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From: Commander, Naval Facilities Engineering Command

Subj: 1, 4 DIOXANE GUIDANCE/FREQUENTLY ASKED QUESTIONS

Ref: (a) Department of Defense Manual (DODM), 4715.20. Defense Environmental Restoration Program (DERP) Management, March 2012

Encl: (1) 1, 4 Dioxane Guidance/Frequently Asked Questions, August 2018

1. In accordance with reference (a), guidance and procedures for addressing 1,4 Dioxane under the Environmental Restoration, Navy (ER,N) Program and Navy Base Realignment and Closure (BRAC) Program are provided in enclosure (1). As many Navy installations have been receiving requests to evaluate 1, 4 Dioxane at cleanup sites, this 1,4 Dioxane Frequently Asked Questions (FAQ) Guidance assists with identifying issues and promoting a consistent approach for dealing with this contaminant at Navy Environmental Restoration (ER) sites.

2. The main objective of the 1, 4 Dioxane FAQ Guidance is to assist Remedial Project Managers (RPMs) with programmatic and technical issues related to 1, 4 Dioxane at Naval ER sites. These issues include: investigation, sampling and risk assessment methodology, along with regulatory requirements and remedy considerations.

3. The Headquarters point of contact is Ms. Kim P. Brown, who can be reached at kim.brown@navy.mil or (202) 685-0096. Technical questions can also be directed to Mr. Tim Reisch at timothy.reisch@navy.mil or (757) 322-4130 and Ms. Jennifer Corack at jennifer.corack@navy.mil or (757) 322-4335.

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1,4-DIOXANE
GUIDANCE/FREQUENTLY ASKED QUESTIONS

Objective/Purpose

The main objective of this document is to assist Naval Facilities Engineering Command (NAVFAC) Remedial Project Managers (RPMs) with programmatic and technical issues related to 1,4-dioxane at Department of the Navy (DON) Environmental Restoration (ER) sites. These issues include: investigation, sampling, regulatory standards, risk assessment, and remedy considerations. Frequently asked questions are presented to give general guidance. However, the NAVFAC RPM should discuss site-specific conditions with their respective Facilities Engineering Command (FEC) ER Manager to determine the appropriate response.

Applicability

The guidance and procedures in this document apply to actions taken under the Defense Environmental Response Program (DERP) and funded from the Environmental Restoration, Navy (ER,N) and Base Realignment and Closure (BRAC) accounts.

Organization of this Document

The remainder of this document answers the following frequently asked questions (FAQs).

FAQ – General/Definitions

G1. What is 1,4-dioxane and how was it used?
G2. How does this contaminant behave in the environment?
G3. Why is 1,4-dioxane now being considered and sampled at DERP sites?

FAQ - Investigation

INV1. Should we sample for 1,4-dioxane even if the regulators are not asking to include it as a contaminant of potential concern?
INV2. Where within a groundwater plume do we expect to see 1,4-dioxane?
INV3. What should be done if 1,1,1-TCA or daughter products are detected, but 1,4-dioxane was never analyzed?
INV4. Is 1,4-dioxane usually associated with trichloroethylene (TCE)?

FAQ - Sampling

S1. If we think that 1,4-dioxane may be present, what media should be tested?
S2. Are there special sampling techniques?
S3. What analytical method should be used for 1,4-dioxane?

FAQ – Regulatory Standards

RS1. Are there Federal standards for 1,4-dioxane?
RS2. Are there state-specific groundwater criteria for 1,4-dioxane?

FAQ – Risk Assessment

RA1. What human health toxicity values exist for 1,4-dioxane?
RA2. What ecological toxicity reference values exist for 1,4-dioxane?

FAQ – Remedy Considerations

RE1. What types of remedial options should be considered in addressing 1,4-dioxane?
RE2. Are the cleanup options for 1,4-dioxane the same as those needed to address 1,1,1-TCA and/or 1,1-DCE?

FAQ – General/Definitions

G1. What is 1,4-dioxane and how was it used?

1,4-Dioxane is a listed hazardous substance as indicated in 40 CFR 302.4. It is a synthetic industrial chemical and a stable, clear liquid at ambient temperatures and dissolves almost completely in water. 1,4-Dioxane has been primarily used as a stabilizer in chlorinated solvents, most notably 1,1,1-trichloroethane (1,1,1-TCA). The stabilizer scavenges hydrochloric acid produced by the hydrolysis of solvents and oils and prevents degradation of the solvent. 1,4-Dioxane has been added to many grades of 1,1,1-TCA at 2 to 3 percent by volume, and in some instances, up to 8 percent (Mohr, 2001). 1,4-Dioxane is also used as a solvent for chemical processing and can be formed as a byproduct in the manufacture of adhesives, cleaning and detergent preparations, cosmetics, deodorant fumigants, emulsions and polishing compositions, varnishes, and waxes. It has been used as a laboratory reagent and is found in plastic, rubber, insecticides, and herbicides (ATSDR, 2012).

