

August 4, 2008

Dr. Resha M. Putzrath, DABT
Designated Federal Officer, Science Advisory Board (MC- 1400F)
U.S. Environmental Protection Agency Headquarter, Ariel Rios Building
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460

Subject: Information Supporting Inclusion of 1,4-dioxane in CCL3

Dear Dr. Putzrath and the SAB Drinking Water Committee:

I am writing to provide context, background, and data in support of including 1,4-dioxane on the Contaminant Candidate 3 List. My testimony stems from five years of reviewing existing literature and data on the occurrence and origin of 1,4-dioxane in drinking water, as well as its fate and transport characteristics, laboratory analysis, toxicology and risk characterization, and treatability. I am compiling my research into a reference volume for publication by the Taylor & Francis Group in 2009. I am testifying as an individual; my verbal testimony will be a brief summary of the information provided below.

1,4-Dioxane is an under-examined and largely overlooked contaminant that should be included on CCL3 because it is likely to be much more prevalent than is now realized owing to its widespread industrial use. Because 1,4-dioxane requires analysis by specialized laboratory method enhancements not usually employed in the course of routine drinking water analysis, most water utilities do not currently test for 1,4-dioxane. Where water utilities have tested for 1,4-dioxane because of its discovery at solvent release sites near water supply wells, 1,4-dioxane has often been detected. Water utility operators have been surprised to discover that they have been serving drinking water with 1,4-dioxane concentrations considerably higher than state and federal drinking water advisory standards, which range from 3 to 85 ppb. Several utilities are finding persistent occurrence of low concentrations of 1,4-dioxane and report this to their customers in their Consumer Confidence Reports (CCRs). Table 1 lists some examples of 1,4-dioxane occurrence in drinking water sources.

Table 1 presents known detections of 1,4-dioxane in drinking water; however, it is by no means inclusive of all detections. A highly correlated association with methyl chloroform occurrence was shown in a survey of 1,4-dioxane detections in drinking water sources in Japan (Abe, 1999). A survey of analytical results in the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program, including more than 5,000 wells between 1985 and 2002, indicated a 7% frequency of detection for methyl chloroform (Moran et al, 2007). While broad generalizations must be tested at the scale of drinking water source contamination, the findings of Abe and Moran taken together suggest a strong likelihood that there are many more drinking water sources impacted by 1,4-dioxane that have not yet been discovered because 1,4-dioxane is not commonly included in drinking water analyses. Where production wells have a history of detections of methyl chloroform and its breakdown products, 1,1-dichloroethylene and 1,2-dichloroethane, screening level testing for 1,4-dioxane is advisable.

The main source of 1,4-dioxane in water supply wells is groundwater contamination from industrial vapor degreasing operations that used methyl chloroform (1,1,1-trichloroethane).¹ 1,4-dioxane was an additive used to stabilize methyl chloroform against reaction with aluminum in manufactured products subjected to vapor degreasing. 1,4-dioxane was added to methyl chloroform beginning in the mid-1960s through the early 1990s. Methyl chloroform was the most widely used chlorinated solvent in the 1970s and 1980s. For example in 1985, about 750 million pounds of methyl chloroform were employed in industry; in the same year, 90% of all 1,4-dioxane produced in the U.S. was employed to stabilize methyl chloroform. While 1,4-dioxane was added to methyl chloroform in relatively small amounts, generally 2 to 3 percent by volume, it became concentrated in vapor degreasing operations due to boiling point differences, so that its final concentration in the solvent wastes that were often released to soil and groundwater ranged from 10 to 25% by volume. 1,4-dioxane concentrations at industrial vapor degreasing and solvent recycling facilities have been measured as high as 340,000 ppb.

1,4-Dioxane may also occur as a drinking water contaminant as a by-product from the production of soaps and other products using ethoxylated surfactants, from the production of polyester resins and plastics, and from the production of cellulose acetate membranes such as those used in reverse osmosis and kidney dialysis filters. There are many other smaller sources of 1,4-dioxane; consequently, many landfills report 1,4-dioxane present in leachate and underlying groundwater, and low concentrations of 1,4-dioxane have been found in municipal wastewater influent and in reclaimed wastewater.

