GROUNDWATER INFORMATION SHEET

Perchlorate

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The purpose of this groundwater information sheet is to provide general information regarding a specific constituent of concern (COC). The following information is pulled from a variety of sources and data relates mainly to drinking water. For additional information, the reader is encouraged to consult the references cited at the end of the information sheet.

GENERAL INFORMATION	
Constituent of Concern	Perchlorate
Aliases	Dissociated anion of perchlorate salts. Includes: ammonium, potassium, magnesium or sodium Perchlorate
Chemical Formula	ClO_4^-
CAS No.	Perchlorate: ammonium 7790-98-9, potassium 7778-74-7, magnesium 10034-81-8, and sodium 7601-89-0
Storet No.	A-031
Summary	The California Department of Health Services (DHS) is required to adopt a maximum contaminant level (MCL) for perchlorate. Until an MCL is finalized, DHS uses an advisory action level (AL) of 6 micrograms per liter (μg/L). Common anthropogenic sources of perchlorate include perchlorate salts used in industrial and military applications. Perchlorate is highly soluble in water, highly mobile, and once released, is persistent in groundwater. Based upon data provided by the DHS through August 2003, 354 drinking water wells (of approximately 6500 sources sampled) have detections of perchlorate, of which 248 exceeded the AL. Most perchlorate detections have occurred in Los Angeles, San Bernardino, and Riverside Counties.

REGULATORY AND WATER QUALITY LEVELS[1]		
Type	**Agency**	**Concentration**
Federal MCL	US EPA, Region 9	No MCL set
State MCL	DHS	No MCL set Expected Early 2005
State AL	DHS	6 µg/L
Detection Limit for Purposes of Reporting (DLR)	DHS	4 µg/L
Others: Preliminary Remediation Goal – Tap Water Public Health Goal (PHG)	 US EPA, Region 9 OEHHA	 3.6 µg/L 6 µg/L

[1]These levels generally relate to drinking water, other water quality levels may exist. For further information, see A Compilation of Water Quality Goals (Marshack, 2003).

SUMMARY OF DETECTIONS IN PUBLIC DRINKING WATER WELLS[2]	
Detection Type	**Number of Groundwater Sources**
Number of public drinking water wells[3] with detections (≥ 4 µg/L)	354 of approximately 6500 sampled
Number of public drinking water wells[3] with AL exceedences (≥ 6 µg/L)	248 of approximately 6500 sampled
Top 3 counties having public drinking water wells[3] with perchlorate detections	Los Angeles, San Bernardino, Riverside

[2]Based on DHS data collected from 1997-2003 (Geotracker). See Figures 1 and 2.
[3]In general, drinking water from active and standby wells is treated or blended so consumers are not exposed to water exceeding MCLs or State AL. Individual private (domestic) wells and wells for small water systems not regulated by DHS are not included in these figures.

ANALYTICAL INFORMATION	
Analytical Test Methods	US EPA Method 314.0
Method Detection Limit	1 µg/L
Known Limitations to Analytical Methods	Ion chromatography (IC) is the state-of-the-art technology for perchlorate analysis. Historical methods based on gravimetry, spectrophotometry, or atomic absorption lack the selectivity, specificity, and sensitivity for perchlorate that IC analysis provides. Before 1997, the IC method used to analyze for perchlorate (Aerojet method) had a method detection limit (MDL) of 100µg/L. In 1997, the DHS developed and introduced what became US EPA Method 314.0, which has an MDL of 4µg/L. In 1998, the Dionex AS-11 method was developed by the Air Force Research Laboratory/Operational Toxicology Branch (AFRL/HEST), which has an MDL of <1µg/L. These methods depend upon retention time in a standard to identify any peak with the same or similar retention time as perchlorate in a water sample. The robustness of the existing IC methods for perchlorate in water analysis with high total dissolved solids is questionable. Research is underway that will evaluate the variability, reproducibility, accuracy and precision of the IC methods across laboratories and to determine the appropriate concentration ranges for measurement.
Public Drinking Water Testing Requirements	In January 2001, DHS identified perchlorate as an unregulated chemical requiring monitoring (Title 22, California Code of Regulations §64450). It is "unregulated" by DHS because it has no drinking water standard or MCL. As a result of the DHS monitoring requirement, public water systems began collecting information on the presence of perchlorate in their drinking water supplies. These data are needed to enable DHS to ascertain the extent to which perchlorate is present in drinking water supplies, and to determine treatment costs, in case a drinking water MCL specific for perchlorate is determined to be appropriate. As of March 2004, 6500 drinking water sources in California have been sampled for perchlorate with 354 detections, of which 252 exceeded the AL (DHS website, March 2004)

