA Inventory Update Reporting
2002	100-500	EPA Inventory Update Reporting

A review of both 1,4-dioxane and 1,1,1-TCA production data support the expected 1,4-dioxane use trends, with 1,4-dioxane production appearing to track very well with the increased use of 1,1,1-TCA as the primary solvent in industrial degreasing and cleaning operations in the United States in the 1980s, as well as the phasing out of 1,1,1-TCA production and use beginning in 1994. These trends further support the conclusion that 1,4-dioxane's primary use was as a solvent stabilizer in 1,1,1-TCA, and to a far lesser extent potentially as a solvent or stabilizer in other chlorinated solvents.[21,22.23]

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[19] The Accelerated Phase-Out of Class I Ozone Depleting Substances, Ozone Depletion Rules and Regulations, EPA.

[20] FY2002 Secretary of Defense Environmental Security Awards, Lake City Army Ammunition Plant, Independence, MO, Army Nomination for Pollution Prevention – Industrial Installation.

[21] 1,4-Dioxane Fact Sheet: Support Document, EPA OPPT, EPA-749-F-95-010a, February 1995.

Because of the strength of evidence linking 1,4-dioxane to 1,1,1-TCA use, it is reasonable to presume that information related to the past storage, use and disposal of 1,1,1-TCA solvent, and/or the known contamination of groundwater or soil with1,1,1-TCA, may serve as useful surrogates to aid RPMs in responding to future site-specific requests to evaluate the potential for 1,4-dioxane contamination.

Toxicology of 1,4-Dioxane

Toxicology is the study of the adverse effects of chemical, physical or biological agents on living organisms and the ecosystem. The primary routes of human exposure that may lead to adverse effects from 1,4-dioxane are the inhalation and ingestion pathways, and to a lesser extent dermal contact. While the database of information used to determine the toxicity of 1,4-dioxane is derived primarily from research on laboratory animals, a limited number of human health studies have been conducted.

Available human information is derived from occupational studies in which exposure was assumed to be primarily through the inhalation pathway but may have also involved dermal exposure. Information regarding oral exposure of humans to 1,4-dioxane is lacking. Although limited information exists regarding the health effects of 1,4-dioxane in humans, available data are sufficient to identify the liver and kidneys as the target organs for 1,4-dioxane toxicity following short-term exposure to relatively high amounts of 1,4-dioxane, regardless of the route of exposure.[24] This observation has been corroborated in studies in animals.

In its September 2007 draft toxicological profile for 1,4-dioxane, the Agency for Toxic Substances and Disease Registry (ATSDR) noted that the limited environmental monitoring data available suggests that the levels of 1,4-dioxane that are normally found in environmental media or to which the general population might otherwise be exposed are orders of magnitude lower than those used in experimental studies with animals.[25] A brief overview of adverse effects from acute and chronic exposures to 1,4-dioxane, and a summary of associated cancer risks, is provided below.

Acute Non-Cancer Effects

Acute, or short-term, exposure to low levels of 1,4-dioxane for short periods of time has been reported to cause irritation of the upper respiratory passages, coughing, irritation of eyes, drowsiness, vertigo, headache, anorexia, stomach pains, and nausea in humans. Repeated, short-term inhalation exposure to very high levels can cause kidney and liver damage, and possibly death.[26]

Laboratory animal studies in rats, mice, rabbits, and guinea pigs have demonstrated 1,4-dioxane has a moderate acute toxicity via the inhalation or dermal exposure pathways, and low to moderate acute toxicity via the ingestion pathway. Rabbits injected with 1,4-dioxane were observed to experience convulsions, collapse, and other adverse effects to the kidneys and liver. Similar studies on rats, mice, rabbits, and guinea pigs support the acute toxicity findings.

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[22] Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications, EPA 542-R-06-009, November 2006.

[23] Draft Solvent Stabilizers White Paper, Santa Clara Valley Water District, T. Mohr, June 2001.

[24] Draft Toxicological Profile for 1,4-Dioxane, U.S. Department of Health and Human Services, Public Health Service, ATSDR, September 2007.

[25] Ibid.

[26] Ibid.

A few cases of delayed lethal effects in humans after inhalation exposure in the workplace have been reported. Exposure levels associated with the lethal effects are uncertain, and in these cases dermal contact with the chemical was also believed to have occurred. Studies conducted during the late 1950s estimated a lethal inhalation exposure level of greater than 470 ppm after 5 days.[27]

An ATSDR Minimal Risk Level (MRL) is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse, non-cancer health effects over specified exposure durations. They are intended to serve as screening levels, and are used by ATSDR health risk assessors to identify contaminants and potential health effects that may be of concern at hazardous waste sites. A No Observable Adverse Effects Level (NOAEL) is an exposure level at which there are no statistically or biologically significant increases in the frequency or severity of adverse effects between the exposed population and its appropriate control; some effects may be produced at this level, but they are not considered as adverse, or as precursors to adverse effects.[28]

Based primarily on NOAELs, ATSDR has independently developed MRLs for 1,4-dioxane.[29] An acute inhalation MRL of 2 ppm based on a NOAEL of 20 ppm for eye and respiratory effects in volunteers. Likewise, an acute oral ingestion MRL of 4 mg/kg/day (or ppm) has been established based on a NOAEL of 370 mg 1,4-dioxane/kg/day for nasal effects in rats.

Chronic Non-Cancer Effects

The database of studies on chronic exposure to 1,4-dioxane is quite limited. Available chronic oral exposure studies with laboratory animals do indicate, however, that 1,4-dioxane can, at high doses and over long exposure times, cause damage to the liver.[30] While such liver damage may lead to tumor formation, tumor formation seems to follow cellular damage or death, and the weight of evidence suggests 1,4-dioxane has limited genetic toxicity.[31] In terms of chronic human exposure, an occupational study of workers exposed via the inhalation pathway to 1,4-dioxane found no adverse effects in workers exposed to airborne concentrations of 1,4-dioxane ranging from 0.006 to 14.3 ppm for an average of 25 years.[32]

ATSDR has established a chronic inhalation MRL of 1 ppm based on a NOAEL of 111 ppm for liver effects in rats and the application of a physiologically-based pharmacokinetic (PBPK) model. By using physiological, biochemical, and physiochemical data to construct mathematical representations of processes associated with the absorption, distribution, metabolism, and elimination of compounds, PBPK models are useful tools for predicting internal doses of chemicals to target organs, can be used to extrapolate across species and exposure scenarios, and can address various sources of uncertainty in health risk assessments.[33] A chronic ingestion MRL of 0.1 mg/kg/day (or ppm) has also been established based on the results of a

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[27] Draft Toxicological Profile for 1,4-Dioxane, U.S. Department of Health and Human Services, Public Health Service, ATSDR, September 2007.

[28] EPA Terms of Environment: Glossary, Abbreviations and Acronyms, NOAEL.

[29] Draft Toxicological Profile for 1,4-Dioxane, U.S. Department of Health and Human Services, Public Health Service, ATSDR, September 2007.

[30] Ibid.

[31] Background Document for the Development of WHO Guidelines for Drinking Water, 1,4-Dioxane, World Health Organization, WHO/SDE/WSH/04.08/120, July 2004

[32] Draft Toxicological Profile for 1,4-Dioxane, U.S. Department of Health and Human Services, Public Health Service, ATSDR, September 2007.

[33] Approaches for the Application of Physiologically Based Pharmacokinetic (PBPK) Models and Supporting Data in Risk Assessment, EPA/600/R-05/043F, September 2006.

two year ingestion study in rats, a NOAEL of 9.6 mg/kg/day for liver effects, and the application of an uncertainty factor of 100.

Cancer Risk

Limited and inconclusive human data exist with respect to associations between chronic 1,4-dioxane exposure and incidence of cancer. In a study of 165 workers exposed to 1,4-dioxane at airborne concentrations ranging from less than 25 ppm to 75 ppm during manufacture and processing operations, the observed number of cancer deaths were not significantly different from the expected death rate.[34] Results were inconclusive according to study authors, primarily because of the small sample size and relatively short exposure duration. An additional study of 74 workers working in a manufacturing plant with an estimated exposure of 0.006 ppm to 14.3 ppm 1,4-dioxane also revealed no significant difference in chromosomal irregularities.[35]

- While EPA classifies 1,4-dioxane as a probable human carcinogen, human risks from lifetime exposures to contaminated water appear low according to EPA studies.
- EPA estimates that an individual drinking water containing 1,4-dioxane at an average concentration of 3.0 µg/L over his or her entire lifetime has no more than a 1:1,000,000 chance of developing cancer as a result.

EPA's current cancer slope factor for ingestion is 0.011 mg/kg/day, which translates to no more than a 1:1,000,000 risk of developing cancer from consumption of drinking water containing 1,4-dioxane at a concentration of 3 µg/L.[36] The slope factor was derived in 1990 based upon the dose-response data for nasal cavity tumors in rats. The application of PBPK models suggest that the IRIS cancer slope factor significantly overestimates 1,4-dioxane's potential cancer risk and associated safe drinking water concentration.[37,]

1,4-Dioxane and EPA's Integrated Risk Information System

The EPA's Integrated Risk Information System (IRIS) IRIS is the official Agency database of human health effects that may result from exposure to various substances found in the environment. Initially developed for EPA staff in response to a growing demand for consistent information on chemical substances for use in risk assessments, decision-making and regulatory activities, the adequacy of the database is assessed by EPA on a regular basis. Each year, the EPA develops a list of priority chemical substances and an annual agenda to guide the IRIS program in determining the adequacy of the database and updating it with new scientific data. Combined with site-specific exposure assessment information, the summary health effects data in IRIS is used by most federal, state, and local organizations as the primary source of information for evaluating the potential public health risks from exposure to environmental contaminants.

As part of its IRIS chemical prioritization process, a screening level literature review was conducted to determine the adequacy of the 1,4-dioxane database. EPA's IRIS Track system indicates the literature search was initiated in 2004, and resulted in an EPA determination that the existing 1,4-dioxane

- EPA is re-evaluating the human health risks associated with exposure to 1,4-dioxane.
- A revised risk assessment document is expected to undergo external peer review and public comment in September 2008.
- A final 1,4-dioxane health risk assessment document is expected to be completed June 2009.

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[34] Draft Toxicological Profile for 1,4-Dioxane, U.S. Department of Health and Human Services, Public Health Service, ATSDR, September 2007.

[35] Ibid.

[36] EPA Integrated Risk Information System, 1,4-Dioxane, Carcinogenicity Assessment for Lifetime Exposure.

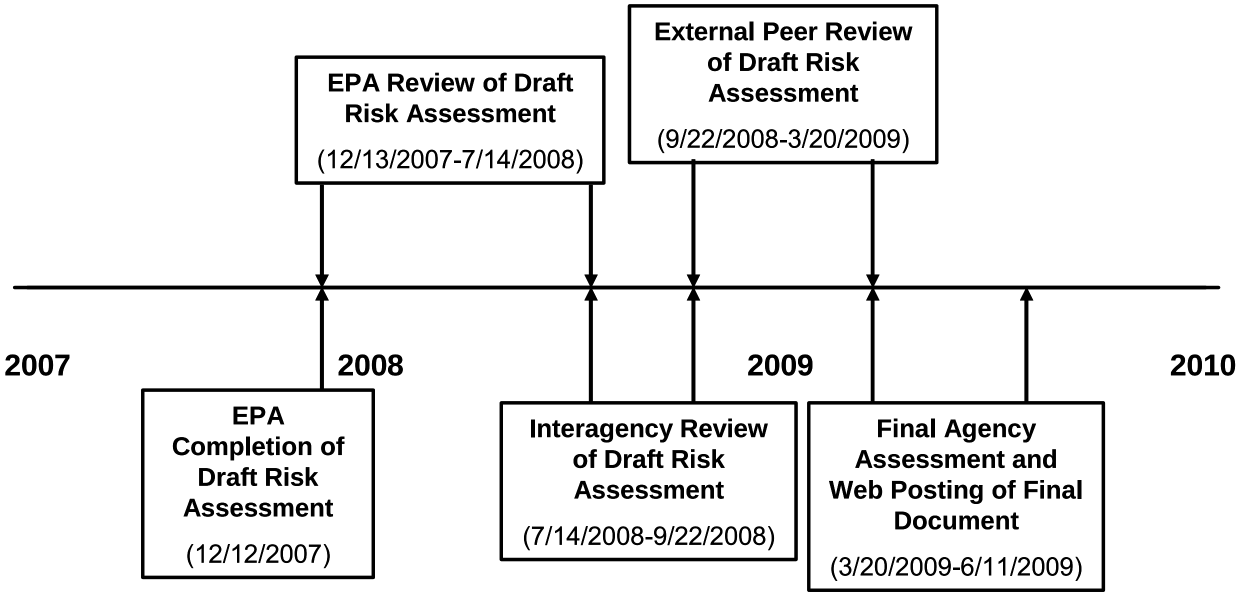
[37] An Updated Evaluation of the Carcinogenic Potential of 1,4-Dioxane, Stickney, Sager, Clarkson, et al, Regulatory Toxicology and Pharmacology 38 (2003) 183-195

database was inadequate, and the agency needed to review new scientific data on its cancer and non-cancer health effects.

EPA's draft revision to its 1,4-dioxane assessment was initiated in July 2004, and completed in December 2007. After completion of the draft, an internal Agency peer consultation of revised IRIS risk values for 1,4-dioxane was initiated, with of the Agency review completed in July 2008. Upon completion of EPA's internal reviews, the draft document was made available for interagency review with an expected completion date of September 2008. After completion of the interagency review, the document will undergo an external peer review and public comment period, currently expected to start in September 2008 and be completed by March 2009. The process of final review and approval of the revised document by the agency's Office of Research and Development (ORD) and National Center for Environmental Assessment (NCEA) is scheduled to commence by March 2009 and end three months later in June 2009.[38] Once finalized, the document will be posted on the World Wide Web no later than June 2009. The IRIS Substance Assessment Tracking System (IRIS Track) timeline for completion of the 1,4-dioxane risk assessment, current as of August 2008, is depicted graphically as Figure 1.

