

Contaminant Update and Book Review: Environmental Investigation and Remediation: 1,4-Dioxane and Other Solvent Stabilizers

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For those working with chlorinated solvents, there has been continued interest in the solvent stabilizer, 1,4-dioxane. The story of the sleuthing required to evaluate this seemingly ubiquitous chemical is worthy of a book, and in fact this article includes a review of Tom Mohr's 2010 book published by CRC as well as an update on the latest information on 1,4-dioxane.

First, some information about 1,4-dioxane. The compound is a solvent stabilizer frequently found at chlorinated solvent sites where methyl chloroform (1,1,1-trichloroethane) was used for degreasing and cleaning. Although 1,4-dioxane has been a constituent of methyl chloroform wastes for decades, recent improvements to analytical methods allowed its detection in the parts per billion range beginning in 1997. The properties that made 1,4-dioxane difficult to chemically analyze in the past also make it difficult to remediate. For example, 1,4-dioxane is fully miscible in water which makes containment difficult, or at least expensive. Successful remedial technologies must take into account the challenging chemical and physical properties unique to 1,4-dioxane and other solvent stabilizers. 1,4-dioxane is among the most mobile organic contaminants in the saturated zone. As a result, it may be found farther downgradient than the leading edge of a chlorinated solvent plume. The combination of a wider spatial occurrence and different approaches for remedial technologies as compared to other potential comingled contaminants make 1,4-dioxane a potentially problematic contaminant, particularly if it is discovered late in the investigation process after remedial design has already been completed. In some cases, discovery of 1,4-dioxane has required expanded monitoring networks, larger capture zones, and the addition of new treatment technologies to the treatment train (US EPA, 2006).

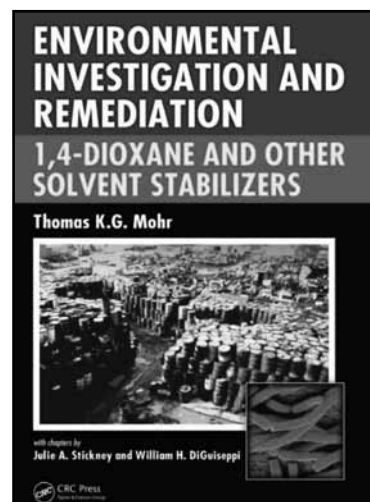
The compound is continuing to make news in 2013. Recent events related to

1,4-dioxane include the January 2013, Proctor & Gamble response to the compound. After getting sued, Proctor and Gamble committed to remove 1,4-dioxane from their laundry detergent line. The book review (described below) covers the history of this issue going back to the 1970s. Also in 2013, the EPA requirement for UCMR3 (unregulated contaminant monitoring requirements) starts. This requirement is related in part, to Mr. Mohr's testimony to the National Research Council's drinking water committee. Now 1,4-dioxane is included in the recommendations, so starting in 2013, more than 30,000 public water systems will have to test for 1,4-dioxane.

An article in the January 23, 2013 issue of an EPA newsletter, *Inside EPA*, notes that the Air Force has decided to do a system wide test for 1,4-dioxane at existing solvent release sites with monitoring wells, using a lower level analytical method. Intrinsic biodegradation of 1,4-dioxane was confirmed at an air force facility near Tucson, Arizona using evidence from baited biotrap and several molecular tools. The study found that the rate of biodegradation of 1,4-dioxane was not high enough to impede the progress of the six-mile long plume.

In November 2010, California lowered the Drinking Water Notification level from 3 to 1 µg/L in response to the US EPA's 2009 toxicity review of 1,4-dioxane. Massachusetts is regulating the solvent stabilizer at 0.5 µg/L. New Hampshire and Massachusetts are now requiring labs to be capable of reporting 1,4-dioxane at 0.20 µg/L by SW846 8270 SIM. State of Washington remediation caseworkers advise they are applying a cleanup level of 0.45 µg/L for 1,4-dioxane at some sites.

The compound is ubiquitous, and until a few years ago, largely overlooked as a groundwater contaminant. Even by the late 1990s, 1,4-dioxane escaped notice by almost all regulators and scientists,



except for Tom Mohr, a regulator and hydrogeologist of the Santa Clara Valley Water District located in the heart of Silicon Valley in San Jose, California. Because the solvent stabilizers as a class of chemicals were largely unanalyzed and therefore unregulated, agreement from the regulatory community in the late 1990s was mixed. Mr. Mohr was credited with being one of the first regulators to evaluate 1,4-dioxane and other solvent stabilizers and to draw attention to the need to understand and regulate these compounds.