PERCHLORATE OCCURRENCE	
Anthropogenic Sources	Perchlorate originates as a contaminant in the environment from the release of solid salts of ammonium, potassium, or sodium perchlorate. The vast majority (approximately 90 percent) of locations where perchlorate has been detected in the groundwater are associated with the manufacturing or testing of solid rocket fuels for the Department of Defense (DOD) and the National Aeronautics and Space Administration (NASA), and with the manufacture of ammonium perchlorate. Perchlorate salts are also used in: fireworks; matches; automotive air bag inflators; nuclear reactors; electronic tubes; lubricating oil; the tanning and finishing of leather; as a fixer for fabric and dyes; electroplating; aluminum refining; rubber manufacture; the production of paints and enamels. Perchlorate is also reported to have been present in certain types of fertilizers. In addition, perchlorate has been detected at hazardous waste sites. Potassium perchlorate has been used therapeutically to treat hyperthyroidism resulting from an autoimmune condition known as Graves' disease. Diagnosis of thyroid hormone production has used potassium perchlorate in some clinical settings.
Natural Sources	Perchlorate is reported to be present in some caliche formations in Chile that are used to produce nitrate fertilizers.

History of Occurrence	Several hundred drinking water wells were sampled by DHS for perchlorate beginning February 1997. Perchlorate was first detected in drinking water wells (up to 260 µg/L) near the Aerojet site in Sacramento County. Groundwater treated to remove volatile organic chemicals (such as trichloroethylene) was re-injected into the groundwater. Perchlorate, also in the contaminated shallow groundwater, has been present in the re-injected water at concentrations up to 8,000 µg/L. Perchlorate was also detected (up to 159 µg/L) in drinking water wells in Los Angeles County. Several sites have been identified as potential sources of contamination, including Aerojet (Azusa), Whittaker-Bermite (Santa Clarita), and Jet Propulsion Laboratory (Pasadena). DHS also found perchlorate in drinking water wells in Riverside (up to 29 µg/L) and San Bernardino County drinking water wells (up to 325 µg/L) and in 24 agricultural wells (up to 221 µg/L). The perchlorate contamination is associated with a TCE plume at the former operation site of the Lockheed Propulsion Company. Perchlorate was detected at 270 µg/L in an inactive well near former fireworks manufacturing site near Rialto. Colorado River water sampling has shown perchlorate concentrations from 5 to 9 µg/L. The river is an important source of California's drinking and agricultural irrigation water. The perchlorate impact is associated with contamination from ammonium perchlorate manufacturers near Las Vegas, Nevada. Other locations of groundwater contamination by perchlorate: • an explosives manufacturing facility near Lincoln, at 1,200 and 67,000 µg/L. • United Technologies in Santa Clara, up to 180,000 µg/L. • Whittaker Ordnance Facility (near Hollister in San Benito County), up to 88 µg/L; an agricultural well in the vicinity at 34 µg/L, and a private well, 810 µg/L.
Contaminant Transport Characteristics	Perchlorate is highly soluble and mobile in groundwater, and is resistant to degradation in that environment. Perchlorate and concentrated solutions of perchlorate are denser than water (ammonium perchlorate at 1.95 g/ml), which allows it to sink. The persistence of perchlorate in groundwater results primarily from its chemical stability (very inert) and its relative resistance to biodegradation (stable at low concentrations).