1,4-Dioxane is persistent and highly mobile once released to the subsurface because it is completely miscible, strongly resists biodegradation, and has a low propensity for sorption to organic matter and mineral surfaces. Its hydrophilic nature makes it among the fastest migrating subsurface contaminants, and also makes it resistant to conventional methods for both laboratory analysis and drinking water or wastewater treatment. Specialized laboratory methods can now reliably detect 1,4-dioxane at concentrations near or below advisory action levels, using isotope dilution and single ion mode analysis by GC/MS. EPA's National Exposure and Research Laboratory is currently developing Method 522 for analysis of 1,4-dioxane and several other solvent stabilizer compounds. Treatment of 1,4-dioxane is with ultraviolet light or advanced oxidation, both of which are prohibitively expensive for most drinking water utilities. Conventional treatment technologies employed to remove volatile chlorinated solvents, e.g. air stripping and granular activated carbon, are ineffective at removing 1,4-dioxane. Consequently, drinking water wells and remediation systems designed to remove contamination by chlorinated solvents do not significantly remove 1,4-dioxane, and it ends up in drinking water. In Bally, Pennsylvania, the town's only well was equipped with a treatment train for removal of chlorinated solvents and returned to service following discovery of solvent contamination. Several years later, EPA and Pennsylvania DEP staff learned that 1,4-dioxane may be present and detected it at up to 77 ppb, more than 10 times the US EPA Region 3 Risk Based Concentration for 1,4-dioxane in drinking water (6.1 ppb).

1,4-Dioxane is currently categorized in IRIS as a probable human carcinogen (Class IIB), and several states have adopted advisory guidance levels. Colorado adopted an MCL for 1,4-dioxane at 6.1 ppb in March 2005, after hearing testimony opposing regulation because of the non-linear dose-response seen in toxicological assays of 1,4-dioxane. California has a Notification Level of 3 ppb, while Michigan's action level is 85 ppb. Michigan sought to set an MCL at 35 ppb but declined to do so following testimony from water utilities and industry advocating more aggressive regulation and no regulation, respectively. The carcinogenicity and toxicity of 1,4-dioxane remain somewhat uncertain, with physiologically-based pharmacokinetic model studies suggesting that concentration range seen in the drinking water detections listed in Table 1 may be too low to produce toxic effects, and Colorado

¹ Details and citations for unattributed statements in this letter can be found in the 2001 White Paper I prepared on solvent stabilizers http://www.valleywater.org/Water/Water_Quality/Protecting_your_water/Solvents/PDFs/SolventStabilizers.pdf

adopting an MCL at 6.1 ppb². In 2004, EPA's National Center for Environmental Assessment in the Office of Research and Development began a review of the Integrated Risk Information System (IRIS) health assessment for 1,4-dioxane; the review is slated for completion by February 2009. 1,4-Dioxane is a tumor promoter, but is not considered by itself to be a complete carcinogen (Stickney, et al, 2003). A further area of uncertainty for health risk assessments of 1,4-dioxane in drinking water is the possible synergistic effects of co-contaminants that may act as tumor initiators.

In summary, I recommend that the Science Advisory Board's Drinking Water Committee consider retaining 1,4-dioxane in the final CCL3 list, for the following reasons:

- 1,4-Dioxane is likely to be a real public health concern, considering the examples that have already played out (e.g. Bally, Pennsylvania), and the general lack of testing for its presence in drinking water.
- Billions of pounds of methyl chloroform, the solvent to which 1,4-dioxane was added as a solvent stabilizer, were used throughout USA in the 1970s and 1980s, and a growing number of solvent release sites have discovered high concentrations of 1,4-dioxane in solvent-contaminated groundwater.
- 1,4-Dioxane is hydrophilic and extremely mobile; it is among the fastest moving groundwater contaminants and likely to arrive at public supply wells ahead of solvent contamination.
- Drinking water surveys report a high frequency of methyl chloroform occurrence (7%), to which 1,4-dioxane occurrence is highly correlated.
- In spite of uncertainties in the health effects data for 1,4-dioxane, Colorado has adopted a legal standard, while many states regulate 1,4-dioxane in drinking water and contamination sites with advisory levels used to set cleanup levels. The states address the toxicological uncertainties by applying a conservative approach to setting advisory standards.
- Sensitive and reliable laboratory methods are now commercially available, and US EPA is developing additional methods targeting 1,4-dioxane and other solvent stabilizers

Thank you for considering these comments. If you require any additional supporting documentation, please contact me.

Sincerely,

Original signed by

Thomas K.G. Mohr, P.G., E.G., H.G.
Hydrogeologist

References:

- Abe, A., 1999, "Distribution of 1,4-dioxane in relation to possible sources in the water environment." *The Science of the Total Environment* 227(1999): 41-48.
- Moran, M. J., J. S. Zogorski, et al, 2007, "Chlorinated Solvents in Groundwater of the United States." *Environmental Science and Technology* 41(1):74-81.
- Stickney, J.A., Sager, S.L., et al (2003), An updated evaluation of the carcinogenic potential of 1,4-dioxane. *Regulatory Toxicology and Pharmacology* 38(2003): 183-195.

² The Colorado MCL will be lowered to 3.2 ppb in March 2010 if EPA's IRIS review does not provide compelling reasons to do otherwise.