G2. How does this contaminant behave in the environment?

1,4-Dioxane can be released into the air, water, and soil at places where it is produced or used as a solvent stabilizer. If released to the air, 1,4-dioxane would be present as a vapor. 1,4-Dioxane is completely miscible in water and does not bioaccumulate in the food chain (Mohr, 2001). Its low log K_{ow} (-0.27) indicates high mobility in soils (EPA, CLU-IN). However, at some soil release sites, such as disposal pits, residuals of this chemical have been found concentrated within silts and clays in the unsaturated zone as opposed to any surrounding sands, and should be considered for conceptual site model (CSM) development (Mohr et al., 2010). 1,4-Dioxane has a low Henry's Law Constant (4.88×10^{-6}) and is unlikely to form a vapor plume in the vadose zone above a dissolved phase plume, which means soil gas measurement techniques will not be useful for tracking it (EPA, CLU-IN).

1,4-Dioxane is more soluble in water than volatile organic chemicals and it can disperse further in groundwater. Due to its properties, 1,4-dioxane maintains an aqueous state without forming a non-aqueous phase. In groundwater, 1,4-dioxane can sometimes form the leading edge of a contaminant plume traveling faster, farther, and wider via groundwater flow than chlorinated volatile organic compounds such as 1,1,1-TCA, 1,1-dichloroethene (1,1-DCE), 1,1-dichloroethane (1,1-DCA), and vinyl chloride (ATSDR, 2012).

G3. Why is 1,4-dioxane being considered a potential contaminant and analyzed for at DERP sites?

Although 1,4-dioxane is a listed hazardous substance, historically, it was not common knowledge that 1,4-dioxane was added as a stabilizer to certain solvents. This, combined

with increased understanding of potential health effects from exposure, have heightened awareness about the possible presence of 1,4-dioxane at sites with solvent releases.

FAQ - Investigation

INV1. Should we sample for 1,4-dioxane even if the regulators are not asking to include it as a chemical of potential concern?

Yes, if the CSM suggests the potential for 1,4-dioxane to have been released by DON to the environment, then ER,N or BRAC funds can be used to investigate, and if necessary, perform restoration of impacted media. Before sampling for 1,4-dioxane, the CSM should support the potential presence of 1,4-dioxane, which may be suggested if groundwater and/or surface water contains the chlorinated solvents 1,1,1-TCA, 1,1-DCE or 1,1-DCA. In addition, the CSM should have adequate groundwater data (direction, flow rate, etc.) to direct a sampling effort. RPMs are encouraged to contact NAVFAC technical support for more guidance.

INV2. Where within a groundwater plume do we expect to see 1,4-dioxane?

1,4-Dioxane can sometimes migrate farther in groundwater, ahead of solvents such as 1,1,1-TCA or its breakdown products (e.g., 1,1-DCE and 1,1-DCA). Therefore, it may be co-located with a chlorinated solvent plume but can also be found at the leading edge of a chlorinated solvent plume.

Since 1,4-dioxane is miscible and does not form a dense non-aqueous phase, it does not "stratify" as chlorinated solvents do (i.e., higher concentrations are not found toward the bottom of an aquifer).

INV3. What should be done if 1,1,1-TCA or daughter products are detected, but 1,4-dioxane was never analyzed?

Since 1,4-dioxane was included as a stabilizer for 1,1,1-TCA, it should be analyzed for if 1,1,1-TCA or its daughter products are detected.

INV4. Is 1,4-dioxane associated with trichloroethylene (TCE)?

This answer is still being actively researched by numerous entities. It is unlikely that a definitive answer will be available in the short-term. The only way to be certain is to analyze for 1,4-dioxane. The data can then be used to update the conceptual site model and help inform site management decisions. Teams will have to make a risk management decision that balances the site CSM with other important project-specific factors such as budget, etc.

FAQ - Sampling

S1. If we think that 1,4-dioxane may have been released to the environment by DON, what media should be tested?