Completion of the review and establishment of revised IRIS risk should provide RPMs, risk assessors, and policy makers with significantly more certainty with regard to assessment and management of 1,4-dioxane risks by reducing the wide variability among current state-specific risk factors. The establishment of an RfD and/or RfC for 1,4-dioxane may also play a role in the potential revision of other regulatory levels not under the jurisdiction of EPA, such as occupational exposure levels or safe levels for consumer products.

Figure 1. 1,4-Dioxane IRIS Track Review Timeline



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[38] Detailed Tracking Report for IRIS Substance Assessment, EPA IRIS Substance Assessment Tracking System, 1,4-Dioxane.

1,4-Dioxane and Solvent Cleaning Activities

Because cold-cleaning and vapor-degreasing processes using 1,1,1-TCA solvent were widely employed in the past to maintain military and industrial equipment, an understanding of the basics of solvent cleaning processes will provide RPMs, risk assessors, and other Air Force environmental professionals with insight into how environmental releases 1,4-dioxane may have occurred in the past. While a general overview of solvent-cleaning processes is provided below, the overview focuses on vapor-degreasing because fundamental differences in the processes, as discussed below, suggest 1,4-dioxane would be expected to be found in higher concentrations in vapor degreasing wastes.

The Vapor Degreasing Processes

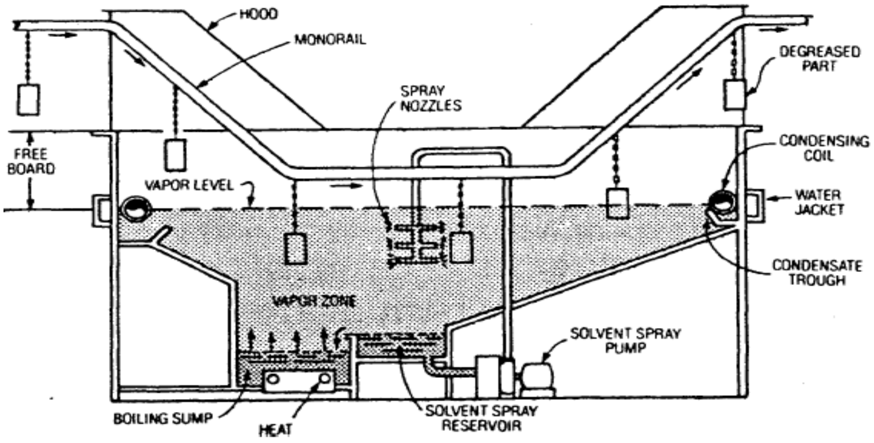
There are two general types of vapor degreasers – immersion units and vapor/spray units. An immersion unit usually has two solvent-filled sumps - a boil sump, and a condensate sump which is filled with clean, distilled solvent and is often used for final rinsing of cleaned products. Parts to be cleaned are lowered into the boil sump for a short period of time then transferred (beneath the vapor line) to the condensate sump for a short period of time. The parts are then raised out of the condensate sump and held in the vapor zone until the solvent has completely drained off the part.

In vapor/spray units, the solvent is boiled in the very bottom of a one-sump degreaser. A perforated metal stand that holds a metal basket filled with dirty parts to be cleaned is usually located just above the boiling solvent. Unlike an immersion unit, the basket or parts are not directly immersed in solvent. Instead, the vapor produced by the boiling solvent envelopes the parts and removes oil, dirt and grease. The oil and grease, now diluted in the condensing liquid, drips back into the boiling solvent below.

Near the top of either type of degreasing unit is a set of condensate coils that catch the vapor before it escapes from the unit, and cools and condenses it back to its liquid form. As 1,1,1-TCA is subject to hydrolysis in the presence of water and can produce acids that discolor solvent and may corrode parts and equipment, a water separator is used to remove excess moisture. The clean vapor condensate is collected in a trough, passed through a water separator, and returned to the boiling sump or condensate sump for reuse. The dissolved oils, dirt and grease collect in the bottom of the unit in concentrated sludges, or “still bottoms”.

Figure 2 below illustrates a typical vapor/spray degreasing unit used in industrial O&M operations, such as may occur at motor pools, depots and logistic centers.

Figure 2. A Typical Vapor/Spray Degreasing Unit



<u>Concentration of 1,4-Dioxane in Vapor Degreasing Unit Still Bottoms</u>

In vapor degreasing units solvent stabilizers such as 1,4-dioxane partition between the vapor phase and boiling liquid phase according to their boiling points, a characteristic that has important implications for the composition of the resulting still bottoms. Because 1,4-dioxane has a boiling point (101° C) that is nearly 30° higher than 1,1,1-TCA (74° C) and a vapor pressure of 30 vs. 100 mm Hg at 20° C, it vaporizes less readily and tends to become more highly concentrated in the still bottoms. In addition, while vapor degreasers recycle the majority of process solvent, operational guidance typically calls for the regular addition of new solvent to restore solvent performance, thus further concentrating 1,4-dioxane in the still bottoms. Mohr reports studies conducted on 1,1,1-TCA vapor degreasing units have shown that 1,4-dioxane may be measured in still bottoms at concentrations in excess of 35% greater than its original concentration in the feed solvent, and that spent 1,1,1-TCA may contain 1,4-dioxane concentrations over 150% of its original concentration, or up to approximately 10% by volume.[39]

- 1,1,1-TCA vapor degreasing waste solvent and still bottoms may contain 1,4-dioxane at concentrations over 135% of their original formulations.
- The concentration of 1,4-dioxane in still bottoms and vapor degreasing wastes suggests a greater potential for its detection at 1,1,1-TCA release or waste disposal sites.

Environmental Fate and Transport of 1,4-Dioxane

Although domestic production of 1,4-dioxane has fallen significantly in the past decade, it is being discovered more frequently at sites contaminated with chlorinated solvents due to advances in analytical detection methodologies that have allowed for its detection at low ppb concentrations. 1,4-dioxane can enter the environment through solvent spills, storage unit leaks, and/or solvent/solvent waste disposal practices. While usage spills and storage leaks are legitimate environmental release pathways, it is more probable that environmental releases of 1,4-dioxane that may have occurred as a result of Air Force activities would be associated with the disposal of spent solvents. Once an environmental release occurred 1,4-dioxane would quickly migrate to underlying groundwater based on its physical and chemical properties. A

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[39] Draft Solvent Stabilizers White Paper, Santa Clara Valley Water District, T. Mohr, June 2001

brief overview of important physical and chemical properties that govern the general behavior of 1,4-dioxane, its fate and transport in the environment, and its subsequent treatability by various remedial technologies, is provided below.

- 1,4-dioxane is characterized by a high solubility and low affinity for sorption to soils and organic matter.
- Because of these properties, it readily leaches from and through soil following its release.
- It dissolves nearly completely in groundwater and moves quickly in the subsurface.
- Once in groundwater, 1,4-dioxane migrates rapidly and in advance of the leading edge of associated host solvent plumes.

Physical and Chemical Properties of 1,4-Dioxane

1,4-dioxane is a colorless, volatile, flammable, cyclic ether with a mild odor. It is fully miscible with water, most organic solvents, aromatic hydrocarbons, and oils, and as an ether is not expected to hydrolyze significantly. Key physical/chemical properties of 1,4-dioxane and its expected 1,1,1-TCA solvent host are presented in Table 3. [40,41,42,] Placing information for both chemicals in a single table allows for a side-by-side comparison of important properties and parameters (such as boiling point, vapor pressure, Henry's Law constant, K_{oc}, K_{ow}, and bioconcentration factor) which can assist readers in more quickly understanding how the two contaminants behave with regard to waste stream generation, environmental fate and transport, and the selection of potential remedial technologies.

Table 3. Physical and Chemical Properties of 1,4-Dioxand and 1,1,1-TCA

Property	1,4-Dioxane	1,1,1-TCA
CAS #	123-91-1	71-55-6
Molecular Formula	$C_4H_8O_2$	$C_2H_3Cl_3$
Solubility (mg/L)	Soluble in water, most organic solvents, aromatic hydrocarbons, and oils	1500
Molecular Weight (g/moll)	88.1	133.4
Boiling Point (° C @ 760 mm Hg)	101.3	74.1
Vapor Pressure (mm Hg @ 20° C)	30	124
Henry's Law Constant (atm-m^3/mol)	4.80×10^{-6}	1.72×10^{-2}
Log Organic Carbon Partition Coefficient (K_{oc})	1.23	2.03
Log Octanol/Water Partition Coefficient (K_{ow})	-0.27	2.49
Specific Gravity (@ 20° C)	1.03	1.34
Vapor Density (air = 1)	3.03	4.63
Log Bioconcentration Factor	- 0.44	0.95

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[40] 1,4-Dioxane Fact Sheet: Support Document, EPA OPPT, EPA-749-F-95-010a, February 1995.

[41] Toxicological Profile for 1,1,1-Trichloroethane, U.S. Department of Health and Human Services, ATSDR, July 2006.

[42] Draft Solvent Stabilizers White Paper, Santa Clara Valley Water District, T. Mohr, June 2001.

Expected Behavior in the Environment

The low log organic carbon partition coefficient (K_{oc}) of 1.23 suggest 1,4-dioxane will not significantly sorb to soil organic matter or suspended sediments, and should readily leach from soils to groundwater. Laboratory column studies have confirmed that 1,4-dioxane can rapidly diffuse through low permeability soils and is expected to easily pass through silts and clays.[43] With a K_{oc} of 2.03 1,1,1-TCA would also not be expected to appreciably sorb to soil organic matter or suspended sediments, and should readily leach from soils to groundwater.

1,4-dioxane's low log octanol/water partition coefficient (K_{ow}) of -0.27 indicates that it is expected to migrate much more quickly through the subsurface and in groundwater than its chlorinated solvent host (which has a K_{ow} of 2.49), will move ahead of the leading edge of the associated chlorinated solvent plume or its breakdown products, and thus generate a larger area of groundwater impact.

While a moderate vapor pressure of 30 mm Hg at 20° C indicates 1,4-dioxane should readily volatilize from dry soil, its estimated Henry's Law constant of 4.88×10^{-6} atm-m^3/mol indicates volatilization from moist soils will be slow, and 1,4-dioxane is unlikely to form a vapor plume in the vadose zone above a dissolved phase plume, essentially rendering soil gas measurement techniques ineffective in tracking it.[44] With a vapor pressure of 123 mm Hg and a Henry's Law constant of 1.72×10^{-2} atm-m^3/mol, 1,1,1-TCA exists in the vapor phase in the atmosphere, and is expected to rapidly re-volatilize from water and moist soils.

Additionally, 1,4-dioxane is not known to significantly bioaccumulate, does not readily biodegrade under normal ambient conditions, and has an estimated atmospheric half-life of 1-3 days.[45] In other words, 1,4-dioxane is very soluble in water, does not sorb well to soil particles, does not readily biodegrade, is very mobile in groundwater, and is expected to be difficult to treat by common remedial processes.

Simulated Transport in the Environment

Mohr reports the transport and biotransformation of 1,1,1-TCA and transport of 1,4-dioxane without biotransformation have been modeled using EPA's BIOCHLOR model to determine the expected rates of migration of 1,4-dioxane and 1,1,1-TCA in groundwater.[46] While the modeling exercise was not intended to represent the true behavior of a mixture of 1,4-dioxane and 1,1,1-TCA under real-world field conditions, it was believed the exercise would provide a reasonable simulation of the relative mobility and persistence of 1,4-dioxane in contrast to its 1,1,1-TCA host solvent.

In the modeling effort, the assumption was 1,4-dioxane would persist over larger distances from the release point relative to 1,1,1-TCA because of differences in physical/chemical properties, such as its miscibility, its lower sorption and its negligible biodegradation. Even at extremely low concentrations, the model predicted 1,4-dioxane would travel at least 2-3 times further than 1,1,1-TCA and other chloroethanes. Mohr reports laboratory column studies and analyses of actual plume behavior indicate that because of its solubility and low affinity for sorption to soils and organic matter 1,4-dioxane is also expected to pass more quickly through soils than other solvents.

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[43] Ibid.

[44] Contaminant Focus - 1,4-Dioxane Chemistry and Behavior, EPA Technology Innovation Program.

[45] Draft Toxicological Profile,for 1,4-Dioxane, U.S. Department of Health and Human Services, ATSDR, September 2007.

[46] Contaminant Focus - 1,4-Dioxane Chemistry and Behavior, EPA Technology Innovation Program.

Observed Migration in the Environment

While the fate and transport of 1,4-dioxane in the environment are highly dependent upon site-specific conditions at the release site, the predictions of transport models and laboratory column studies with regard to the expected movement of 1,4-dioxane relative to host solvents appear to be supported by available data on the known occurrence and distribution of the chemical at solvent release sites. Sampling and monitoring data from solvent-contaminated sites in Indiana, California, and Canada and other locations indicate that 1,4-dioxane does, indeed, move quickly in the subsurface, and travels well in advance of associated solvent plumes.

At the Seymour, Indiana, Superfund Site, 1,4-dioxane was found to extend approximately three quarters of a mile northwest of the site boundary, while by comparison other chlorinated and volatile hydrocarbon compounds have moved only a few hundred feet.[47] As another example, a 1,4-dioxane plume at the Safety Kleen solvent recycling facility in Silicon Valley, CA, has been shown to have migrated approximately 300 feet while the other volatile and chlorinated organics associated with the release have migrated less than 50 feet.[48] Similarly, a 1,4-dioxane plume at the Gloucester Landfill in Ontario, Canada, is known to lead a 1,1,1-TCA plume by approximately 500 feet.[49]

Based upon these and other observations, it is not unreasonable to expect similar trends to be observed at Air Force or other DoD sites with documented environmental releases of 1,1,1-TCA, or which were responsible for the disposal of 1,1,1-TCA solvent cleaning and degreasing wastes.

