



ENVIRONMENTAL TOOL BOX



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PERCHLORATE

Is it Naturally Occurring or Anthropogenic?



Photograph of Magnesium Batteries

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Sources of Perchlorate

Sources of perchlorate in the environment include anthropogenic (man-made) and naturally occurring. The bulk of anthropogenic sources are associated with military and industrial applications. Perchlorate is also present in fertilizers and as a naturally occurring salt in geologic formations associated with arid depositional environments in the United States, Bolivia and Chile.

Military and Industrial Sources

Perchlorate has been produced in the United States since the 1900s. In the 1940s and 1950s, perchlorates' strong oxidative properties were recognized and used in the production of explosives and propellants. Since World War II, millions of pounds of perchlorate have been synthesized for use by the military in the United States. The United States Environmental Protection Agency (U.S. EPA) estimates approximately 90% of ammonium perchlorate manufactured in the United States is used by the Department of Defense, its contractors and the National Aeronautics and Space Administration. The bulk of manufactured perchlorate is used in rocket and missile engine solid propellants.

Military sources of perchlorate include solid rocket fuels, signal flares, colored and white smoke generators, numerous types of munitions, artillery tracers, incendiary delays, and railway torpedoes. Historical sources of potassium and ammonium perchlorate associated with World War II munitions produced by the United

States and their percentage of perchlorate include high intensity signal flares (50%), mortar rounds (12%), railway torpedoes (5-12%) and ground burst projectile simulators (40%). Contemporary military products containing perchlorate include 3-inch chaff mortar shells (12%), hand-held parade flares (52%), parachute suspended illumination flares from 3-inch mortar rounds (12%) and booby trap illumination flares (73%).

Non-military sources of perchlorate include match manufacturing, tanneries, aluminum, refining, explosive bolts, signal and road flares, seismic explosives, fireworks, gas drying agent, fixer for fabrics and dyes, paint and enamel production, magnesium batteries, air bag inflators for automobiles, lubricating oils, methamphetamine laboratories, an ingredient of bleaching powder used in paper and pulp processing and calico printing, and cloud seeding.

The association of perchlorate with methamphetamine laboratories is interesting. The Bureau of Narcotics Enforcement has revealed that large quantities of unburned highway flares and unburned matches have been found at methamphetamine facilities. Red phosphorous (used as a catalyst in the production of methamphetamine) is obtained by dissolving highway flare striker caps or striker pads from match books.

The presence of perchlorate in fertilizer mined from caliche and brines with high sodium nitrate concentrations from Chile's Atacama Desert deposits has been known since 1886.

Perchlorate in Fertilizer

These deposits contain the largest known natural reservoir of perchlorate and have been used for fertilizer since 1830 with peak production in 1930. The ores and brines from these Chilean deposits have been exported throughout the world with an estimated worldwide production of about 23 million metric tons (in terms of nitrogen).

In 2003, the U.S. EPA analyzed nitrate fertilizers for the presence of perchlorate. Their initial findings indicated that other than Chilean nitrates, most fertilizers do not contain perchlorate. Other investigators have reported the presence of perchlorate in fertilizers not derived from Chilean nitrate deposits. In 2003, perchlorate in the parts per billion concentration range were detected in "bloodmeal" and "fishmeal" fertilizers.

Naturally Occurring Sources of Perchlorate

In addition to the presence of perchlorate in Chilean deposits that are used for fertilizer, other naturally occurring deposits of perchlorate include the following types of deposits and locations: New Mexico potash, Canadian potash, Bolivian playa crusts, evaporative deposits in Searles Lake, California, deposits in West Texas and New Mexico, and marine deposits in the Mission Valley Formation, San Diego.



Road Cut of Marine Layer Containing Naturally Occurring Perchlorate in San Diego, California

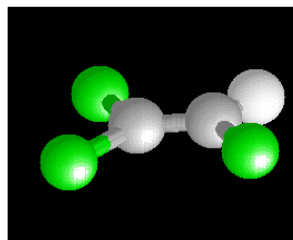
Perchlorate has been detected in public water systems, private wells, irrigation wells, and wells monitored by the United States Geologic Survey over a 60,000 square mile area in 56 counties in West Texas. Ten wells in the eastern counties of New Mexico covering an area of 6,800 square miles were included in this testing. Perchlorate concentrations in groundwater from portions of the West Texas study area (Gaines and Dawson Counties) consistently measured over 20 ug/l with some samples with concentrations of nearly 60 ug/l. For 560 public water system wells sampled in 54 of the 56 Texas counties, 46% contained perchlorate > 0.5 ug/l and 18% contained perchlorate > 4 ug/l. Analysis of 76 private wells

resulted in 47% of the wells detecting perchlorate with 23 of the 36 wells having concentrations above 4 ug/l. All ten New Mexico wells had detectable concentrations of perchlorate (i.e., above 0.5 ug/l) and 60% of the wells had concentrations above 4 ug/l.

Isotopic analysis of oxygen and chlorine can provide information regarding the source of the perchlorate as well as potentially distinguishing between anthropogenic and naturally occurring perchlorate. The advent of a new class of bifunctional anion exchange resins and resin regeneration techniques provides the ability to extract perchlorate from environmental samples. The ability to concentrate small concentrations of perchlorate provides the basis to distinguish between perchlorate reagents, naturally occurring perchlorate salt deposits, salt derived fertilizers, and perchlorate enriched surface and groundwater.

TCE – What is the Real Risk?

TCE (trichloroethylene) is a chemical whose regulatory and toxicological history is complex and continuously changing, primarily due to the limitations inherent of modern toxicology. The effect of TCE on animals and the extrapolation of these results for humans is a common nexus point for which tremendous uncertainty exists. The following is a brief history of key toxicological milestones for TCE.