Typically sampling for 1,4-dioxane will be limited to groundwater. Given 1,4-dioxane's physical and chemical properties (e.g., low estimated organic carbon partition coefficient, low Henry's Law Constant) it readily desorbs to groundwater and, therefore, is not often found in soil. However, depending on the CSM (e.g., recent release, moist soil layers, fine grained material), it may be appropriate to sample soil for 1,4-dioxane.

S2. Are there special sampling techniques?

Since 1,4-dioxane has been found in many detergents, projects should ensure quality control measures (e.g., equipment blanks) are in place to verify the cleanliness of the sampling equipment.

There are many sampling methodologies available, depending on the media and required detection limits (EPA, 2017); refer to the EPA website which lists the approved standard methods by media and associated detection limits: https://clu-in.org/contaminantfocus/default.focus/sec/1,4-Dioxane/cat/Detection_and_Site_Characterization/.

S3. What analytical method should be used for 1,4-dioxane?

There are many analytical methodologies available, however, the media and the limit of quantitation (LOQ) needed must be considered in order to select the most appropriate method for the project.

Two EPA methods, SW-846 Methods 8270 and 8260, are commonly used, with modifications (e.g., isotope dilution, selective ion monitoring [SIM], large volume injection), to detect 1,4-dioxane in media other than drinking water. It is important to verify if the laboratory's LOQs are capable of achieving all of the State advisory/guidance levels listed in Table 1. Due to the significant bias that can result from the sample preparation procedures associated with SW-846 Method 8270, it is currently recommended that SW-846 Methods 8260 be utilized for all media other than drinking water.

If a 1,4-dioxane plume impacts drinking water and the drinking water should be sampled, it should be prepared and analyzed using EPA Method 522. This method was developed specifically for the analysis of 1,4-dioxane in drinking water and is capable of achieving a LOQ well below the current health advisory level. EPA Method 522 is not equipped to eliminate interferences common to ground water, surface water, and soil samples, and

does not include soil sample preparation processes. Therefore, it cannot be used for these media.

FAQ – Regulatory Standards

RS1. Are there Federal standards for 1,4-dioxane?

There are currently no federal drinking water standards (i.e., Maximum Contaminant Levels [MCLs]) for 1,4-dioxane in drinking water.

EPA has established non-regulatory health advisory levels for 1,4-dioxane in drinking water. Health advisories are informal technical guidance for unregulated contaminants. The lifetime health advisory, which is based on noncarcinogenic effects, is 200 micrograms per liter (µg/L). The health advisory based on an excess cancer risk of 1 in 10,000 is 35 µg/L.

RS2. Are there state-specific groundwater criteria for 1,4-dioxane?

Several states have developed standards and guidance for either drinking water or groundwater. See Table 1 below.

Table 1. State Standards and Guidelines for 1,4-Dioxane in Water[1]

State	Type of Guidance (Regulatory Citation)	Matrix	Concentration (µg/L)
AK	Pollution Control Regulations (18 AAC 75, NOV 2017)	Groundwater	4.6
CA	Notification Level (not promulgated, JUL 2018)	Drinking Water	1
CO	Groundwater Quality Standard (5 CCR 1002-41, DEC 2016)	Groundwater	0.35
CT	Action Level (not promulgated, FEB 2013)	Drinking Water	3
DE	Uniform Risk-Based Remediation Standard (not promulgated, DEC 1999)	Ground Water	6.0
FL	Health Advisory Level (not promulgated, AUG 2016)	Drinking Water	0.35
HI	Environmental Action Level (not promulgated, NOV 2016)	Groundwater	0.67
IN	Screening Level (not promulgated, MAR 2016)	Groundwater	4.6
MA	Drinking Water Guidelines (310 CMR 22.00, Spring 2017)	Drinking water	0.3
ME	Maximum Exposure Guidelines (not promulgated, DEC 2016)	Drinking Water	4
MI	Residential Drinking Water Criteria (R.299.44, DEC 2013)	Drinking Water	7.2
NH	Ambient Groundwater Quality Standard (AGQS) (PART Env-Or 603, OCT 2011)	Groundwater	3
NJ	Interim specific groundwater quality criterion (N.J.A.C. 7:9C-1.9(c), JAN 2018)	Groundwater	0.4
NY	Maximum Contaminant Level (10 NYCRR 5-6.10, JAN 2018)	Public Water Supply	50
NC	Groundwater Quality Standard (15A NCAC 02L .0202, APR 2013)	Groundwater	3
TX	Protective Concentration Levels (PCLs) (not promulgated, MAR 2017)	Groundwater	9.1
VT	Health Advisory (not promulgated, JAN 2018)	Drinking Water	0.3
WA	Groundwater Quality Criteria (WAC 173-200-040, 2003)	Groundwater	7.0
WI	Enforcement Standard (NR 140, MAY 2017)	Groundwater	3

[1]RPMs should consult with Navy legal counsel to determine if state levels are considered current applicable or relevant and appropriate requirements (ARARs). RPMs need to verify if the values above are current.