Analytical Methodologies

Because of the overall lack of promulgated regulatory standards, unless specifically requested to do so, most laboratories do not analyze and report 1,4-dioxane or other solvent stabilizers when conducting laboratory analysis of common solvents. While not routinely included in laboratory analysis, the presence of 1,4-dioxane in liquid and solid media can be detected using gas chromatography/mass spectrometry (GC/MS)-based methods such as EPA Methods 8260, 8270, 1624.[50] Several methods are capable of detecting 1,4-dioxane in solid and liquid samples. While determination of 1,4-dioxane in water at low detection levels is accomplished most often using a modified Method 8270, at this point there does not appear to be a preference specified by regulators as to which, if any, of the methodologies is preferred. A brief overview of analytical methodologies available for use in quantifying 1,4-dioxane and associated analytical costs are provided in the following sections.

Laboratory Analyses

- Unless specifically requested to do so, most laboratories do not currently analyze and report 1,4-dioxane when conducting laboratory analysis of common solvents.
- 1,4-dioxane can be detected at low levels using GC/MS methods at a cost of $90-$275 per sample.
- Because of chemical/physical characteristics that are more similar to semi-volatile vs. volatile organic compounds, EPA Method 8270 is often a preferred methodology.
- Analysis of 1,4-dioxane should be conducted in accordance with the AFCEE QAPP to ensure the data are scientifically valid and defensible.

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[47] Seymour, Indiana, Superfund Site, Five Year Report, EPA Region 5, March 2002.

[48] Draft Solvent Stabilizers White Paper, Santa Clara Valley Water District, T. Mohr, June 2001.

[49] Occurrence and Treatment of 1,4-Dioxane in Aqueous Environments, M. Zenker, R. Borden, M. Barlaz, Environmental Engineering Science, Sep 2003, Vol. 20 No. 5: 423:432.

[50] Toxicological Profile for 1,4-Dioxane, U.S. Department of Health and Human Services, Public Health Service, ATSDR, July 2006.

EPA Method 8260 (Volatile Organic Compounds by GC/MS)

EPA Method 8260 is used to assess the concentration of volatile organic compounds (VOCs) in a variety of samples, including surface, ground and drinking water; soils and sediments; aqueous sludges; waste solvents; spent carbon and catalysts; and air sampling media.

Under this method, samples are introduced into the GC by direct injection following dilution, concentration by azeotropic distillation, or closed system vacuum distillation.[51] The use of Method 8260 coupled with conventional EPA purge–and-trap procedures for the extraction of VOCs from soil or water (Methods 5030 or 5035) results in method detection limits as high as 100 ppb, primarily due to the high water solubility of 1,4-dioxane and the associated poor purging efficiencies.[52] As an alternative, Method 8260 coupled with azeotrophic distillation (Method 5031) can be used with volatile, water-soluble compounds that are difficult to trap and purge. This approach is reported to be capable of achieving detection limits of 12 ppb for 1,4-dioxane.[53] Detection limits as low as 3 ppb have also been reported when using Method 8260 in Selective Ion Monitoring (SIM) mode.[54]

EPA Method 8270 (Semi-Volatile Organic Compounds by GC/MS)

EPA Method 8270 is used to assess the concentration of semi-volatile organic compounds (SVOCs) in a variety of matrices, including surface, ground, and drinking water; soils and sediments; numerous solid waste matrices; and air sampling media. Because of its chemical and physical properties, several commercial laboratories contacted during an informal survey conducted by Booz Allen Hamilton in October/November 2006 recommended treating 1,4-dioxane as a SVOC versus a VOC, and analyzing for its presence using EPA Method 8270 to reliably achieve low ppb detection levels.

Method 8270 requires sample preparation in order to extract 1,4-dioxane from water, soil sediment, and waste samples. Available sample preparation methods include Method 3520 for aqueous samples, Method 3540 or 3550 for soil/sediment samples, and Method 3540, 3560, or 3580 for other solid waste samples. The samples are extracted with a volatile solvent and then concentrated by evaporation. When using Method 8270 the extracted sample is introduced into the GC to separate 1,4-dioxane from other analytes and detected by MS. The relatively low volatility of 1,4-dioxane is a key factor that leads to poor recoveries during the concentration step. While typical detection limits for Method 8270 are approximately 10 ppb for aqueous samples, Method 8270 modified with isotope dilution and optimized for 1,4-dioxane has been reported to achieve a detection limit of 1 ppb; even lower limits may be achieved when using Method 8270 in SIM mode.[55]

EPA Method 1624 (Volatile Organic Compounds by Isotope Dilution GC/MS)

EPA Method 1624 utilizes isotopic dilution GC/MS to assess the concentration of 1,4-dioxane in water and in industrial and municipal discharges. [56] In this method, isotopically labeled 1,4-dioxane-d_8 is added to the sample as an isotope dilution standard. The sample is introduced into the GC where it is purged with an inert gas. After purging, the trap is backflushed and heated, the 1,4-dioxane is separated by GC, and then detected by MS. The labeled compounds serve to correct the variability of the analytical technique. Although EPA has established a

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[51] Ibid

[52] Sampling for 1,4-Dioxane at Ft Lewis, USACE/HTRW, 17 September 2004.

[53] Ibid

[54] Personal Communication, Commercial Analytical Laboratory Service, November 2006.

[55] Sampling for 1,4-Dioxane at Ft Lewis, USACE/HTRW, 17 September 2004.

[56] Toxicological Profile for 1,4-Dioxane, U.S. Department of Health and Human Services, Public Health Service, ATSDR, July 2006.

detection limit of 10 ppb for this method, a commercial laboratory contacted as part of this analysis reported the method can consistently achieve a 1 ppb detection limit.[57]

Analytical Costs

Analytical costs for 1,4-dioxane are dependent upon the number of samples to be analyzed, the method by which the sample is prepared and introduced into the analytical equipment, and the type of analytical equipment employed. A range of analytical costs that can be expected for the three methods discussed above was obtained by reviewing available literature, and supplemented by an informal survey of several commercial laboratories. Current prices provided for analysis of 1,4-dioxane were reported to range from $90 - $140 per sample using Method 1624 or Method 8260, and from $150 - $275 per sample using Method 8270.

Quality Assurance Considerations

Ensuring the quality and accuracy of data used in assessing risks and choosing appropriate management strategies is of utmost importance when dealing with an emerging contaminant. DoD experience with other emerging contaminants such as perchlorate has demonstrated that ensuring the quality and accuracy of sampling data that is reported out to regulators and the public can go a long way in alleviating stakeholder concerns about the potential risks to human health and the environment posed by the contaminant. The laboratory compound should have a documented quality assurance/quality control (QA/QC) system that complies with the latest approved versions of the DoD Environmental Data Quality Workgroup (EDQW) and AFCEE Quality Assurance Project Plan (QAPP) and the DoD Quality Systems Manual for Environmental Laboratories (DoD QSM) to ensure the analytical protocols and documentation requirements needed to generate scientifically valid and defensible data are implemented; have appropriate State certifications; and be accredited by a nationally recognized accreditation body such as National Environmental Laboratory Accreditation Program (NELAP) for the applicable test method.

When selecting a laboratory to analyze for 1,4-dioxane, RPMs should ask for documentation demonstrating the ability of the laboratory to achieve the project-specific method reporting limit using the specified method in each matrix to be analyzed. In addition, RPMs should verify the laboratory's performance with blind whole-volume samples, particularly for new projects. The DoD QSM and AFCEE QAPP establish the analytical protocols and documentation requirements necessary to ensure the data are collected, reviewed and assessed in a consistent manner to meet the overall project goals and that the data are scientifically valid and defensible.[58,59] The AFCEE QAPP guidance presents, in specific terms, the policies, organization, functions, and QA/QC requirements designed to achieve the data quality goals to be described in the approved project Sampling and Analysis Plan (SAP).

Remedial Technology Options

Conventional *ex situ* pump-and-treat systems involving the use of air stripping or granular activated carbon that are routinely used to remediate chlorinated solvents and VOCs have proven to be generally ineffective at removing 1,4-dioxane from contaminated water supplies to levels below 10 µg/l (10 ppb).[60,61] In fact, unless specifically designed to address 1,4-dioxane contamination, most systems currently being used to remediate chlorinated solvent plumes that

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[57] Personal Communication, Commercial Analytical Laboratory Service, October 2006.

[58] DoD Quality Systems Manual for Environmental Laboratories, Final Version 3, January 2006.

[59] AFCEE Quality Assurance Project Plan, v.4.0.02, May 2006.

[60] Sampling for 1,4-Dioxane at Ft Lewis, USACE/HTRW, 17 September 2004

[61] Contaminant Focus - 1,4-Dioxane Chemistry and Behavior, EPA Technology Innovation Program

may include 1,4-dioxane as a constituent are likely discharging or re-injecting it into the environment. Advanced oxidation processes (AOPs) using hydrogen peroxide (H_2O_2) and ultraviolet light (UV) or ozone (O_3) have been applied successfully to destroy 1,4-dioxane but are typically more expensive to install and operate (particularly if installation occurs after initial site characterization and remedial design decisions have been made), may have issues with adequate light penetration in the treated water supply, may unintentionally mobilize unwanted contaminants, and may not be effective at removing other co-contaminants.

- Air stripping and sorption systems used to remove its chlorinated co-contaminant are generally ineffective in treating 1,4-dioxane, and may discharge or reinject untreated 1,4-dioxane into the environment.
- Advanced oxidation processes are effective at treating 1,4-dioxane but have high capital and O&M costs, may mobilize unwanted contaminants such as bromate, and may not remove co-contaminants.
- Bioremediation and phytodegradation processes show promise but are still under investigation and may require co-metabolites to function properly.
- Evaluation of monitored natural attenuation studies suggest natural degradation processes should continue to be investigated as a less intrusive, regulator accepted remediation process.

The potential presence of 1,4-dioxane as a co-contaminant in 1,1,1-TCA solvent waste plumes means a treatment system specifically designed for the remediation of both the 1,1,1-TCA solvent and 1,4-dioxane components of the plume will be necessary to achieve the treatment levels currently requested by regulators. As discussed later in this document, such treatment level goals generally range from 3 – 85 ppb, with the majority falling under 10 ppb. A brief overview of 1,4-dioxane remedial technology options and their effectiveness is provided below.

Conventional Pump-and-Treat Technologies

Conventional pump-and-treat technologies commonly used for the remediation of chlorinated solvents and other volatile organic plumes typically involve the use of air stripping and/or sorption by granular activated carbon (GAC).

Air stripping is a process which involves the mass transfer of volatile contaminants from water to air via aeration methods such as packed towers, diffused aeration, tray aeration, and spray aeration. The ability of air stripping to remove an organic compound is based upon the chemical's ability to efficiently transfer from the liquid and gaseous phase, defined by the Henry's Law constant.

Sorption systems are used to remove soluble organic and inorganic compounds in extracted groundwater. In GAC systems, the ability of the system to remove a contaminant is dependent upon the contaminant's carbon adsorption coefficient, K_{oc}. In typical systems, water to be treated is introduced at the top of a carbon column, flows downward through the carbon bed, and is withdrawn at the bottom of the column. Spent carbon must be removed periodically, and virgin or regenerated carbon added to the system to ensure its effectiveness.

1,4-dioxane and 1,1,1-TCA have significantly different properties that impact the ability of conventional pump-and-treat technologies to remove contamination from treat waste streams. 1,1,1-TCA is less soluble, has a higher Henry's Law Constant, and has a significantly higher K_{oc} than 1,4-dioxane, making 1,1,1-TCA a good candidate for removal by air stripping and/or carbon adsorption. These technologies, however, do not achieve high removal efficiencies when applied to 1,4-dioxane contaminated waste streams due to differences in chemical and physical characteristics. Relative to 1,1,1-TCA, 1,4-dioxane has a low Henry's Law constant (making it a difficult compound to air-strip) and a low K_{oc} value (meaning it is not expected to be readily sorbed by GAC systems.)

Bench-scale treatability testing has been conducted to evaluate the effectiveness of removal of 1,4-dioxane from groundwater using a variety of sorbants, including Activated Tri-Base pelletized carbon (which contains three different types of carbon in a single pellet), surfactant modified zeolites (SMZ), SMZ with zero valent iron (SMZ/ZVI), and a proprietary macro-porous polymer. Testing indicated that the two zeolite formulations and the macro-porous polymer were ineffective for removal of 1,4-dioxane.[62] Only the Activated Tri-Base carbon showed effective 1,4-dioxane adsorption, but did so only at usage rates far in excess of what would be cost effective or logistically achievable for the test site.

Advanced Oxidation Processes

At this time, the most effective remedial technology for 1,4-dioxane appears to be advanced oxidation processes. These processes appear capable of handling 1,4-dioxane influent concentrations as high as several thousand ppb while achieving effluent concentrations that are generally less than 10 ppb.

Advanced oxidation processes are *ex situ*, destructive processes that oxidize organic constituents in water by creating hydroxyl radicals (^{-}OH) through the addition of strong oxidizers such as H_2O_2 and irradiation with UV light. The hydroxyl radicals then attack the targeted organic molecule. The reaction is aided by the direct photolysis of the organic molecule by the UV light, which can break or activate certain bonds making the molecule more susceptible to oxidation. The EPA reports variation of the process using H_2O_2 and ferrous iron (Fenton's Reagent) and ozone with UV may also be effective at removing 1,4-dioxane.[63] Use of an ozone system, however, requires the waste stream being treated to be maintained at a low pH and to be retained within the system for a relatively long retention time to ensure the destruction of 1,4-dioxane. Similarly, the use of Fenton's Reagent also requires a retention time of several hours to achieve desired destruction efficiencies.[64] UV oxidation is generally accomplished using low pressure lamps operating at 65 watts of electricity for ozone systems, and lamps operating at 15kW to 60kW for hydrogen peroxide systems.

The main advantage of advanced oxidation processes is they are destructive in nature, as opposed to air stripping or carbon adsorption in which contaminants are extracted and concentrated in a separate phase, thus creating a secondary solid waste stream requiring subsequent treatment and disposal. Potential disadvantages include the need to: control common water quality parameters (such as pH) through the use of large volumes of chemicals; remove compounds in the water being treated to ensure the effective transmission of UV light; the possible formation of bromate (itself classified as a B2 Probable Human Carcinogen) if the treated water contains bromide; the mobilization of hexavalent chromium if the treated soil contains trivalent chromium; and the potential formation of undesirable decomposition products such as aldehydes and organic acids in the treated waste stream.