Health Effects

The scientific information on the health effects of TCE originates from animal studies and from humans exposed to high concentration in the course of their work. The epidemiologic research on TCE is complicated by the lack of quantitative exposure information and the presence of other chemical exposures among workers studied.

Non-Cancer effects. Acute (short-term) and chronic (long-term) inhalation exposure to trichloroethylene can affect the human central nervous system (CNS), with symptoms such as dizziness, headaches, confusion, euphoria, facial numbness, and weakness. Liver, kidney, immunological, endocrine, and developmental effects have also been reported in humans.

Cancer effects. In experimental rodent studies, high doses of TCE administered to mice resulted in tumors of the lungs, liver, and testes. Other possible cancers associated with exposure to high levels of TCE include cancer of the bladder, stomach, prostate, kidney, and pulmonary system. No clear dose-response relationship appeared for any of the cancers associated with TCE exposure. Even more, such studies may not be relevant for humans, due to different mechanisms and required trigger dosage, and should be assessed with precaution.

Table with Chronology of Key TCE Toxicology Events

Date	Discussion
1985	U.S. EPA classified TCE as a probable human carcinogen.
1989	U.S. EPA withdraws the official assessment of TCE's potential carcinogenicity and TCE toxicity values from the Integrated Risk Information System (IRIS), pending on the resolution of several issues raised by the Science Advisory Board (SAB).
1998	EPA undertakes a project to reevaluate the toxicity of TCE under the Integrated Risk Information System Program. The EPA's cancer guidelines of 1999 propose TCE as "highly likely to produce cancer in humans." These findings are consistent with those of the International Agency on Research of Cancer (IARC) and the National Toxicology Program; The IARC (1995) places TCE in Group 2A, a category summarized as probably carcinogenic, based on limited human evidence and sufficient animal evidence.
2001	EPA presented a revised assessment in August 2001 (The U.S. EPA's 2001 Draft TCE Risk Assessment) for SAB review – the agency proposes a range of toxicity values more stringent than the withdrawn values, suggesting that TCE should be regarded as between 2 and 65 times more potent than it had been before. The assessment document discusses the possibility that children and developing fetuses have different susceptibilities to TCE toxicity, and considered the role of other volatile organic compounds and TCE metabolites.
2002	The SAB issues a written review of an EPA 2001 Assessment document in December 2002 (Review of Draft TCE Risk Assessment: Synthesis and Characterization: A SAB Report, EPA_SAB-EHC-03-002, December 2002) – requesting revision, clarification and strengthening of EPA's analysis. EPA asks a National Academy of Sciences panel to review the topic, and a finalized assessment is not expected until 2006. In the interim, the withdrawn toxicity values are still in use.
2005	The current TCE limits are: for water MCL: 0.005 mg/L. For air, the withdrawn value (EPA 1989) is 1.43 ug/m ³ . The more conservative "new provisional value" (EPA 2001) for indoor air (assuming a cancer risk of 10 ⁻⁶) is 0.021 ug/m ³ , while the less conservative "new provisional value" is higher (0.43 ug/m ³). The California EPA Air Toxics Hot Spots Program (2002) recommends a different TCE air value of 1.2 ug/m ³ , and the Colorado Department of Public Health and Environment (CDPHE) us a value of 0.016 ug/m ³ .

Challenge To Use Of Isotopic Methods For Source Identification Of TCE

In 1993, principles were established in what is commonly referred to as *Daubert* regarding the courts ability to be a "gate keeper" to expert witness testimony (*Daubert v. Merrell Dow Pharmacy, Inc.*, 509 U.S., 113 S. Ct. 2786, 125 L. Ed. 2d 469). According to the criteria set forth in *Daubert*, the court has the ability to determine whether the methodology is the product of reliable principles and methods and whether the technique has been subjected to peer review and publication. The court can also evaluate whether the technique enjoys general acceptance within a relevant scientific community.

Daubert challenges have become commonplace as a legal technique to exclude unreliable expert witness testimony. An example of the implementation of these principles to the reliance of forensic evidence is found in the matter of *Mejdrech v. The Lockformer Company* (United States District Court, N.D. Illinois, Eastern Division). In this case, the court considered the reliability of testimony regarding the use of chlorine and carbon isotopic ratios to identify potential sources of TCE in soil and groundwater samples. The purpose of this analysis was to examine whether differences in chlorine isotope ratios in the two class areas (LeClerc & Mejdrech) originated from a known TCE release at the Lockformer Company property.

In the subject case, the court found that opinions regarding the use of chlorine and carbon isotopic ratios for TCE source apportionment did not meet the reliability requirements as set forth in *Daubert*. The court found that the technique was not tested or subject to peer review or publication, it appeared to sustain a high potential rate of error and did not enjoy general acceptance within the relevant scientific community.

Tree Rings for Dating Contaminant Releases

An emerging forensic technique (dendroecology) is available for age dating a contaminant release. The basis of this method is that tree ring widths are dependent on environmental conditions. Environmental stresses (a petroleum release) in the vicinity of a tree may therefore be identified from a core from the tree. The tree rings provide the means to date the arrival of the contaminant. For petroleum hydrocarbons, the presence of sulfur and vanadium in the sample are useful indicators. For chlorinated solvents, chlorine is used. Lead is an especially useful indicator which with other indicators of stress, such as calcium, can indicate when a release occurred. Potential translocation issues associated with many contaminants are minimized with lead. The cost of this technique is about \$400 and takes 3-4 weeks.



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