FAQ – Risk Assessment

RA1. What human health toxicity values exist for 1,4-dioxane?

The EPA Integrated Risk Information System (IRIS) database includes toxicity values to evaluate both carcinogenic and noncarcinogenic health effects. The toxicity levels can be used to derive screening values, as listed in EPA Regional Screening Level (RSL) tables. The specific values are not provided here as the tables are updated frequently; therefore, it is best to check the most recent version. The EPA RSLs are available online at: http://www.epa.gov/region09/superfund/prg/.

RA2. What ecological toxicity reference values exist for 1,4-dioxane?

Currently, the available information on ecotoxicity is limited to acute effect levels which are not typically evaluated as part of a CERCLA ecological risk assessment. RPMs are encouraged to check with NAVFAC technical support regarding any updated or new levels that should be considered.

FAQ – Remedy Considerations

RE1. What types of remedial options should be considered in addressing 1,4-dioxane?

Due to its physical properties (e.g., high solubility), 1,4-dioxane is difficult to separate from water. Therefore, it does not respond to air stripping or granular activated carbon adsorption. Several options are summarized in the EPA fact sheet (EPA, 2017). Researchers are developing new treatment technologies for 1,4-dioxane, but advanced oxidation processes involving hydrogen peroxide and ultraviolet light or ozone have been applied successfully by groundwater extraction and treatment systems.

Researchers are investigating additional options such as:

- phytoremediation (via phytovolatization),
- in-situ chemical oxidation (ISCO) using sodium persulfate under alkaline and high heat conditions, or with iron-activated hydrogen peroxide, and
- bioremediation, particularly aerobic metabolic and aerobic cometabolic, and
- monitored natural attenuation (MNA)

RE2. Are the cleanup options for 1,4-dioxane the same as those needed to address 1,1,1-TCA and/or 1,1-DCE?

No, not all technologies (e.g., air stripping and granular activated carbon adsorption) that can remediate chlorinated VOCs (1,1,1-TCA, 1,1-DCE) are effective for treating 1,4-dioxane. However, technologies that target 1,4-dioxane, such as advanced oxidation, can

be effective at treating chlorinated VOCs such as 1,1,1-TCA and 1,1-DCE. EPA considers groundwater extraction and treatment as a remediation option, which can also be used to address 1,1,1-TCA or 1,1-DCE (EPA, 2017). Oxidation processes involving hydrogen peroxide with ultraviolet (UV) light or ozone can be added to existing groundwater extraction and treatment systems to target 1,4-dioxane. However, Navy optimization policy (NAVFAC, 2012) stresses to consider other remedial options besides installing new groundwater extraction and treatment systems. If there are no other feasible options, then written justification needs to be provided to NAVFAC Headquarters.

References

Agency for Toxic Substances and Disease Registry (ATSDR), 2012. Toxicological profile for 1,4-dioxane. April.

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Mahendra, S., and Alvarez-Cohen, L., 2006. Kinetics of 1,4-dioxane biodegradation by monooxygenase-expressing bacteria. Environ. Sci. Technol. 40, 5435–5442.

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Mohr T, Stickney J, and Diguiseppi, B. 2010. Environmental investigation and remediation: 1,4-dioxane and other solvent stabilizers. CRC Press, Boca Raton, FL.

Naval Facilities Engineering Command (NAVFAC), 2012. Policy for Optimizing Remedial and Removal Actions at all Department of Navy (DON) Environmental Restoration Program Sites. April.

United States Environmental Protection Agency (EPA), 2008. Contaminant Candidate List 3. February. www.epa.gov/safewater/ccl/ccl3.html

EPA, 2017. Technical Fact Sheet-1,4-Dioxane. November. http://www2.epa.gov/fedfac/technical-fact-sheet-14-dioxane

EPA Contaminated Site Cleanup Information (CLU-IN), 1,4-Dioxane website http://clu-in.org/contaminantfocus/default.focus/sec/1,4-Dioxane/cat/Overview/

EPA Drinking Water Treatability Database website http://iaspub.epa.gov/tdb/pages/contaminant/contaminantOverview.do?contaminantId=10860