Although advanced oxidation processes can be used to treat and destroy 1,4-dioxane, they are generally not capable of reducing 1,1,1-TCA and other chlorinated co-contaminants to desired

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[62] Treatment Options for Remediation of 1,4-Dioxane in Groundwater, William DiGuiseppi, P.G. and Caroline Whitesides, P.G, Environmental Engineer, Vol. 43 No.2, May 2007.

[63] Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications, EPA 542-R-06-009, November 2006.

[64] Sampling for 1,4-Dioxane at Ft Lewis, USACE/HTRW, 17 September 2004.

levels by themselves.[65] This means that an integrated treatment train with components that individually target the co-contaminant host solvent and 1,4-dioxane elements of a plume (most likely in the form of air stripping and/or GAC used in conjunction with advanced oxidation may be necessary to ensure that both the co-contaminant and 1,4-dioxane are removed from the treatment stream prior to its discharge. Recent studies indicate, however, that use of activated persulfate agents in AOP systems may be capable of simultaneously treating 1,4-dioxane and its chlorinated co-contaminants.[66]

Bioremediation

Bioreactors are an *ex situ* form of biological treatment in which contaminated process wastewater or extracted groundwater is pumped into an aboveground reactor vessel (*i.e.*, bioreactor) and placed into direct contact with microorganisms. These microorganisms remove the contaminant by consuming it as a food source. Careful control of environmental conditions (pH, temperature, oxygen content, nutrient sources, etc.), hydraulic flow, and residency time of the contaminated water supply in the bioreactor is necessary to support the growth of the microorganisms.

Aerobic bioreactors have been used for decades in the treatment of municipal and industrial wastewater. Common system designs include fluidized bed reactors (FBR), continuous-stirred tank or suspended growth reactors, and fixed-film or packed-bed reactors. Laboratory-scale studies have demonstrated the ability of *ex situ* trickling-bed filters to effectively biodegrade cyclic ethers such as 1,4-dioxane, and a fixed film moving bed bioreactor system has been deployed for that purpose at the Lowry Landfill Superfund Site outside of Denver, Colorado.[67,68] Despite the name, the Lowry Landfill Superfund site is in no way associated with the nearby former Lowry AFB.

The landfill was used to dispose of municipal and industrial waste, including liquid industrial waste containing spent solvents and 1,4-dioxane. Contaminated groundwater recovered at the site was historically treated on-site before being discharged to the Denver Metro Water Reclamation Facility. A treatment train consisting of equalization, chemical softening, pH adjustment, filtration, UV/Oxidation, and GAC was employed, but was unable to reduce 1,4-dioxane levels to below Colorado regulatory limits due to poor UV transmittance, hydroxyl scavenging, and poor sorption on GAC.[69] The inability to reduce 1,4-dioxane concentrations to permitted levels resulted in the evaluation of a number of alternative technologies, including biological treatment.

Pilot studies demonstrated the ability of aerobic bioreactors to reduce 1,4-dioxane from blended water supplies with influent concentrations of 8,000 to 12,000 ppb to effluent concentrations of less than 200 ppb. Reductions occurred in 12-15 hours, and required the presence of tetrahydrofuran (THF) as a co-metabolite. Based on the results of the bench and pilot scale testing, a full-scale system was designed, constructed and operated at the Site. The full-scale system, a fixed film, moving bed bioreactor, has been in operation at the Lowry Landfill site

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[65] 1,4-Dioxane - - A Little Known Compound – Changing the Investigation and Remediation of TCA Impacts, D. Walsom and B. Tuncliffe, XCG Consultants Ltd., Environmental Science and Engineering, May 2002.

[66] Emerging Contaminant Spotlight: 1,4-Dioxane, Peroxygen Talk, FMC Environmental Solutions, July 2006

[67] Biodegradation of 1,4-Dioxane Using Trickling Filter, M. Zenker, R. Borden and M. Barlaz, Journal of Environmental Engineering, Vol. 130, Issue 9, September 2004.

[68] Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications, EPA 542-R-06-009, November 2006.

[69] Full-Scale Treatment of 1,4-Dioxane Using a Bioreactor, T. Shangraw and W. Plaehn, Federal Remediation Technology Roundtable, December 2006.

since 2004. It has demonstrated the ability to treat up to 10 gallons per minute (gpm) of blended influent waters containing 10,000 to 25,000 µg/L of 1,4-dioxane and 10,000 to 60,000 µg/L of THF. It is currently operating at an influent flow rate of approximately 6 gpm, and is reducing 1,4-dioxane to near detection limits of 1 µg/L at reactor temperatures of approximately 23°C, approximately a 99.9% reduction.[70] The robustness of the reactor system has enabled the site to eliminate the ineffective UV-Oxidation system, significantly reducing activated carbon usage, and lower operating and maintenance requirements without compromising plant reliability..

In situ bioremediation of groundwater eliminates the need for aboveground treatment by using biological processes to destroy or transform contaminants in groundwater. Preliminary information suggests that propane-utilizing aerobic bacteria (propanotrophs) may have the ability to co-metabolically degrade 1,4-dioxane using enzyme systems designed to oxidize propane.[71] Use of propanotrophs for *in situ* bioremediation of 1,4-dioxane would require amending the groundwater with both propane and oxygen. Degradation of 1,4-dioxane would occur after depletion of the propane. As part of EPA's recent evaluation of treatment technologies for 1,4-dioxane the Agency noted that while dioxane should theoretically be amenable to removal from soil using in situ processes, no full- or pilot-scale *in situ* projects were identified as part of the evaluation.[72] However, the Department of Defense's Strategic Environmental Research and Development Program (SERDP) is currently funding research to develop a better understanding of the mechanisms and effects of bacterial degradation on the fate and persistence of 1,4-dioxane in the environment. [73,74]

Two complementary SERDP projects are seeking to: develop a mechanistic understanding of the enzymes, pathways, and kinetics of biodegradation of 1,4-dioxane by evaluating bacteria expressing oxygenase enzymes; evaluate the effects of contaminant mixtures and different redox and chemical/physical conditions and treatment regimes on biodegradation rates; identify and isolate new 1,4-dioxane degrading microbes from environmental microcosms; and confirm that biodegradation pathways observed in pure bacterial cultures actually occur in environmental samples. As was the case with previous SERDP funding of critical perchlorate biodegradation studies, the successful completion of these projects is expected to generate important biochemical and mechanistic information that will support the further development, optimization, and potential availability of cost-effective *ex situ* and *in situ* biodegradation processes to remediate 1,4-dioxane contamination.

Phytoremediation

Limited evidence suggests that 1,4-dioxane may be amenable for removal from soil and shallow groundwater via phytoremediation. Phytoremediation uses natural plant processes and microorganisms associated with the root system to remove, contain, or degrade environmental contaminants in soil, sediment, and water. Phytoremediation processes expected to be important for remediation of 1,4-dioxane include, but are not limited to, phytovolatilization

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[70] Full-Scale Treatment of 1,4-Dioxane Using a Bioreactor – A Progress Report, W. Plaehn, T. Shangraw, D. Wilmoth, S. Richtel, The Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 2008.

[71] Dioxane-Degrading Propanotrophs for In Situ Bioremediation, M. Findlay, D. Smoler and S. Fogel, Bioremediation Consulting, Inc.

[72] Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications, EPA 542-R-06-009, November 2006.

[73] Oxygenase Catalyzed Biodegradation of Emerging Water Contaminants: 1,4-Dioxane and N-Nitrosodimethylamine, CU 1417, Strategic Environmental Research and Development Program.

[74] Biodegradation of 1,4-Dioxane, CU 1422, Strategic Environmental Research and Development Program.

through the leaves and rhizodegradation through the root system. These processes are expected to work together as part of a single plant system to remove 1,4-dioxane although one may exert a greater influence on contaminant removal.

Using a model for coupled transport of water, heat, and solutes in the soil-plant-atmosphere, French researchers have simulated the phytoremediation of 1,4-dioxane by a poplar tree cutting.[75] The model indicates that up to 30% of the 1,4-dioxane in soil is removed within a period of seven days, resulting mainly from root uptake; approximately 60% of the 1,4-dioxane mass is expected to reside within the stem, 28% in the leaves, and 12% in the roots. The modeling results appear consistent with previous studies that used hybrid poplar tree cuttings to remove 1,4-dioxane from contaminated water.[76] The limited data suggest that phytoremediation has potential to be a cost-effective means of remediating 1,4-dioxane.

Monitored Natural Attenuation

Monitored natural attenuation (MNA) is an accepted remedial approach for many organic compounds, chlorinated solvents and petroleum contaminants. Attenuation mechanisms typically include some form of biodegradation, sorption, dilution, dispersion, volatilization or chemical reactions with soil and groundwater. It has been reported that solute fate and transport modeling to simulate observed 1,4-dioxane plume migration characteristics at an industrial site in the southeast United States generated data suggesting a seven year degradation half life at the site. The results of the modeling were used to support the selection of MNA, which was approved by the state agency as the proposed groundwater remedy for the site.[77]

Treatment of 1,4-Dioxane in Soil

Because of its chemical and physical properties, 1,4-dioxane is not expected to sorb to soil and organic matter. However, because of its hydrophilic properties, the use of *in* or *ex situ* solvent extraction processes using water as the solvent would be expected to remove 1,4-dioxane from soils for further treatment. Evidence that 1,4-dioxane is amenable to biological reduction suggests that biotreatment processes such as composting may prove to be effective at remediating contaminated soils. In *ex situ* processes, contaminated soils are excavated, mixed with additional soil and/or bacteria to enhance the rate of contaminant degradation, and placed in aboveground enclosures or treatment cells. *In situ* processes typically require the addition of a carbon source for contaminant degrading bacteria and may be active or passive depending upon whether the carbon source is applied directly to the undisturbed soil surface (passive) or physically mixed into the soil surface layer (active). While researchers in Japan have recently isolated a soil fungus capable of using 1,4-dioxane and many kinds of cyclic ethers as the sole source of carbon and identified ethylene glycol as a degradation product, no full- or pilot-scale projects involving the bioremediation of 1,4-dioxane in soil have been identified.[78]

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[75] Phytoremediation: Modeling Plant Uptake and Contaminant Transport in the Soil-Plant-Atmosphere Continuum, Ying Ouyang, St Johns River Water Management District, Palatka, FL, Journal of Hydrology, Vol 266, pp. 66-82, 2002.

[76] Phytoremediation of 1,4-dioxane by Hybrid Poplars, E.W. Aitchison, J.L. Schnoor, S.L. Kelley, and P.J. Alvarez, Proceedings of the 12th Annual Conference on Hazardous Waste Research, Kansas City, MO, May 1997.

[77] Treatment Options for Remediation of 1,4-Dioxane in Groundwater, William DiGuiseppi, P.G. and Caroline Whitesides, P.G, Environmental Engineer, Vol. 43 No.2, May 2007.

[78] Degradation of 1,4-Dioxane and Cyclic Ethers by an Isolated Fungus, K. Nakamiya, S. Hashimoto, H. Ito, J. Edmonds, and M. Morita, National Institute for Environmental Studies, Applied Environmental Microbiology, 71(3): 1254–1258, March 2005.

An overview of current remedial technology options for the ex situ and in situ degradation of 1,4-dioxane are summarized in Table 4.[79]

Table 4. Overview of *In* and *Ex Situ* Remedial Technology Options

Technology	Degradation Mechanisms	Technology Status (Bench, Pilot or Full Scale)	Effectiveness
***Ex Situ* – Pump and Treat**			
Aeration/air stripping	Volatilization	Full	Poor
GAC adsorption	Adsorption	Full	Moderate (~50%) (Poor)
Aerobic Bioremediation	Aerobic biodegradation in the obligate presence of THF, 20°-25°C	Full	Good to Very Good
RBC with THF	Aerobic biodegradation	Full	Low to moderate (limited data)
O_3/H_2O_2	Aerobic biodegradation	Bench	Good
UV/H_2O_2	Advanced Oxidation Process	Bench	Good
UV/sodium peroxydisulfate	Advanced Oxidation Process	Full	Good
UV/TiO_2 catalyst,	Advanced Oxidation Process	Bench	Good
Fenton's Reagent	Advanced Oxidation Process	Bench	Good
$UV/H_2O_2/O_3$	Advanced Oxidation Process	Bench	Good
In Situ			
Phytoremediation/Hybrid Poplars	Direct uptake Indigenous root-zone Microorganisms (minimal)	Bench	Good for shallow subsurface
Aerobic Bioremediation	Aerobic biodegradation in the obligate presence of THF - Aerobically at 35°C with THF	Bench	Possible but no evidence in ambient subsurface conditions
Aerobic Cometabolic Bioremediation	Cultured propanotroph, indigenous propanotrophs may be effective	Field, additional Bench ongoing	10 mg/L degraded in several hours
Anaerobic Bioremediation	Anaerobic biodegradation	Hypothetical	Poor
Bioaugmentation	*Actinomycete strain)*	Bench	Possible and under study
Phytoremediation/ Bioaugmentation	Poplar and bioaugmentation with CB1190 in poplar root zone	Bench	Good for shallow subsurface
Chemical Oxidation	Fenton's Reagent	Bench	Good
Chemical Oxidation	Persulfate with FMC catalyst	Bench	Good
Chemical Oxidation	Persulfate with Fe2+	Bench	Moderate
Chemical Oxidation	Persulfate	Bench	Poor
Chemical Oxidation	Zero-Valent Iron	Hypothetical	Low, but possible using nano-scale iron
Iron filing PRB	Zero-Valent Iron	Hypothetical	Low
MNA	Natural attenuation	Full	TBD; highly depends

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[79] Information obtained from professional judgment analysis as provided in email from B. DiGuiseppi, Earthtech, to E. Becvar, AFCEE, 28 May 2007, updated to reflect Lowry Landfill 2008 performance data.

