



RISK BULLETIN

Emergent Chemicals in Groundwater: An Ever Constant Changing Landscape

INTRODUCTION

Unregulated and emerging chemical contaminants present numerous technical challenges to environmental and public health professionals.

This fact sheet provides a brief overview of technical issues associated with emergent chemicals, particularly those present in groundwater in California.



Over the past four decades, increasingly sensitive analytical techniques have chronicled the emergence of specific chemicals in actual or potential sources of drinking water.

As the ability to detect these agents has improved, the number of contaminants regulated under various environmental statutes has also increased. This has resulted in increased first and third party liability for property owners completing site characterization and remediation projects, professional liability for consulting firms providing due diligence services, and potential products liability for public water supply utilities.

The term “emergent chemicals” is used by the United States Environmental Protection Agency (USEPA) and other regulatory agencies to identify

a group of chemicals associated with explosives and solvent release sites. Of particular concern to the California Regional Water Quality Control Board (RWQCB) is groundwater contamination at former/active military facilities as well as industrial facilities. In California, “emergent chemicals” include 1,4-Dioxane, N-nitrosodimethylamine (NDMA), Hexavalent Chromium, 1,2,3-Trichloropropane (1,2,3-TCP), Polybrominated diphenyl ether (PBDE), and Perchlorate.

Recent experiences with MTBE and perchlorate have increased awareness of groundwater supply vulnerability. Detections of emergent chemicals have been most frequently linked to former military sites that have impacted numerous drinking water supply wells. This has resulted in the installation of treatment systems or the permanent shutdown of water supply wells.

The presence of emergent chemicals can increase the costs of effective remediation as well as cause reassessment of cleanup remedies. Due to the prevalence of these chemicals in groundwater, the RWQCB has required sampling for these chemicals at active remediation sites that involve pump and treat systems, regardless of whether an identified potential source exists. Sites within the boundaries and the immediate vicinity of National Priority List (i.e., Superfund) and military sites may also be required to sample for these chemicals if a potential source for these chemicals is identified. Emergent chemicals have been detected in groundwater throughout California at locations such as the Burbank Superfund site, San Fernando Valley Superfund site, and San Gabriel Valley Superfund site.

SOURCES OF EMERGENT CHEMICALS

Potential Source Areas Associated with Explosives

- Ordnance detonation/disposal sites;
- Missile/rocket test sites and launch pads;
- Catch basins, waste sumps, clarifiers, and settling ponds;
- Decommissioned missile silos;
- Suspected areas where chemicals and pesticides were stored, used, transferred, processed, incinerated, or disposed;
- Firing and bombing ranges, and
- Mock battle-training locations.

Potential Source Areas Associated with Solvent Release Sites

- Catch basins, waste sumps, clarifiers, and settling ponds;
- Paint maintenance, hobby shops, plating shops, and degreasing activities;
- Weapons maintenance or cleaning areas;
- Known release sites and
- Suspected areas where these chemicals and pesticides were stored, used, transferred, processed, incinerated, or disposed.

EMERGENT CHEMICALS AND HEALTH CONCERNS

1,4-Dioxane – A synthetic industrial chemical that is used as a solvent in products such as paints and lacquers and in processes such as organic chemical manufacturing. It was used in the past primarily with 1,1,1-TCA, as a stabilizer and corrosion inhibitor. It has been found in groundwater throughout California and the United States. Groundwater investigations at solvent release sites have not typically included 1,4-dioxane as a target analyte because it was not detectable at low concentrations in a standard laboratory scan. 1,4-dioxane is classified as a probable carcinogen by the USEPA. Some states now have established enforceable cleanup goals.

Colorado became the first state to establish an enforceable standard for 1,4-dioxane in groundwater at 6.1 ug/l. The cleanup goal will be reduced to 3.2 ug/l by March 2010. For California, the health-based advisory level for 1,4-dioxane in drinking water is 3 ug/l. Currently ex-situ advanced oxidation processes have been the most effective remediation option.