REMEDIATION & TREATMENT TECHNOLOGIES

Treatment of perchlorate contamination in water is complicated because conventional filtration, sedimentation, and air stripping technologies cannot remove the perchlorate anion. Since 1997, much progress has been made in perchlorate treatment technologies. However, no single treatment technique is effective in every case and the best solution may be a combination of treatment technologies.

Physical Removal Technologies

Ion Exchange – a process with two similar applications of the same technology:

- Water softening: removes ions from the water and replacing them with sodium (Na^+) and chloride (Cl^-) ions. This technique is employed at Aerojet Sacramento.
- Deionization: ions are removed and replaced with hydrogen (H^+) and hydroxyl (OH^-) ions, which can combine to form water.

Ion exchange treatment has been successful in reducing perchlorate concentrations in water from 75 ppb to less than detectable levels at the San Gabriel Valley Superfund sites. This process concentrates the perchlorate into brine, which must be disposed or treated. Ion exchange is the preferred large-scale treatment method used by most utilities.

Membrane Techniques:

- **Reverse Osmosis and Nanofiltration -** use semi-permeable membrane, allowing the water to pass through it, while retaining perchlorate. RO and NF can be costly due to the energy use and perchlorate disposal. Typically used on small-scale systems.
- **Electrodialysis** – an electrically driven membrane separation process that separates ions from water. The process is based on the property of ion exchange membranes to selectively reject anions or cations.

Other Treatment Technologies

Biological – Effective and fast-reaction treatment technology has been successful in reducing concentrations in water from 75 ppb to less than detectable levels at the San Gabriel Valley Superfund sites and at Aerojet Sacramento. Biological fluidized bed reactors (FBR) use naturally occurring microorganisms to destroy perchlorate molecules (to oxygen and chloride) while attached to a hydraulically fluidized bed of sand or granular activated carbon media. Regulatory barriers and the hardiness of the bacteria have been considered problematic, but additional microbe removal using oxidation and/or granular activated carbon has been effective when added downstream the FBR.

Biochemical - A highly effective and fast-reaction technique that produces no toxic by-products. Biochemical reduction is expensive, high maintenance, difficult to implement and the enzymes used in the reaction are expensive and unstudied.

Chemical - A reducing agent transfers electrons to the chlorine atom (of perchlorate anion) converting it to chloride. Chemical reduction is expensive, slow, and it produces toxic by-products that are hard to remove.

Electrochemical - A well-known technique and has non-toxic by-products on the positive side, but construction costs are high, uses a lot of power to the electrolysis of water, the process is slow, and a safety concern.

HEALTH EFFECT INFORMATION

In the body, perchlorate interferes with the uptake of iodine by the thyroid gland, causing disruption of thyroid hormone production. Thyroid hormones help to regulate the body's metabolism and physical growth. Inhibited thyroid function can result in hypothyroidism and, in rare cases, thyroid tumors. Pregnant women and their developing fetuses may suffer the most serious health effects from perchlorate contamination in drinking water, particularly in the first and second trimesters of pregnancy. During this period, the fetal thyroid is not yet fully functional, so the mother's thyroid must be able to produce enough extra hormones to enable her baby's brain to develop properly. Because pregnancy already places a strain on the maternal endocrine system, pregnant mothers and their fetuses are particularly susceptible to perchlorate's inhibition of iodine intake. Women with critically low levels of iodine can miscarry, or their developing fetuses can suffer congenital hypothyroidism, which may stunt the fetus's physical growth and impede proper development of its central nervous system. Even moderate to mild iodine deficiency during pregnancy has been linked to impaired brain development and lower IQs for children born under these conditions (OEHHA, 2002).