Technology	Degradation Mechanisms	Technology Status (Bench, Pilot or Full Scale)	Effectiveness
			on site conditions

EPA reports that of the 14 systems currently in place across the country to address 1,4-dioxane contamination in soil and groundwater, 12 projects currently use advanced oxidation systems. Additional perspective on 1,4-dioxane issues, the applicability of remedial technology options for its treatment, and details on their application at specific sites across the countray is available in an overview document developed by EPA's Office of Superfund Remediation and Technology Innovation (OSRTI) document *Treatment Technologies for 1,4-Dioxane – Fundamentals and Field Applications.*[80]

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Remedial Cost Implications

The cost associated with installing and operating a remedial system is highly dependent upon site-specific variables including, but not limited to: the size and geological characteristics of the site, the number of wells or boreholes to be installed, the total volume of water and/or amount of soil to be treated, the need to control the soil and water chemistry, the presence of co-contaminants and, of course, the cleanup goals established for the site.

New or additional site characterization and remedial design choices may be necessary if RPMs are asked by regulators to analyze for and manage 1,4-dioxane after initial site characterization and remedial design choices have already been made based on the presence of other chlorinated solvents or contaminants. In some cases, the discovery of 1,4-dioxane has already resulted in expanded monitoring networks, additional analytical costs, larger capture zones, and the addition of new technologies to existing treatment trains. For instance, in the September 2005 Five Year Report for the King of Prussia Superfund Site in Winslow Township, New Jersey, EPA Region 3 recommended modifying the site's operations and maintenance (O&M) plan to add 1,4-dioxane to the sampling protocol due to the known presence of 1,1,1-TCA in groundwater at the site. [81]

An overview of general remedial cost implications that can be expected for 1,4-dioxane is provided below. Because most technologies currently treating 1,4-dioxane contaminated groundwater are ex situ in nature, and limited cost and performance data for in situ treatment is available, the discussion focuses on technologies that could be expected to be employed to simultaneously treat 1,4-dioxane and its chlorinated solvent host in a treatment train.

<u>Site Characterization and Remedial Design</u>

Regulatory requests to assess for the presence of 1,4-dioxane are in many cases expected to occur well after site characterization and remedial design for other contaminants has already been completed. Consequently, RPMs can expect to incur new or additional costs for characterizing 1,4-dioxane release sites and choosing an appropriate remedy. As an example, consider the case of a fictitious site that had previously characterized 1,1,1-TCA contamination, chose an appropriate remedy based upon the extent of the contamination and potential exposure pathways, and was issued a formal record of decision (ROD). Under such a scenario,

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[80] Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications, Office of Superfund Remediation Technology Innovation, EPA 542-R-06-009, November 2006

[81] Second Five Year Report for the King of Prussia Superfund Site, Winslow Township, NJ, EPA Region 3, September 2005

if the site was asked by regulators to assess for the potential of 1,4-dioxane after issuance of the ROD it would require a larger monitoring network and therefore greater associated costs. Additional costs could be expected to be incurred from the need to re-sample the characterized 1,1,1-TCA plume for the presence of 1,4-dioxane. Because the chemical is reasonably expected to be associated with 1,1,1-TCA there may be an opportunity to leverage existing knowledge of site conditions to minimize those costs, however the site would also need to conduct new sampling in advance of the plume due to the expectation that 1,4-dioxane contamination would exceed the 1,1,1-TCA plume length. New costs could also be expected due to the need to reassess, and potentially replace or modify, the existing remedy choice to allow treatment of 1,4-dioxane and co-contaminants.

Treatment Trains

Conventional pump-and-treat technologies (*e.g.*, air stripping, GAC) are generally ineffective at treating 1,4-dioxane but may be required to treat its host solvent plume. A major operating cost of air strippers is the electricity required for the groundwater pump, the sump discharge pump, and the air blower. Depending on plume size, pump electrical draw, and site difficulty, O&M costs can be expected to range from \$0.40 - \$3.40/1,000 gallons for air stripping.[82] Costs associated with liquid phase GAC are dependent upon flow rates, contaminant concentration, mass loading, and discharge levels. They are generally lower with lower influent concentration levels and higher flow rates. At flow rates of approximately 100,000 gallons/day costs are expected to range from \$1.20 to \$6.30 per 1,000 gallons treated.[83]

The capital costs of an AOP system are expected to be significantly higher than those associated with air stripping and/or GAC systems. At a contaminated commercial site in Canada the re-engineering of an existing air stripping system to add an AOP system specifically to treat 1,4-dioxane increased the capital costs of the system by a factor of three.[84] O&M costs are also expected to significantly increase with AOPs due to the need to control the water chemistry through regular use of large volumes of reactive chemicals such as H_2O_2, sodium hydroxide (NaOH), and sulfuric acid (H_2SO_4) to adjust pH, and sodium bisulfate ($NaHSO_4$) to remove excess H_2O_2 prior to discharge; and high electrical demand and consumption associated with the use of UV lights.

The electrical demand associated with the UV/H_20_2 system previously used at the Pall-Gelman Sciences release site in Ann Arbor, Michigan, to treat one of the country's largest 1,4-dioxane-contaminated groundwater plume averaged 660kW-hr/day, or about \$850/day, for an overall cost of approximately \$3.50/1,000 gallons.[85] Because of the excessive operating cost, an O_3/H_2O_2 system was installed in 2005 to reduce H_2O_2 consumption by 50%, and eliminate the need for H_2SO_4 and NaOH.

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[82] Federal Remediation Technology Roundtable, Screening Matrix and Reference Guide, Ex Situ GW Remediation Technology, 4.45 Air Stripping.

[83] Federal Remediation Technology Roundtable, Screening Matrix and Reference Guide, Ex Situ GW Remediation Technology,4.51 Granular Activated Carbon (GAC)/Liquid Phase Adsorption .

[84] 1,4-Dioxane - - A Little Known Compound – Changing the Investigation and Remediation of TCA Impacts, D. Walsom and B. Tuncliffe, XCG Consultants Ltd., Environmental Science and Engineering, May 2002.

[85] Ultraviolet and Hydrogen Peroxide Treatment Removes 1,4-Dioxane from Multiple Aquifers, EPA Technology News and Trends, January 2005

For comparative purposes, representative costs of applying air stripping, GAC and AOP technologies as part of a treatment train for another cyclic ether groundwater contaminant, methyl tert-butyl ether (MTBE), are provided in Table 5.[86]

Table 5. Comparative Costs of Air Stripping, Sorption and AOP Systems

Technology (flow gpm)	Capital ($1000)	O&M ($1000 Annual)
Air Stripping		
60	$50-100	$50-60
600	$200-700	$80-280
6000	$2000-7000	$250-1400
GAC		
60	$150-234	$61-127
600	$1000	$161-665
6000	$6000	$1000-5000
AOP		
H_2O_2/UV		
60	$177-266	$54-108
600	$266-1300	$157-551
6000	$1000-10,000	$930-4210
H_2O_2/O_3		
60	$144-622	$47-64
600	$1666-1888	$123-239
6000	$8000-9775	$1101-1725

State and Federal Regulatory Guidelines, Action Levels, and Remediation Targets

Although the EPA is currently evaluating the toxicological studies that were used to derive the current cancer slope factor new data thay may be used to support the development of a new slope factor, and potentially an RfD, is being analyzed. However, as additional detections of the chemical have occurred across the country some EPA Regions and various states have established (or are at least investigating) their own screening levels, action levels, health advisories, and cleanup targets for 1,4-dioxane in drinking water, groundwater, and soils.

In September 2004, Colorado became the first state to establish an enforceable regulatory standard for 1,4-dioxane. Currently set at 6.1 ppb, the standard will fall to 3.1 ppb after March 2010. As of January 2007, 18 states, 3 EPA Regions, and the EPA NCEA have established some type of action level for 1,4-dioxane in drinking water, groundwater, surface water, and soils. While most of these levels have not undergone the scrutiny of a public rulemaking and are not enforceable on their own, they are being used to establish site-specific cleanup goals.

An expanded overview of federal and state guidance for 1,4-dioxane in soil and water identified by EPA in its previously referenced November 2006 document is provided in Table 6 below. It should be noted that while there is a great deal of variability in the levels, most state levels are less than the commonly reported 10 ppb effluent concentration that can be expected to be

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[86] Remediation Innovative Technology Seminar, Management of Secondary Treatment Trains, Naval Facilities Engineering Service Center, October 2001

achieved by most AOP remedial processes, as well as the effluent concentration currently being achieved through the use of *ex situ* bioreactor technology at the Lowry Landfill Superfund Site.

Table 6. State and EPA Regulatory Guidelines, Action Levels and Remediation Targets for 1,4-Dioxane

Jurisdiction	Guidance Type	Media	Level/Use
Arizona	Soil Remediation Level	Soil	400 ppm (400 ppm) (residential)
			1,700 ppm (non-residential)
	Advisory Level	Drinking Water	3 ppb
California	Advisory Level	Drinking Water	3 ppb
		Soil	0.0018 ppm (residential, industrial)
Colorado	Water Quality Standards	Groundwater, Surface Water	6.1 ppb (Mar 2005 – Mar 2010) 3.2 ppb (Mar 2010)
Connecticut	Comparison Value for Risk Assessments	Drinking Water	20 ppb
Delaware	Remediation Standard	Groundwater	6 ppb
		Soil	0.6 ppm (critical water resource area) 58-520 ppm (non-critical water resource area)
Florida	Groundwater Cleanup Target Levels	Groundwater	3.2 ppb
	Surface Water Cleanup Target Levels	Surface Water	120 ppb
	Soil Cleanup Target Levels	Soil	38 ppm (direct exposure – commercial/industrial) 23 ppm (direct exposure – residential) 0.01 ppm (leachability – groundwater) 0.5 ppm (leachability – surface water)
Illinois	Groundwater Remediation Objective	Groundwater	1 µg/l (acceptable detection limit – carcinogens)
Iowa	Soil Standard	Soil	280 ppm
Maine	Maximum Exposure Guideline	Drinking Water	32 ppb
Massachusetts	Drinking Water Guidelines	Drinking Water	3 ppb
	Massachusetts Contingency Plan Groundwater Standards	Groundwater	3 ppb(proposed current/future drinking water) 6000 ppb (proposed shallow/potential vapor intrusion) 50000 ppb (proposed ecological risk)
		Soil	0.005 ppm (direct contact and leaching)
Michigan	Cleanup Criteria/Screening	Drinking Water	350 ppb (industrial)

Jurisdiction	Guidance Type	Media	Level/Use
	Levels		85 ppb (residential)
		Soil	7 ppm (drinking water protection – industrial) 56 ppm (groundwater/surface water interface – industrial)
Missouri	Target Concentrations	Groundwater	3 ppb
		Soil	150-590 ppm (direct exposure) 0.01 ppm (leaching to groundwater)
Oregon	Risk Based Concentrations for Chlorinated Solvents	Soil	53 ppm (residential – soil ingestion, dermal contact) 140 ppm (urban residential – soil ingestion, dermal contact) 0.23 ppm (residential – leaching to groundwater) 0.41 ppm (urban residential – leaching to groundwater)
	Level II Screening Level for Ecological Risk Assessment	Soil	63 ppm (mammals)
		Surface Water	4 mg/l (mammals)
Pennsylvania	Media Specific Concentrations for Organic Regulated Substances	Groundwater	5.6 ppb (used aquifers – residential) 24 ppb (used aquifers – non-residential) 56 ppb (non-use aquifers – residential) 240 ppb (non-use aquifers – non-residential)
		Soil	210 – 240 ppm (direct contact – non-residential) 41 ppm (direct contact – residential) 0.31 – 240 ppm (groundwater protection – non-residential) 0.0073 – 56 ppm (groundwater protection – residential)
South Carolina	Drinking Water Health Advisory	Drinking Water	70 ppb (monthly average)
Texas	Protected Concentration Levels	Groundwater	18.6 ppb (commercial/industrial) 8.3 ppb (residential)
		Soil	2,600 ppm (total combined pathways – industrial) 552 ppm (total combined pathways – residential) 0.36 ppm (groundwater protection – industrial) 0.083 ppm (groundwater protection – residential)
West Virginia	Risk-Based Concentrations	Groundwater	6.1 ppb
		Soil	5200 ppm (industrial) 58 ppm (residential)
Wyoming	Soil Cleanup Level	Soil	44 ppm (residential)
EPA NCEA	Health Based Advisory Level	Tap Water	3 ppb
	Cancer Slope Factor		1.1×10^{-2} (ppm/day)$^{-1}$

Jurisdiction	Guidance Type	Media	Level/Use
EPA Region 3	Risk-Based Concentrations	Tap Water	6.1 ppb
		Soil	260 ppm (industrial) 58 ppm (residential) 0.0013 – 0.0026 ppm (groundwater protection)
EPA Region 6	Screening Levels	Tap Water	6.1 µg/l
		Soil	170 – 520 ppm (industrial) 44 ppm (residential)
EPA Region 9	Preliminary Remediation Goal (PRG)	Tap Water	6.1 ppb
		Soil	160 ppm (industrial) 44 ppm (residential)

Other Environmental, Safety and Health Guidance

When used as a solvent stabilizer, 1,4-dioxane itself is considered a hazardous substance regulated under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA); a CERCLA reportable quantity of 100 lbs has been established for the chemical. In addition, emissions of 1,4-dioxane are also regulated as a hazardous air pollutant (HAP) under the Clean Air Act and its implementing guidance. As a Clean Air Act HAP, total emissions of 1,4-dioxane are limited to 10 tons per year if it represents the lone HAP emitted by a source, or if it is one of multiple HAPs emitted by a source, the total aggregated emissions of all HAPs are limited to 25 tons per year. Other organizations have also established guidance levels for 1,4-dioxane, in most instances based on occupational, environmental, and other exposure concerns. The American Council on Governmental Industrial Hygienists (ACGIH), the National Institute of Occupational Safety and Health (NIOSH), and the Occupational Safety and Health Administration (OSHA) have all established guidelines to limit workplace exposures.[87] When used in consumer products, 1,4-dioxane does not meet the regulatory definition of a solvent, but is regulated by the Food and Drug Administration (FDA) under the Federal Food, Drug, and Cosmetics Act. Additionally, the ATSDR has developed Minimal Risk Levels to guide health risk assessments for 1,4-dioxane. These other environmental, safety and health guidelines are presented in Table 6.