Table 1: 1,4-dioxane Detections in Drinking Water

Location	Maximum Detected Concentration	Year	Ref
Kitchener, Ontario, Canada	285 ppb in a single well ^a 31 ppb in finished water	2005	1
Nakdong River, South Korea	119 ppb in raw river water 92 ppb in treated river water	2003	2
Tama District, Tokyo, Japan	113 ppb in a well; detected in >70% of 338 wells tested; average in deep wells = 4.5 ppb	2005	3
Kanagawa Prefecture, Japan	95 ppb in a production well ^a	1997	4
Bally, Pennsylvania	24 – 77 ppb in a single well (30 – 50 ppb more frequent range)	2004	5
Ann Arbor, Michigan	3 - 38 ppb in four single family domestic wells; earlier results up to 71 ppb in a single domestic well	2007	6
Banning, California	35 ppb in a single well ^a	2005	7
Durham Meadows, Connecticut	27 ppb in a single well, unfiltered 27 ppb in a GAC-filtered well ^d	2004	8
Santa Monica, California	22 ppb in a single well ^a	2002	9
Spokane, Washington	13.8 ppb in a single well ^c	2006	10
Fountain Valley, California	7.7 ppb	2006	11a
Downey, California	5.6 ppb in a single well; average 4 ppb in 4 wells with detections of 8 total in system ^{a b}	2005	12
Japan: Detected in 39 of 91 raw water samples from drinking water treatment plants; 22 out of 29 groundwater samples contained 1,4-dioxane	5.52 ppb maximum detected in groundwater; average of 22 detections in groundwater was 1.0 ppb	2006	17
Irvine, California	5 ppb ^a	2007	11b
Tucson, Arizona	2.3 ppb	2003	12
Huntington, Suffolk County, New York	2.3 ppb	2007	13
Centerport/Cold Spring Harbor/Halesite, Suffolk County, New York	2.2 ppb	2007	13
City of Commerce, California	2.2 ppb maximum; detections in four wells ^a	2004	14
Ann Arbor, Michigan	2 ppb in a single well ^c	2001	15
Bayport/Bellport/Blue Point/Bohemia/Brookhaven, Suffolk County, New York	1.9 ppb	2007	13
Bell Gardens, California	1.92 ppb in a single well; average 1.7 ppb ^a	2003	21
Huntington/Huntington Bay, Suffolk County, New York	1.5 ppb	2007	13
Kanagawa Prefecture, Japan	0.2 – 1.5 ppb in tap water	1995	17
Kings Park/ Northport/Asharoken/Crab Meadow/Eatons Neck/Fort Salonga, Suffolk County, New York	1.4 ppb	2007	13
Commack/Kings Park/Northport, Suffolk County, New York	1.1 ppb	2007	13
Bellport/Bohemia/Brentwood/Centerreach/Islip/Coram/Deer Park/Farmingville/Hauppage/Islandia, Suffolk County, New York	1.0 ppb	2007	13
City of Clare, Michigan	1.0 ppb	2006	18
Commack/East Commack/Kings Park/ Suffolk County, New York	0.8 ppb	2007	13

Amityville/Babylon/BayShore/Brentwood, Suffolk County, New York	0.7 ppb	2007	13
The Netherlands	0.5 ppb	1999	19
Niigata Prefecture, Japan	0.39 ppb in river water used to supply drinking water	2002	20

Notes:

a) water utilities often manage wells by blending impacted wells with clean water from unimpacted wells, so that tap water in homes remains below regulatory thresholds or advisory action levels, if not laboratory detection levels. **b)** Only 15% of the Bellflower/Norwalk/Park Water Company System water supply comes from groundwater; its main source is imported surface water from the Metropolitan Water District of Southern California. The surface water/groundwater mix for other water systems on this list was not evaluated. **c)** ATSDR conducted a Health Consultation for the maximum 1,4-dioxane occurrence of 13.8 ppb in a well supplying 34 homes near the Colbert Landfill in Spokane, Washington; the review concluded that no apparent public health hazard exists for all routes of exposure to all exposed populations at this concentration. **d)** GAC = Granular Activated Carbon; GAC does not effectively remove 1,4-dioxane at economical rates; **e)** Ann Arbor well was not in service at time of detection; it remains off-line.

References: 1) Regional Municipality of Waterloo, 2005; 2) Park et al, 2005; 3) Suzuki, et al, 2005; 4) Abe, 1999; 5) USEPA, 2004a; 6) MDEQ, 2007; 7) City of Banning, 2005; 8) USEPA, 2004b; 9) City of Santa Monica, 2002; 10) WSDOH, 2006; 11a) City of Fountain Valley, 2006; 11b) IRWD, 2007; 12) CWSC, 2004; 13) Tucson Water, 2003; 14) SCWA, 2007; 15) City of Ann Arbor, 2001; 16) SCWC, 2004; 17) Abe, 1997; 18) City of Clare, 2007; 18) Simazaki, et al, 2006; 19) VROM, 1999; 20) Kawata et al, 2003; 21) Bellflower/Norwalk/Park Water Company, 2005. Complete citations furnished upon request.