N-nitrosodimethylamine (NDMA) – A semi-volatile organic compound that is highly soluble in water. NDMA has been used in production of liquid rocket fuels, as an additive for lubricants, as a softener for copolymers, and as disinfection by-product of wastewater treatment. NDMA can also be directly discharged by industries from industrial applications such as circuit-board shops, metal fabrication, and rubber manufacturing. NDMA is primarily known as an industrial contaminant commonly found with perchlorate and is a breakdown product from hydrazine, an intermediate in rocket fuel production. NDMA is classified as a probable human carcinogen. The USEPA does not currently regulate NDMA. The California Department of Health Services has set the drinking water action level at 10 ng/l (ppt). There have been cleanup requirements associated with NDMA at various Superfund sites. The Arizona Department of Environmental Quality has started to include NDMA on monitoring lists for NPDES permits. Ultraviolet light and advanced oxidation treatment has been found to be effective in removing NDMA from groundwater (e.g., San Gabriel Valley Superfund site),

Hexavalent Chromium – Chromium is a naturally occurring metallic element that can be found in water and soils. The most common forms of chromium are trivalent (Cr+3) and hexavalent (Cr+6). Trivalent chromium has very low toxicity. Hexavalent chromium is a very soluble, non-reactive compound in groundwater and highly toxic to organisms and plants. The existence of hexavalent chromium in the environment is associated with industrial waste from metal plating

operations, chrome plating, leather tanning, steel making, and dyes and pigments. Hexavalent chromium is a carcinogen. Studies of workers exposed to hexavalent chromium by inhalation have shown an increase in cancers. Current scientific evidence shows it to be more toxic when inhaled than ingested. The USEPA has established a drinking water Maximum Contaminant Level (MCL) of 100 ug/l for total chromium (the aggregate of trivalent and hexavalent). In California, a risk-based drinking water standard has been established for total chromium at 50 ug/l. Effective remediation treatment methods include ion exchange, reverse osmosis, and lime softening.

1,2,3 Trichloropropane (1,2,3-TCP) – This chemical is man-made and has been primarily used as a solvent and extracting agent. In industry, 1,2,3-TCP has been used as a paint and varnish remover, a cleaning and degreasing agent, a maintenance solvent and a chemical intermediate. 1,2,3-TCP is a heavy liquid with a strong acrid odor similar to chloroform. The chemical dissolves quickly in air and can be persistent in groundwater. The chemical is listed as reasonably anticipated to be a human carcinogen by the National Toxicology Program. The California Department of Health Services (CDHS) considers 1,2,3-TCP as “known to cause cancer” and established a 5 ppt notification level. The chemical was not a common analyte prior to 2001 when California listed it as an unregulated chemical requiring monitoring. Since 2001, at least 84 water sources in 16 counties have reported concentrations above the notification level. The highest level detected in groundwater in California was 57 ug/l in 2001 at the Burbank Superfund Site Operable Unit. CDHS will be developing a Public Health Goal action level, which is the first step in developing a drinking water standard. Effective remediation treatment systems include bioremediation, chemical oxidation, and soil vapor extraction.

Polybrominated diphenyl ether (PBDE) – This is in the family of flame-retardant chemicals used in a variety of products such as: computer printers, cell phones, televisions, toasters, microwave ovens, furniture, plastic foam, and carpeting. The chemical may be used in a viscous liquid to powder form. It has been found at nine Superfund sites. There is currently little toxicity data available, but has a high potential for bioaccumulation and is a concern due to its structural similarity to PCBs. In 2003, California passed a state-wide ban on manufacturing and use of flame retardant chemicals commonly known as PBDEs. The ban covered two forms of PBDEs, octa- and penta-. Implementation of the ban was initially set for 2006; however, intense lobbying by the chemical industry pushed it back to year 2008. The chemicals are potent thyroid disruptors and may lead to development of Attention Deficit Hyperactivity Disorder (ADHD). In 2007, the state of Washington became the first government entity in the world to ban the deca- form of PBDE. California is still developing relative exposure levels (RELs) for PBDE. There are currently no Federal or California MCLs for PBDE. Limited information exists on groundwater remediation system efficacy.



Perchlorate - Perchlorate and its salts (e.g., ammonium perchlorate) are used in solid propellant for rockets, missiles, and fireworks. Perchlorate has a number of industrial uses and is used in matches, flares, pyrotechnics, ordnance, explosives, air bag initiators, paints and enamels, leather tanning, engine oil testing, electropolishing and electroplating. Perchlorate contamination has been found in groundwater in over 35 states, most notably in Arizona,

Arkansas, California, Maryland, Massachusetts, Nevada, New York, Texas and Utah. Perchlorate interferes with iodide uptake into the human thyroid gland. The RWQCB has been active in requiring remediation sites in the Los Angeles region to expand chemical analysis to include perchlorate in quarterly or semi-annual groundwater monitoring requirements. Prior to 2007, USEPA had not established a perchlorate MCL and only Massachusetts had established a state MCL (2 ug/l). In August 2006, California DHS established 6 ug/l as a Public Health Goal (PHG) and proposed a state MCL. Consumer notification is required at concentrations greater than 6 ug/l. Once the standard is adopted, drinking water sources exceeding this limit must be eliminated. The most effective treatment technology for perchlorate in groundwater is ion exchange and reverse osmosis.