Table 6. Other 1,4-Dioxane Environmental, Safety and Health Guidelines

Organization	Description	Level
EPA	CERCLA Reportable Quantity	100 lbs
	RCRA Hazardous waste identification (listed waste – discarded commercial chemical product)	U108
	CAA Hazardous Air Pollutant	
ATSDR	Minimal Risk Level (Inhalation – Acute)	2 ppm
	Minimal Risk Level (Inhalation – Chronic)	1 ppm
	Minimal Risk Level (Oral – Acute)	4 ppm/day
	Minimal Risk Level (Oral – Chronic)	0.1 ppm/day
ACGIH	Threshold Limit Value	20 ppm
NIOSH	Recommended Exposure Level (Ceiling)	1 ppm
	Immediately Dangerous to Life and Health	500 ppm
OSHA	Permissible Exposure Limit (general)	100 ppm
FDA	Consumer Product Limitation	10 ppm

The OSWER Directive on Toxicity Criteria for CERCLA Risk Assessments

The EPA's Office of Solid Waste and Emergency Response (OSWER) provides policy, guidance, and direction for the Agency's solid waste and emergency response programs. OSWER Directive 9285.7-53 (December 5, 2003) provides explicit instructions on the use of human health toxicity values in risk assessments at CERCLA sites.[88] Toxicity values consist of cancer potency factors for evaluating risks of cancer associated with a dose of a chemical, and

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[87] Eleventh Report on Carcinogens, Substance Profile – 1,4-Dioxane, U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program, January 2005.

[88] OSWER Directive 9285.7-53, Human Health Toxicity Values in Superfund Risk Assessments, December 2003

RfDs or RfCs for evaluating hazards associated with exposures to chemicals that may cause health effects other than cancer.

OSWER Directive on Toxicity Criteria

- Three tiered hierarchy approach based on data quality - draft toxicity assessments are not appropriate for use until they have undergone peer review, have had comments addressed, and are publicly available
- Tier 1 – EPA's IRIS database as containing the highest quality data
- Tier 2 – In the absence of IRIS values use EPA PPRTVs
- Tier 3 – in the absence of IRIS values or EPA PPRTVs, use state or other peer-reviewed data
- RPMs and risk assessors should employ an approach for assessing 1,4-dioxane risks that is consistent with the OSWER crtiteria
- If conflicts arise regarding application of such an approach, immediately notifiy your major command, coordinate with the Regional Environmental Office, and report the matter up through the chain-of-command.

The directive updated EPA's hierarchy of human health toxicity values and provided guidance on the sources of toxicity information that EPA believes should generally be used when performing human health risk assessments at Superfund sites. A tiered hierarchy approach based on the quality of the underlying database and the extent to which the toxicity values have undergone peer review was developed to provide a consistent approach for selecting toxicity values for use in risk assessments, particularly when no IRIS values have been developed for the chemical in question. The highest quality (Tier 1) data is that contained in EPA's IRIS database. In the absence of IRIS values, EPA's Provisional Peer Reviewed Toxicity Values (PPRTVs) are identified as the next highest quality (Tier 2) data. Finally, in the absence of formal IRIS values or PPRTVs for a chemical, other non-EPA toxicity (Tier 3) data can be used, with special consideration given to current, publicly available data that has undergone peer review, such as those used to develop formal state toxicity or criteria values.

OSWER Directive 9285.7-53 specifically states "In general, draft toxicity assessments are not appropriate for use until they have been through peer review, the peer review comments have been addressed in a revised draft, and the revised draft is publicly available". However, there are some agencies applying and requiring that the draft toxicity assessments be used in health risk assessments. In light of the numerous state-specific action levels and the lack of formal federal regulatory standards, if asked to assess potential risks from 1,4-dioxane RPMs and risk assessors should employ an approach for identifying and selecting peer-reviewed toxicity values that is consistent with the methodology of the OSWER directive. Such an approach will support Air Force personnel in making consistent and informed decisions regarding risk assessment and mitigation strategies, while minimizing opportunities for data of questionable or lesser quality to drive assessment and response activities. If conflict regarding the application of such an approach occurs, RPMs and risk assessors should immediately notify their Major Command and coordinate with their Regional Environmental Office, and seek additional guidance as necessary through the chain-of-command.

Potential of Air Force Environmental Releases of 1,4-Dioxane

A recent assessment conducted by the DoD Emerging Contaminants Directorate concluded that 1,4-dioxane risks to the Military Services are primarily associated with the presence of 1,4-dioxane at legacy environmental contamination sites, and from the continued presence of low levels of 1,4-dioxane in materials and products still used by DoD or their contractors, such as deicing fluids and waterproofing materials for small arms ammunition shell casings.[89] Because

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[89] Phase I Impact Assessment for 1,4-Dioxane, Deputy Undersecretary of Defense for Installations and Environment, Emerging Contaminants Directorate, April 2007

of pending EPA regulatory activities, it was recommended that 1,4-dioxane remain on a chemical watch list and that regulatory activities relative to 1,4-dioxane continue to be monitored.

The following section discusses the potential for Air Force environmental releases of 1,4-dioxane, focusing on its expected association with legacy environmental contamination sites. Having made the DoD chemical watch list, Service acquisition and material management practices should be conducted in a manner that acknowledges the potential for 1,4-dioxane releases from current materials use, and appropriate management practices to minimize the possibility of environmental releases should be implemented.

Past environmental management and waste disposal practices employed by public and private sector organizations are known to have caused widespread contamination of soil, sediment and groundwater with industrial solvents. Routine waste disposal practices previously accepted by regulators often involved disposing of organic and chlorinated solvent wastes by pouring them directly on the ground or into unlined pits/trenches for evaporation or burning, where they often seeped out and contaminated surrounding soils, groundwater and surface water. As waste management and disposal practices matured, public agencies sometimes required solvents and solvent wastes to be stored in underground tanks, and many of those tanks and associated piping are also known to have leaked.

The 1995 Report to Congress on the DoD Ozone Depleting Substance Reduction Program noted there were five major solvents used in thousands of applications for military weapon systems, platforms, and facilities across the Services – 1,1,1-TCA, carbon tetrachloride (CCl_4), and three variations of chlorofluorocarbons (CFCs).[90] It further noted that nearly two thirds of the DoD-owned equipment specifications and standards directly referenced using one of the chemicals for solvent and miscellaneous cleaning purposes. While the number of actual 1,1,1-TCA specifications was not identified in the Report, because of its historical widespread use for cleaning and degreasing purposes in both the public and private sector, storage and disposal of spent solvents and associated solvent wastes by Air Force personnel is reasonably expected to have contributed to some degree to associated environmental releases of 1,4-dioxane. Efforts to obtain historic Air Force 1,1,1-TCA acquisition and use data to assist in the evaluation of where associated environmental releases of 1,4-dioxane may have occurred were unsuccessful due to limited data.

Air Force Toxic Release Inventory Data

In the absence of acquisition and use information, historic Air Force Toxic Release Inventory (TRI) data were assessed to determine whether reported releases of 1,1,1-TCA could provide greater insight into the extent of its use by the Air Force, and thus better frame the potential for 1,4-dioxane releases. As indicated in the table below, during the six year period of 1994-1999 approximately 624,352 pounds of 1,1,1-TCA was reported released by the Air Force, making it the seventh most prevalent toxic substance released by Air Force operations during that period.[91] Note that during 1994, the first year such data were collected and reported by the DoD and the Military Services, 1,1,1-TCA releases were comparatively even more significant, with 1,1,1-TCA the third most prevalent chemical reported released by the Air Force during that

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[90] Report to Congress, Department of Defense Ozone-Depleting Substance Reduction Program, Deputy Under Secretary of Defense for Environmental Security, August 1995.

[91] Emergency Planning and Community Right-to-Know Act: Air Force Toxic Release Inventory Performance, 11th Annual International Workshop on Solvent Substitution and the Elimination of Toxic Substances and Emissions, Col R. Miller, December 2000.

period and release numbers diminishing significantly in following years due to the phase-out on its production and use.

Table 7. Air Force 1,1,1-TCA Toxic Release Inventory Data

	1994	1995	1996	1997	1998	1999	Total
1,1,1-TCA Releases (lbs)	366,648	127,882	76,501	41,152	12,169	No data	624,352

Given what is known about 1,4-dioxane's role as a stabilizer for 1,1,1-TCA, about trends in solvent use during the 1970s and 1980s, and TRI data that indicate 1,1,1-TCA was the third most prevalent chemical released by the Air Force in 1994, it is clear that large quantities of this chemical were used and released by Air Force in preceding years. Thus there exists the potential for environmental releases of 1,4-dioxane to also have occurred as a result of the use and disposal of 1,1,1-TCA. The significant fall off in use observed after 1994 also support the observations that numerous solvent substitution/elimination and pollution prevention initiatives were being implemented, and that environmental concerns about potential releases of 1,4-dioxane should focus primarily on the role legacy 1,1,1-TCA operations and activities likely played in those releases. Accordingly, the following discussion of potential sources of Air Force environmental releases of 1,4-dioxane focuses on Air Force activities and processes that used and disposed of 1,1,1-TCA as a result of solvent cleaning applications.

Activities/Processes Using 1,1,1-TCA Solvent

The primary operational activities and processes that used 1,1,1-TCA solvent are electronics cleaning, precision cleaning, and metal cleaning. It is believed that consideration of these processes will account for most Air Force use of 1,1,1-TCA, and thus the majority of potential sources of 1,4-dioxane releases. This assumption appears to be supported by experiences in California where the San Francisco Bay Regional Water Quality Board requested 15 electronics manufacturing facilities sample for 1,4-dioxane, and the chemical was found to be present in the majority of the 1,1,1-TCA releases at the sites.[92]

- Electronics cleaning removes contaminants, primarily solder flux residues, from electronics or printed circuit boards
- Precision cleaning removes contaminants from sensitive parts such as optical devices, gyroscopes or hydraulic components that require ultra-high standards of cleanliness due to close tolerances, complex geometries, etc.
- Metal cleaning removes oil or grease from metal parts during maintenance and repair. It can include preparation of surfaces prior to machining or application of surface coatings, as well as stripping of existing surface coatings and adhesives.

Broadly speaking, Air Force processes, activities, and contractor activities conducted on behalf of the Air Force that have the potential to have contributed to environmental releases of 1,4-dioxane include the following:

- Development and acquisition of Air Force aerospace systems
- Performance of depot maintenance, repair/reclamation and overhaul of Air Force aviation motor vehicles and nonroad engines, and aviation electronic assets
- Storage and disposal of spent solvents and solvent wastes

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[92] Survey of 1,4-Dioxane Occurrence at Solvent Release Sites in the San Francisco Bay Area, V. Christian, San Francisco Bay Water Quality Board, 9th Symposium on Groundwater Contaminants, Groundwater Resources Association, December 2003.

More specific examples of equipment, processes and activities that have historically used or treated 1,1,1-TCA or 1,1,1-TCA wastes, and therefore may have potentially contributed to 1,4-dioxane releases are presented in Table 9.[93,94,95,96,97,98]

Table 8. Examples of Military Processes That Are Potential Sources of 1,4-Dioxane Releases

Vapor degreasing solvent distillation/recovery processes	Industrial/municipal waste disposal sites (landfills, waste pit areas, evaporation ponds, etc.)
Manufacture, assembly, and maintenance activities on launch vehicles and solid rocket motors	Manufacture, maintenance and cleaning of tubing for air, fuel, hydraulic and oxygen systems
Conformal surface coating/stripping activities	Electronic component production/cleaning
Electromechanical device cleaning	De-icing and cooling fluids, oil/water separator waste disposal
Maintenance of aircraft, motor vehicle, and aviation ground support equipment (GSE) and components (including engines, engine test cells/hush houses, landing gear/wheel bearings, and brakes)	General purpose small arms, ordnance and fuze maintenance and production
Weapons/weapon system maintenance and cleaning	Operation and maintenance of installation printing plants
Fire training activities	Cleaning agent for penetrator used in non-destructive inspection and oil analysis process

Installations with responsibilities and mission activities other than those specifically identified in Table 8 may also have generated environmental releases of 1,4-dioxane, either directly or indirectly by accepting and disposing of waste such as spent solvents from other Air Force or DoD sources.

Air Force 1,4-Dioxane Case Studies

A brief overview of the experiences of two Air Force installations known to be actively responding to concerns over the presence of 1,4-dioxane in soil and/or groundwater are provided below These serve as case studies for issues RPMs may encounter.

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[93] Joint Service Pollution Prevention Technical Library, Alternatives for Ozone Depleting Substances, Naval Facilities Engineering Service Center.

[94] ODC/EPA 17 Elimination from DoD Technical Data and Gas Turbine Engines, Maj L. DeGarmo, B. Manty, M. McCall, August 1995.

[95] Air Force Center for Environmental Excellence, PRO-ACT Success Story, Spotlight on Tinker AFB, December 1998.

[96] Solid Propellant Environmental Issues, Phase I Final Report, United Technologies Corporation for the Phillips Laboratory Propulsion Directorate, PL-TR-94-3047, December 1996.

[97] Research Triangle Institute, Solvent Alternatives Guide, Alkaline Aqueous Case Studies.

[98] Air Force Center for Environmental Excellence, PRO-ACT Success Story, Pollution Prevention Success Story on Toxic Chemical Substitution at a Printing Plant at Barksdale AFB.

Air Force Plant 44 - Air Force Plant 44 is a defense system manufacturing facility located in Tucson, Arizona. It is currently operated by Raytheon Corporation (formerly Hughes Missile Systems) under lease with the Air Force Aeronautical Systems Center (ASC), and is part of the Tucson International Airport Superfund Site.[99] The principal environmental contaminants of concern at Plant 44 include TCE, 1,1-DCE, 1,4-dioxane, and chromium.

- Past production, maintenance and modification of missile systems at Plant 44 resulted in environmental releases of chlorinated solvents and solvent wastes
- In 2002, 1,4-dioxane was detected in groundwater long after remedies were in place
- Detections occurred at levels of 1 to 54 ppb
- Existing contamination treatment systems were re-injecting 1,4-dioxane back into the underlying aquifer
- Currently implementing extraction and recharge strategy to prevent migration into the regional aquifer
- Some recharge wells have been taken out of service to prevent recharge of contaminated water.