Following the initial detections in 1997, DHS informed drinking water utilities that US EPA had evaluated the health effects of perchlorate as part its Superfund activities (US EPA, 1992, 1995). US EPA used studies on humans as most appropriate for evaluating the health risks of perchlorate to establish a "provisional" reference dose (RfD). Data were derived from medical patients given perchlorate to treat hyperactive thyroid glands (Graves' disease). The release of iodine from the thyroid and inhibition of iodine uptake by the thyroid were the most sensitive indicators of perchlorate effects. For these effects, the US EPA (1992) identified a no observed adverse effect level (NOAEL) of 0.14 mg/kg/day and a 1000-fold uncertainty factor (UF). Later, US EPA reviewed its earlier report and material submitted by the Perchlorate Study Group, and maintained the earlier 1000-fold UF, but also included a 300-fold UF (US EPA, 1995).

The US EPA evaluations corresponded to a range of 4 to 18 μg/L in drinking water. DHS, in cooperation with OEHHA, reviewed the US EPA perchlorate evaluations, and established an AL of 18 μg/L in 1997. DHS reduced its AL level from 18 μg/L to 4 μg/L, equal to the analytical quantitation limit in 2002.

OEHHA released a final PHG of 6 μg/L in March 2004. DHS will use the PHG in proposing a perchlorate MCL (expected late 2004/ early 2005). Until a final MCL is set, the AL set by DHS for perchlorate is 6 μg/L. Perchlorate concentrations at or below 6 μg/L are not considered by DHS and OEHHA to pose a health concern for the public, including children and pregnant women and their developing young.

KEY REFERENCES

1 California Department of Health Services. *Perchlorate in California Drinking Water: Status of Regulations and Monitoring Results* http://www.dhs.cahwnet.gov/org/ps/ddwem/chemicals/perchl/perchlindex.htm (March 12, 2004).
2 California Environmental Protection Agency. Office of Environmental Health Hazard Assessment. Public Health Goal for Perchlorate in Drinking Water http://www.oehha.ca.gov/water/phg/perchphg31204.html (March 2004).
3 California Environmental Protection Agency / Regional Water Quality Control Board, Central Valley Region.. *A Compilation of Water Quality Goals*. Prepared by Jon B. Marshack. http://www.swrcb.ca.gov/rwqcb5/available_documents/wq_goals/index.html (August 2003).
4 U.S. Environmental Protection Agency. Groundwater and Drinking Water. *Drinking Water Contaminant List: Perchlorate* http://www.epa.gov/safewater/perchlorate/perchlorate.html (January 2003).
5 U.S. Environmental Protection Agency. Contaminant Focus: Perchlorate (CLU-IN.ORG) http://clu-in.org/contaminantfocus/default.focus/sec/perchlorate/cat/Overview/ (March 2004).
6 General Electric, Osmonics Technology Web Library http://www.osmonics.com/library/library.htm (March 2004).
7 Calgon Carbon Corporation, http://www.perchlorateinfo.com/index.html (June 2003).
8 U.S. Environmental Protection Agency. *What Techniques Will Work?* Prepared by Edward T. Urbansky http://www.epa.gov/safewater/ccl/perchlorate/pdf/urban.pdf.
9 *Biological Treatment of Perchlorate Contaminated Groundwater Using Fluidized Bed Reactors*, prepared by Paul B. Hatzinger, http://www.clu-in.org/download/contaminantfocus/perchlorate/Envirogen1.pdf (May 2000).
10 Aerojet Sacramento Perchlorate Activities (Fact Sheet supplied through Groundwater Resources Association Website) http://www.grac.org/Aerojet_Perchlorate_Solutions.pdf (May 2003).

FOR MORE INFORMATION, CONTACT: John Borkovich, SWRCB (916) 341-5779

Groundwater Information Sheet: Perchlorate
Figure 1

Active and Standby DHS Wells (248 Total) with at Least One Detection of Perchlorate >= 6 PPB State Action Level

Source: 1984 - 2003 DHS Data
(Map Revised 03/23/04 - Data current to August, 2003)
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Groundwater Information Sheet: Perchlorate
Figure 2

Abandoned, Destroyed, and Inactive DHS Wells (81 Total) with at Least One Detection of Perchlorate >= 6 PPB State Action Level

Source: 1984 - 2003 DHS Data
(Map Revised 03/23/04 - Data current to August, 2003)
Prepared by: B. Wyckoff

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