The book *Environmental Investigation and Remediation: 1,4-Dioxane and other Solvent Stabilizers* by Thomas K.G. Mohr with chapters by Julie A. Stickney and William H. DiGuseppi is certainly the most authoritative book on 1,4-Dioxane and solvent stabilizers ever written. This well researched compilation contains a good summary of 1,4-dioxane and other stabilizers. The book starts out describing the history of chlorinated solvents and why different solvent applications require different solvent stabilizers. The chemistry, use and occurrence of 1,4-dioxane is profiled in great detail, and the environmental fate and transport of about three dozen confirmed solvent stabilizers is examined with more than two dozen tables and an

extensive review of the literature on biodegradation. Chapters on sampling and laboratory analysis, toxicology, risk assessment and regulation, remediation with numerous case studies, forensic application, and regulatory policy round out this 520 page book. Thomas Mohr, well known for his technical expertise at the Santa Clara Valley Water District in San Jose and leadership with the Groundwater Resources Association of California, was one of the first scientists on the groundwater supply side to investigate this chemical of emerging concern in November 2000.

As chlorinated solvent production and uses increased, metal-induced decomposition was noted in the mid 1930s and stabilizers were needed to neutralize acids, supply an antioxidant, and inhibit chlorinated solvent reactions with metal chloride salts. Alcohols and compounds containing oxygen were used as early solvent stabilizers; the more alcohol or other oxygen compounds present, the more effective the stabilizer. 1,4-Dioxane was patented by Dow Chemical to stabilize methyl chloroform (1,1,1-trichloroethane) in 1957. Mohr explains the importance of examining how the uses of solvents prior to their release imparts a variety of properties affecting solvent fate and transport, a practice he calls "contaminant archeology".

Although 1,4-dioxane was used widely in a variety of different industrial applications, it was largely overlooked by the US EPA, state regulatory agencies and groundwater scientists and engineers. 1,4-Dioxane is still not included in routine regulatory drinking water testing lists today, and consequently, is not routinely analyzed in the laboratory when groundwater samples are analyzed for the presence of chlorinated solvent compounds. A sensitive and reliable laboratory analytical method was not widely available until 1997 when the California Department of Health Services developed a method for low-level detection of the compound using isotope dilution. Even at large US EPA Superfund sites impacted by chlorinated solvents, 1,4-dioxane and other solvent stabilizers are not routinely requested laboratory analytes. A new method for drinking water, EPA Method 522, was published in 2008 for use in the 3rd Unregulated Contaminant Monitoring Requirements which include 1,4-dioxane beginning in 2012.

Once discovered, 1,4-dioxane presents difficult and expensive challenges

to remedial project managers. It is often discovered after regulatory orders have been adopted, yet its presence has on numerous occasions required an expansion of the monitoring network, additional treatment technologies, and review of the health risk assessment. Mohr demonstrates that 1,4-Dioxane can be and has been a "ROD-reopener".

The book explains the ongoing controversy and toxicological uncertainty associated with 1,4-dioxane, which exhibits a non-linear dose-response, but regulatory conventions apply a linear extrapolation to determine drinking water limits. In May 2009, after the manuscript was submitted, US EPA released a draft toxicity review, which suggests a steeper cancer slope factor is appropriate, meaning that if adopted, health risk levels could be lowered. This development and 1,4-dioxane's mobility, persistence and remediation challenges make it worthy of regulatory attention.

The importance of this book is that it highlights one of many emerging and recalcitrant compounds brought to our attention in the past decade. The story of 1,4-dioxane is as good an example as any available, to articulate the scientifically interesting, but logically uncomfortable question of whether there are any more important and widespread industrially used chemicals that are currently being overlooked by regulators or not analyzed because they are not on the list of required analytes. Based on the detailed research documented in this book, the unfortunate but likely answer is yes. The 1,4-dioxane story highlights the need for Federal or state regulatory agencies to put more effort into methodical testing and toxicological evaluation of commonly used industrial chemicals that might find their way into drinking water aquifers or food or drink products. The book is a highly recommended for those working with chlorinated solvent sites.

Given the continued challenges with addressing the impacts to groundwater from 1,4-dioxane, new research is being funded by the Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) for remediation of 1,4-dioxane using bioremediation, in-situ chemical oxidation (ISCO), and enhanced soil vapor extraction and other techniques. The understanding of 1,4-dioxane has grown over the past decade, and many of the main ideas are

included in this important book on this solvent stabilizer.

References

Mohr, T.G., Stickney, J.A., and Diguseppi, W.H., 2010, Environmental Investigation and Remediation: 1,4-Dioxane and Other Solvent Stabilizers, CRC Press; Francis & Taylor Group (ISBN978-1-56670-662-9). *www.The14DioxaneBook.com*.

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