Past industrial processes conducted at Plant 44 in conjunction with the production, maintenance and modification of missile systems have included cleaning and degreasing, plating, chemical etching, circuit board production, and surface coating. These processes generated wastewater and general industrial waste which were disposed of at IRP Site 3 in several excavated, unlined pits from the mid-1960s to the late 1970s. Wastes placed into the pits included 1,1,1-TCA, TCE, and other paint sludges, and thinners. [100]

Site investigations at Plant 44 were initiated in the early 1980s following the identification of contamination of the regional drinking water aquifer underlying areas around the airport. In 1985, a ROD was issued, and in 1987 an extensive, regional pump-and-treat system consisting of air stripping and reinjection was installed to contain and remediate the contaminants. During 1992, soil gas surveys detected elevated levels of DCE, 1,1,1-TCA, TCE, and Freon 113 in the vicinity of the disposal pits, and soil vapor extraction systems were installed shortly thereafter to accelerate the removal of VOCs. 1,1,1-TCA has not been detected in any groundwater monitoring wells since February 1989, and 1,1,1-TCA analyses were discontinued after August 1991, TCE and 1,1-DCE continued to be the primary contaminants of concern.

In 2002, 1,4-dioxane and TCE were detected at concentrations ranging from 1 to 54 ppb in an area characterized by relatively low hydraulic conductivity. It was determined that both contaminants likely migrated to that location in the past when overall groundwater contamination was higher, and that the low permeability of the soils trapped the contaminants and prevented their dispersal. It was subsequently determined that because 1,4-dioxane is not effectively remediated with the remedial technologies that were in place, the chemical was inadvertently being reinjected into the contaminated aquifer. In 2004, additional monitoring of the TCE and 1,1-DCE plumes was conducted, with 1,4-dioxane detections being correlated with 1,1-DCE and not TCE. This correlation is not suprising for two reasons: stabilizers for TCE require an antioxidant, a metal inhibitor, and an acid acceptor, and 1,4-dioxane stabilizer used in 1,1,1-TCA contains only a metal inhibitor and an acid acceptor; and 1,1-DCE is a known degradation product of 1,1,1-TCA. Based on the association with 1,1-DCE, additional monitoring was conducted, with a maximum detection of 600 ppb.

In July 2006, the U.S. Geological Survey and ASC entered into an agreement to investigate the extent and degree of 1,4-dioxane contamination in areas north of Plant 44. Of the 34 samples obtained under the agreement, 1,4-dioxane was detected in two thirds at concentrations ranging

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[99] EPA Region 9 Superfund Program, Tucson International Airport Area Site Overview.

[100] Final Remedial Action Completion Report IRP Site 3: Inactive Drainage Channel Disposal Pits, Air Force Plant 44, Tucson, Arizona, U.S. Air Force Aeronautical Systems Center, Wright-Patterson AFB, OH, October 2006.

from 1 to 11 ppb; 14 of the samples contain 1,4-dioxane concentrations that exceeded the EPA Region 9 PRG value of 6.1 ppb. [101] 1,4-dioxane was being addressed at Plant 44 through an extraction and recharge strategy to prevent migration into the regional aquifer. Some recharge wells have been taken out of service to eliminate recharge of 1,4-dioxane contaminated water outside of the extraction well field zone of capture. [102] On 13 July 2007, US EPA Region 9 issued an Administrative Order for Response Action under the Safe Drinking Water Act. As of August 2008, AFP 44 is the only AF cleanup site where 1,4-dioxane is considered to be a driver. Plant 44 officials have initiated a procurement action for a project to install an AOP system at the site that is reportedly capable of removing 1,4-dioxane to less that 2 ppb.[103]

McClellan Air Force Base - The primary mission of the former McClellan AFB in California, was the management, maintenance, and repair of aircraft, electronics, and communication equipment. The O&M of aircraft and related equipment involved the use, storage, and disposal of hazardous materials including industrial solvents, caustic cleansers, paints, metal plating wastes, and a variety of fuel oils and lubricants. Hazardous wastes from operations at McClellan AFB were historically discharged to surface soils on base in burial pits, landfills, sludge/oil pits or burn pits, or piped through a subsurface industrial wastewater line to two former industrial wastewater treatment plants. Sludge from these units was then discharged to surface soils on base. These land disposal practices were discontinued in the late 1970s.[104]

- The primary mission of the former McClellan AFB was the management, maintenance, and repair of aircraft, electronics, and communication equipment and known to be contaminated with 1,1,1-TCA, 1,1-DCE and TCE.
- At the request of regulators, a sampling strategy was developed to assess for the possible presence of 1,4-dioxane.
- 1,4-dioxane was detected at concentrations up to 64 µg/l in groundwater.
- An existing AOP system was activated to treat groundwater, achieving effluent concentrations of ~1,5 µg/l before being destroyed by fire.
- Results of additional sampling conducted during the Summer of 2007 will be used to determine whether 1,4-dioxane is a contaminant of concern, and if additional remedial remedies are needed.

As a consequence of its mission and past waste disposal practices, groundwater, sludge, and soil at McClellan AFB have been contaminated with different VOCs, heavy metals, and chlorinated and non-volatile solvent compounds, including TCE, 1,1.1-TCA, 1,1-DCE, and PCE. Active cleanup began in the mid 1980s, with McClellan AFB steadily expanding its long-term groundwater extraction and treatment system. In July 2002, the Air Force issued an Action Memorandum for a time-critical removal action to ensure that hexavalent chromium in the groundwater treatment plant would meet surface discharge criteria.

In the 2001-2002 timeframe, 1,4-dioxane was identified as an emergent chemical that was a potential constituent in the chlorinated solvents used at McClellan AFB. Air Force officials and regulatory agencies discussed the contaminant, and a sampling strategy was developed to determine if 1,4-dioxane was present in the groundwater, and, if so, its extent. Under the sampling strategy, all locations where VOC samples were being collected would also be subject to analyses for 1,4-dioxane. From the fourth quarter of 2002 until the fourth quarter of 2005, monitoring and extraction wells at McClellan AFB were sampled at least once, and as many as

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[101] Memorandum from N. Melcher, USGS Water Resources Discipline, Arizona Water Science Center to G. Warner, USAF ASC/ENVR, October 3, 2006.

[102] Installation Restoration Program, Summary of Reclamation Well Field and Soil Remediation Operations, July 2005-June 2006, U.S. Air Force Plant 44, Tucson International Airport, U.S. Air Force Aeronautical Systems Center, Wright-Patterson AFB, OH, September 2006.

[103] Proposal for Installation and Testing of an Advanced Oxidation Process System and Accelerated Schedule and Work Plan for Remedial Action, EarthTech, 31 Aug 2007

[104] EPA Superfund CERCLIS Description Report, McClellan AFB.

four times for 1,4-dioxane.[105] As a result 1,4-dioxane was detected in groundwater at concentrations up to 64 ppb, with the highest concentration in Operable Unit D wells.

Based on the occurrence of 1,4-dioxane in the groundwater, an existing AOP system (a UV/oxidation system) was also activated in order to treat 1,4-dioxane; the system treated approximately 10% of the influent to the groundwater treatment plant, primarily from Operable Units C and D. The UV/oxidation system was used to decrease the concentration of 1,4-dioxane in the plant's effluent, which is discharged to a nearby creek. In July 2005, the UV/oxidation system was destroyed by a fire. Because surface water discharge limits have not been established for 1,4-dioxane, and because 1,4-dioxane concentrations associated with the groundwater treatment plant have remained well below EPA Region 9's PRG value of 6.1 ppb (as of January 2007 1.5 ppb in the influent and 1.4 ppb in the effluent) there are currently no plans to replace the unit. A 2006 update to the groundwater monitoring plan includes a revised sampling strategy that focuses on sampling in areas where 1,4-dioxane was detected between 2002 and 2004.[106] Approximately 260 sampling locations are included in the update, although the number is subject to change if the plume expands or contracts. Sampling frequency at these locations vary from semi-annually to every five years, with most assigned a biennial frequency. The next revision of the State Regional Water Quality Board permit which establishes surface water discharge limits may include discharge limits for 1,4-dioxane. The Air Force will re-evaluate the need for additional treatment of 1,4-dioxane at the groundwater treatment plant after the permit is updated.

Related to the effort described above McClellan AFB also completed non-VOC site inspection (SI) and remedial investigation (RI) efforts in 2006 This included activities to identify potential sources and determine the extent of 1,4-dioxane in the groundwater. The SI was performed in 2006, and the RI was completed in the summer of 2007. The SI/RI information was used to develop a non-VOC feasibility study (FS) in 2007 to determine whether 1,4-dioxane is a contaminant of concern and if additional remedies are needed. Based on the analyses, a Non-VOC Proposed Plan (PP) and Non-VOC Record of Decision (ROD) are currently planned for completion in 2008.[107]

As can be seen by the case studies discussed above, the potential for environmental releases of 1,4-dioxane can potentially be greater at Air Force depots/logistic centers and aerospace facilities. However, the general breadth of the equipment, processes, and activities listed, and knowledge that general O&M activities, waste disposal activities, and fire training activities were historically conducted to some degree on many other Air Force installations, suggests focusing exclusively on depots/logistic centers and aerospace facilities may underestimate the extent of the potential occurrence of 1,4-dioxane and associated environmental liabilities.

Analysis of Air Force Environmental Sampling Data

Because 1,4-dioxane has not typically been sampled for and reported as a target analyte in environmental monitoring programs, a robust Air Force database of quantitative 1,4-dioxane analytical results is not available. Based on historic Air Force use of 1,1,1-TCA in solvent cleaning applications and observations of the co-contamination of 1,4-dioxane with 1,1,1-TCA, it is possible a number of Air Force sites across the country have some detectable levels of 1,4-dioxane that have simply not been sampled and analyzed for.

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[105] Personal Correspondence, Air Force Real Property Agency, February 21, 2007.

[106] Ibid

[107] Personal Correspondence, Air Force Real Property Agency, February 21, 2007

As a preliminary screening method to assess for the potential of 1,4-dioxane contamination at Air Force installations, two Air Force environmental data management systems, the Air Force Remedial Information Management System (AFRIMS) and the Air Force Environmental Resources Program Information Management System (ERPIMS), were queried for 1,4-dioxane to provide insight into its spatial distribution and frequency across Air Force installations. [108] Because 1,1,1-TCA was widely used by the Air Force for cleaning and degreasing purposes, has been found at nearly half of all Superfund sites, and the strength of evidence linking 1,4-dioxane to 1,1,1-TCA, the data systems were also queried for 1,1,1-TCA as a means of potentially bounding the extent of possible 1,4-dioxane contamination at Air Force installations. The results of the screening assessment are summarized below.

AFRIMS is an automated tool which allows RPMs at an installation, MAJCOM, and/or Air Staff level to manage funding and schedule site information and management estimates pertaining to the AF Environmental Restoration Account (ERA)-funded environmental cleanup program for Installation Restoration Program (IRP), Military Munitions Response Program (MMRP), and Building Demolition/Debris Removal (BD/DR) sites. AFRIMS information is used to construct various budget submittals, track command performance, and respond to other program information and data requests. Because AFRIMS is not designed to be a comprehensive, analytical database of the occurrence of chemical contaminants on Air Force installations, and because emerging contaminants such as 1,4-dioxane have not typically been sampled for and reported as target analytes in environmental monitoring programs, AFRIMS was expected to contain minimal data on the potential extent of 1,4-dioxane contamination on Air Force installations.

ERPIMS is the Air Force system for validation and management of analytical and other data from environmental projects at all Air Force bases. The database contains analytical chemistry samples, tests, and results as well as hydrogeological information, location descriptions, and monitoring well/sampling site characteristics. One of the largest environmental databases in the United States, ERPIMS contains over 45 million analytical records on approximately 3,000 parameters for 160 Air Force installations. ERPIMS provides summary concentration data for 1,4-dioxane and other emerging contaminants, and allows for an analysis of the tendency of detected concentrations to exceed environmental criteria of concern.

AFRIMS 1,4-Dioxane Data

A query of the AFRIMS database for 1,4-dioxane revealed only two installations which reported 1,4-dioxane detects. Despite known detections of 1,4-dioxane at Plant 44 and the former McClellan AFB, they do not appear in the AFRIMS database. The two Air Force installations that were listed in AFRIMS as having reported 1,4-dioxane detections were Altus AFB, Oklahoma, and Edwards AFB, California.

Information reported by Altus AFB, home of the Air Force Mobility Training Center of Excellence, indicates 1,4-dioxane has been detected in groundwater at three locations, with maximum concentrations ranging from 15 to 110 ppb. The detections are associated with spill sites contaminated by chlorinated solvents, primarily TCE, 1,1,-DCE, PCE, and carbon tetrachloride, and with other chlorinated hydrocarbons detected underneath the aircraft industrial area of the base. 1,4-dioxane has also been detected at Altus AFB in soil at two

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[108] Occurrence of 1,4-Dioxane in Groundwater and Soil Air Force Wide, ERPIMS Data Summary, P. Hunter, P.G., Air Force Center for Engineering and the Environment, January 4, 2007

locations at maximum concentrations ranging from 3,700 to 5,500 µg/kg (3.7-5.5 ppm), well below the EPA Region 6 soil screening level of 170-520 ppm (industrial) and the 44 ppm (residential) level. Soil contamination was detected at spill sites associated with historic storage areas, and at the former waste water treatment facility and its associated drying beds. The data also includes an installation comment that contamination appears to have migrated to the groundwater; presumably this comment was based upon the fact of 1,4-dioxane being detected in groundwater at the location.

Information reported by Edwards AFB, home of the Air Force Flight Test Center, indicates 1,4-dioxane has been detected in groundwater at a maximum concentration of 5.42 ppb. This was under the former exotic fuel storage area and its tanks, ponds, and wash areas. The AFRIMS database is void of results for soil.

AFRIMS 1,1,1-TCA Data

Not surprisingly, significantly more Air Force installations appear in AFRIMS as having sampled for and reported detections of 1,1,1-TCA in soil, groundwater, surface water, and sediment than for 1,4-dioxane. Based upon the review, not all installations that reported 1,4-dioxane detections also sampled for and reported 1,1,1-TCA detections.