TESTING REQUIREMENTS

Listed below are the emergent chemicals of concern and the RWQCB's recommendations with respect to acceptable testing procedures for each of the specified emergent chemicals. The table also summarizes the current action levels/MCLs for the respective chemicals.

For active remediation sites where pump and treat systems were operating, RWQCB issued letters to all PRPs requiring them to sample groundwater influent for these chemicals regardless of the site operational history. The RWQCB also issued letters to all Department of Defense (DOD) sites requiring them to develop source reports identifying any potential areas that stored or used emergent chemicals on their base. The source reports require the military bases to sample for emergent chemicals in soils and groundwater. Due to the presence of emergent chemicals in large Superfund sites such as the San Gabriel Valley area, numerous industrial facilities within the boundaries of the groundwater plumes were also required to sample for emergent chemicals. These developments have the potential to result in increased site investigation and remediation expenses, legal defense expenses, and third party claims.

For future property owners planning on redeveloping former industrial sites or military facilities, there is potential pollution liability if the groundwater beneath the site has not been characterized for emergent chemicals. More attention should be focused on historical operations at the

| CHEMICAL | TESTING PROCEDURE | REPORTING LIMIT | ACTION LEVELS |
|---------------------|--------------------|-----------------|---------------------------------|
| 1,4-Dioxane | USEPA Method 8270 | 2 ug/l | 2 ug/l (California NL) |
| NDMA | USEPA Method 1625 | 0.002 ug/l | 0.010 ug/l (parts per trillion) |
| Hexavalent Chromium | USEPA Method 218.6 | 0.3 ug/l | 50 ug/l (Total Chromium) |
| 1,2,3-TCP | USEPA Method 524.2 | 0.005 ug/l | 0.005 ug/l (CA NL) |
| PBDE | USEPA Method 8270 | 2 ug/l | None |
| Perchlorate | USEPA Method 314.0 | 4 ug/l | 6 ug/l (California PGH) |

LIABILITY AND CLAIMS POTENTIAL

Due to the detections of emergent chemicals in groundwater and drinking water supplies located in California, in 2003 the RWQCB began to require property owners and active/former military installations to sample for these analytes.

site to determine whether there was a potential source for these chemicals that could mandate sampling. There is now also increased potential for sites that have received closure from a regulatory agency to be required to sample for emer-

gent chemicals years later. Property owners that acquire and redevelop contaminated sites may be responsible for any increased costs associated with additional sampling requirements. Furthermore, detections of emergent chemicals on active remediation sites being redeveloped could alter the remediation system design increasing overall project costs and potentially delaying future redevelopment. Delays in development due to unforeseen circumstances surrounding emergent chemicals may potentially result in builder's soft costs and business interruption claims.

Historical data on sampling of emergent chemicals has identified some correlations between the presence of other chemical compounds and emergent chemicals. For instance, a majority of the remediation sites investigated in southern California that contained 1,1,1-trichloroethane



(1,1,1-TCA) in groundwater also detected 1,4-dioxane. As such, there has been an increase in requests by RWQCB to also sample for 1,4-dioxane at sites that contain 1,1,1-TCA. A site in Menlo Park, CA, also identified 1,4-dioxane with 1,1-dichloroethane (1,1-DCE), the abiotic degradation product of 1,1,1-TCA. There has also been correlation with pesticides/herbicides and 1,2,3-TCP since it was

used in soil fumigants. Similarly, the presence of perchlorate and NDMA has been associated with similar uses. The association between common chemical uses can assist risk managers and environmental professionals in generating potential data gaps in site assessments.

CONCLUSIONS

The list of emergent chemicals will constantly be changing based on technological advances and epidemiology. It is imperative that property own-

ers and purchasers undertaking soil and groundwater investigation projects account for the potential historic sources of these chemicals. Agencies such as the RWQCB will continue to pursue potentially responsible parties for any impacted aquifers or drinking water supply wells containing emergent chemicals. Awareness of these chemicals should help decrease the potential claims associated with discovery of unknown pollution conditions or new regulatory agency requirements.

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Information accurate as of January, 2008.



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