A review of AFRIMS data indicates a total of 39 individual sites on 23 active and closed installations and reserve or National Guard locations report 1,1,1-TCA groundwater contamination at maximum concentrations ranging from 70 to 180,000 ppb. Representative processes and activities reported as being associated with the detections include fuel storage/dispensing, fire training, industrial waste pits and lagoons, landfills, paint washout areas, bulk chemical storage, maintenance areas (aircraft/engines/motor vehicles/other mechanical equipment) gun shops, waste solvent/petroleum storage, surface preparation (cleaning, coating, etc.), oil/water separation, and water treatment plants. Of these, industrial waste pits, fire training areas, landfills, surface preparation, and maintenance activities reported higher concentrations of 1,1,1-TCA.

A review of AFRIMS data for sites with reported 1,1,1-TCA in soils revealed 21 active and closed installations and reserve or National Guard locations with 26 individual sites with reported TCA in soil or sediment at concentrations ranging from 75 to 700,000 ppb. Representative processes and activities associated with the detections include solvent cleaning/storage areas; solvent disposal areas such as industrial waste pits and lagoons; maintenance areas (aircraft/engines/motor vehicles/other mechanical equipment); oil/water separators; and landfills.

ERPIMS 1,4-Dioxane Data

AFCEE queried ERPIMS for 1,4-dioxane and conducted a statistical analysis on the results. [109] The analysis indicates that 29 Air Force installations have sampled for 1,4-dioxane in groundwater, approximately 18% of all Air Force installations in the ERPIMS database. Based on available ERPIMS data, this would indicate that approximately 131 active or closed Air Force installations have not yet conducted sampling for 1,4-dioxane.

Of the 29 installations that report having sampled for 1,4-dioxane in groundwater, 10 have sampled at least 40 wells, a number AFCEE believes to be statistically relevant. Of the remaining 19 installations, three have sampled between 21 and 30 wells, and three have

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[109] Occurrence of 1,4-Dioxane in Groundwater and Soil Air Force Wide, ERPIMS Data Summary, P. Hunter, P.G., Air Force Center for Engineering and the Environment, October 23, 2006 and January 4, 2007.

sampled between 10 and 20 wells. The remaining installations have sampled less than 10 wells. Of the 29 installations that have sampled for 1,4-dioxane, eight (or approximately 28%) reported detections as shown in Table 9. Assuming the percentage of installations that have sampled for 1,4-dioxane in groundwater and reported detections is representative of all Air Force installations that report to ERPIMS, up to 36 additional installations (28% of the remaining 131 that have not yet sampled) could be expected to report detections of 1,4-dioxane if asked to sample.

As part of the AFCEE ERPIMS analysis, 1,4-dioxane detections and concentrations were identified across statistically relevant endpoints (such as the 33rd, 50th, 75th, 90th, and 95th percentiles) and compared against EPA's 3 ppb Health Advisory Level and EPA Region 9's 6.1 ppb PRG. The analysis indicated at least 10% of all the groundwater samples collected (both detections and non-detects) at the 29 installations were at concentrations in excess of 6.1 ppb, and 5% were at concentrations in excess of 19 ppb. When the analysis focused only on those groundwater samples with reported detections of 1,4-dioxane, more than 66% of samples were at concentrations in excess of 6.1 ppb; 50% were at concentrations of 12 ppb or more; 25% were at concentrations in excess of 48 ppb; and 10% were at concentrations exceeding 450 ppb.. The installations and the range of reported detections are provided in Table 9.[110]

Table 9. ERPIMS Analysis of Air Force 1,4-Dioxane Sampling Data

Installation	Media	# of Wells Sampled	# of Sampling Events	Range of 1,4-Dioxane Concentrations (ppb)	Comment
Air Force Plant 6, GA	GW	29	185	1.8 - 1700	Majority of samples obtained prior to 2001
Air Force Plant 44, AZ	GW	60	320	1.1 – 650	
Air Force Plant 85, OH	GW	8	10	101 – 421	
Air Force Plant PJKS, CO	GW	4	4	< 1 – 130	130 ppb value believed to be an outlier; other samples less than 1.3 ppb
Altus AFB, OK	GW	58	69	13 – 390,000	
McChord AFB, WA	GW	1	1	8000	Question accuracy of single sample taken in 1990
Travis AFB, CA	GW	7	14	< 1 - 269	
Vandenberg AFB, CA	GW	15	63	< 1 - 3820	

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[110] Occurrence of 1,4-Dioxane in Groundwater and Soil Air Force Wide, ERPIMS Data Summary, P. Hunter, P.G., Air Force Center for Engineering and the Environment, October 23, 2006 and January 4, 2007.

A similar analysis was applied to 1,4-dioxane in soil samples, which were compared against the EPA Region 9 residential PRG value of 44,000 µg/kg. According to the ERPIMS database, 1,4-dioxane was sampled for in soil at 12 Air Force installations. Of the 12 that sampled, three reported 1,4-dioxane detections: Air Force Plant 85, Altus AFB, and Vandenberg AFB. The analysis indicated at least 50% of all soil samples collected at these installations (whether the samples reported detects or non-detects) were at concentrations of 400 µg/kg or more, and 10% were at concentrations of 750 µg/kg. When the analysis focused only on those samples reporting detects 50% of samples were at concentrations of 3,700 µg/kg or more, while 10% were at concentrations of 7,700 µg/kg or more. While above non-detect, the concentrations fall well below EPA Region 9's residential soil PRG value.

ERPIMS 1,1,1-TCA Analysis

A similar analysis of ERPIMS 1,1,1-TCA data was conducted to determine if a correlation exists between 1,1,1-TCA contamination and known 1,4-dioxane contamination. Approximately 70% of the 160 installations in ERPIMS reported having detected 1,1,1-TCA in groundwater samples. By using the 200 ppb drinking water standard for 1,1,1-TCA as a point of departure, AFCEE determined that approximately 0.5% of all groundwater samples (both detections and non-detect) in the database contained TCA at concentrations greater than 200 ppb.

When the analysis was narrowed to consider only those samples reported as detects for 1,1,1-TCA, approximately 10% were at concentrations in excess of 200 ppb. ERPIMS data indicates at least 30 installations that did not report sampling for or detecting 1,4-dioxane reported 90th percentile groundwater 1,1,1-TCA concentrations that are higher than the 1,1,1-TCA concentrations reported by the eight Air Force installations that have actually reported 1,4-dioxane detections. This suggests that if the 30 installations specifically sampled for 1,4-dioxane there would be an increased likelihood of detecting the chemical.

Is There Meaning in the Data?

Because 1,4-dioxane is an analyte that has not historically been sampled for by Air Force installations, insufficient data exists to be able to draw definitive conclusions about the potential extent of its occurrence as a groundwater or soil contaminant at Air Force installations. However, based upon the review and analysis of available AFRIMS and ERPIMS data, some general observations can be made.

The AFCEE review of ERPIMS data indicates that not all installations that reported 1,4-dioxane detections also reported 1,1,1-TCA detections, and that not all installations that reported 1,1,1-TCA at elevated levels sampled for 1,4-dioxane. If used as a representative benchmark across all Air Force installations, the ERPIMS database indicates it is possible that up to 36 of the 131 Air Force installations which have not yet sampled for 1,4-dioxane could be expected to have groundwater contamination at or above EPA Region 9's PRG of 6.1 ppb. From the perspective of soil contamination, given 1,4-dioxane's solubility and sorption characteristics, it is quite possible that detectable levels of 1,4-dioxane in soil are also indicative of some degree of detection in groundwater.

A Possible Approach for Using 1,1,1-TCA Data to Screen for 1,4-Dioxane

While the presence of 1,1,1-TCA as correlated to the potential occurrence of 1,4-dioxane in groundwater is also not a link that has yet been rigorously evaluated, historic production information strongly suggests a positive association exists between 1,4-dioxane and 1,1,1-TCA. In the absence of a robust 1,4-dioxane sampling database, Air Force RPMs may be able to leverage available 1,1,1-TCA data collected during previous site investigations as a tool to screen out areas that are presumed to be less likely to have detections of 1,4-dioxane at or above commonly cited levels of regulatory concern. Such an approach could assist Air Force personnel in focusing their efforts on areas where there is expected to be a greater likelihood of detecting 1,4-dioxane at higher concentrations, and maximize the effective use of limited resources.

Assuming such a link does exists a potential 1,1,1-TCA "level of concern" for groundwater can be estimated to quickly screen candidate sites for the possible presence of 1,4-dioxane. A key assumption in estimating such a level is that 1,4-dioxane was initially present in its 1,1,1-TCA host solvent at a concentration of 3.5%, the approximate mid-point of the 2-5% concentration range often cited in available literature. Under such an assumption, available environmental data indicating the presence of 1,1,1-TCA in groundwater at a concentration of 150 ppb could be viewed as suggesting that an associated 1,4-dioxane concentration of approximately 5.25 ppb may exist in the groundwater, a number that is higher than EPA' Health Advisory level and California's Drinking Water Advisory Level of 3 ppb, but falls just below EPA Region 9's PRG value of 6.1 ppb.

Using a similar approach to soil, 1,1,1-TCA concentrations of 1257 ppm would result in expected 1,4-dioxane soil concentrations of 44 ppm, EPA Region 9's PRG value for residential use. It may be prudent, however, to evaluate for the potential occurrence of 1,4-dioxane in instances where 1,1,1-TCA is detected in soil at significantly lower concentrations. Due to 1,4-dioxane's solubility, mobility, and soil sorption properties, it is likely that 1,4-dioxane originally present in the 1,1,1-TCA detected at the site has already infiltrated the soil and migrated into underlying groundwater.

Summary and Conclusions

The chemical 1,4-dioxane has emerged as a potential contaminant of concern for the Air Force and the other military services. Improved analytical detection capabilities that allow for its detection at low ppb levels in water and soil, and the on-going re-evaluation of its human health and environmental risks by the EPA have resulted in increased interest in the chemical by federal and state regulators. While formal water quality standards and clean up levels have not yet been promulgated at the federal level, at least 18 states and the EPA have established various regulatory guidelines, action levels, and remediation targets that generally fall in the low ppb levels; one state, Colorado, has formally established water quality standards for 1,4-dioxane.

Once released into the environment, the highly soluble 1,4-dioxane does not readily sorb to soil and other organic material, will persist in the environment, will migrate to a great extent, and will quickly move ahead of the leading edge of the associated 1,1,1-TCA plume or its 1,1-DCE breakdown product. Conventional *ex situ* pump-and-treat systems such as air stripping and the use of granular activated carbon that are routinely used to remediate chlorinated solvents and VOCs have proven to be generally ineffective at removing 1,4-dioxane from contaminated water supplies to levels below 10 ppb, and may result in the re-injection of the chemical into groundwater. Advanced oxidation processes are effective at treating 1,4-dioxane but have high capital and O&M costs, can mobilize other unwanted contaminants, and may not remove co-contaminants. Bioremediation, phytodegradation, and monitored natural attenuation processes show promise but are still being investigated as potential remedies, and may require the presence of metabolites such as THF to function properly.

Because 1,4-dioxane was used in the past in large quantities as a stabilizing agent to prevent the degradation of 1,1,1-TCA, the greatest likelihood of detecting it in the environment is associated with the legacy use and disposal of 1,1,1-TCA from solvent cleaning and degreasing operations. Air Force electronics cleaning, precision cleaning, and metal cleaning processes and activities used 1,1,1-TCA as a solvent in significant quantities until the early 1990s, with TRI data for 1994, the year of its production phase-out, indicating 1,1,1-TCA was the Air Force's third most widely used industrial chemical.

Available Air Force environmental sampling data indicate that although few installations have sampled for 1,4-dioxane, many have data for 1,1,1-TCA. Not all installations that reported 1,4-dioxane detections also reported 1,1,1-TCA detections, and not all installations that reported elevated levels of 1,1,1-TCA have sampled for 1,4-dioxane. If available environmental data for 1,4-dioxane and 1,1,1-TCA accurately reflects Air Force-wide conditions, it is possible that other Air Force installations which have not yet sampled for 1,4-dioxane could be expected to have groundwater contamination at or above the EPA Region 9 PRG value of 6.1 ppb.

At this point, only two installations, Air Force Plant 44 and the former McClellan AFB, have been asked to actively address 1,4-dioxane contamination by state regulators. This can reasonably be expected to change after EPA completes its re-assessment of the potential risks associated with exposure to 1,4-dioxane. Upon completion of the revised risk assessment, Air Force RPMs and risk assessors should expect to be asked to sample for 1,4-dioxane more frequently in the future, to define the nature of its risk to human health and the environment, and as appropriate, to evaluate and implement remedial actions to manage any associated risks. If asked by regulators to sample and assess for its presence, RPMs should coordinate a response through their MAJCOMs, and consider consulting the AFCEE REOs to obtain greater insight on state-specific issues that may exist.

Air Force installations and contractor-operated facilities where 1,1,1-TCA is known to have been used in large quantities over many years, and where solvent releases are known to have occurred from spills, leaks, and waste disposal activities, are expected to have an elevated risk of contamination of groundwater and soil by 1,4-dioxane and can be used as surrogate to assist RPMs in defining possible areas of concern and efficiently responding to potential requests to sample.

When assessing for the presence of 1,4-dioxane in environmental samples, seek out laboratories with GC/MS analytical capabilities, and consider the use of analytical procedures for VOCs such as EPA Method 8670. RPMs should verify the laboratory's ability to reliably perform the analysis and ensure it has a QA/QC system that complies with the latest approved versions of the AFCEE Quality Assurance Project Plan and the DoD Quality Systems Manual for Environmental Laboratories. If sampling and analysis indicates the presence of 1,4-dioxane at or near levels of regulatory concern, pending completion of EPA's 1,4-dioxane risk assessment document and the formal establishment of regulatory standards by federal or state officials, RPM should follow the tiered hierarchy specified in OSWER Directive 9285.7-53 when selecting a risk factor.

Because 1,4-dioxane is still a minor constituent of some items procured for use by DoD and the Services, and it has made the DoD MERIT chemical watch list, Service acquisition and material management practices should be conducted in a manner that acknowledges the potential for 1,4-dioxane releases from current materials use.

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