Groundwater Fact Sheet Perchlorate



Constituent of Concern Perchlorate

Synonym

Perchlorate ion (1-). Dissociated anion of perchlorate salts. Includes: ammonium, potassium, magnesium, or sodium perchlorate

Chemical Formula CIO4-

CAS Number

Perchlorate ion 14797-73-0 Perchlorate:

- ammonium 7790-98-9
- potassium 7778-74-7
- magnesium 10034-81-8
- sodium 7601-89-0

Storet Number

A-031

Summary

Perchlorate is a regulated drinking water contaminant with an established State Maximum Contaminant Level (MCL) of 6 micrograms per liter (µg/L). Perchlorate is a monovalent inorganic anion and a chlorine oxyanion. It is a strong oxidizing agent and as such, its salts, in particular ammonium perchlorate, are potentially explosive chemicals. Perchlorate salts may occur naturally, particularly in arid regions, as impurities in nitrate salts or potash ores. Nitrate salts can then be used as natural fertilizers inducing environmental contamination by perchlorate. Common anthropogenic sources of perchlorate include perchlorate salts used in industrial and military applications. It is commonly used as an oxidizer in solid propellants, munitions, fireworks, airbag initiators for vehicles, matches and signal flares. Perchlorate is highly soluble in water, highly mobile, and as such, once released, is very persistent in groundwater.

Based on State Water Resources Control Board (SWRCB) data from 2007 to 2017, 230 active and standby public supply water wells (of 9,341 wells tested, 562 detections) had at least one detection above the MCL. Most detections occurred in three counties, Los Angeles (88), San Bernardino (62) and Riverside (23).

REGULATORY WATER QUALITY LEVELS ¹			
PERCHLORATE			
Туре	Agency	Concentration	
Federal MCL	EPA ²	NA	
State MCL	SWRCB ³	6 μg/L	
Detection Limit for Purposes of Reporting (DLR)	SWRCB ³	4 μg/L	
Public Health Goal (PHG)	OEHHA4	1 μg/L	

¹These levels are generally related to drinking water. Other water quality levels may exist. For further information, see "A Compilation of Water Quality Goals", 17th Edition (SWRCB 2016).

²EPA – United States Environmental Protection Agency

³SWRCB - State Water Resources Control Board.

⁴OEHHA – Office of Environmental Health Hazard Assessment

PERCHLORATE DETECTIONS IN PUBLIC WATER WELL SOURCES⁵

Number of active and standby public water wells with perchlorate concentrations > $6 \mu g/L^6$	230 of 9,341 wells tested with 562 detections
Top 3 counties with perchlorate detection in public wells above the MCL	Los Angeles (88), San Bernardino (62) and Riverside (23)

⁵Based on 2007-2017 public standby and active well (groundwater sources) data collected by the SWRCB. ⁶Water from active and standby wells is typically treated to prevent exposure to chemical concentrations above MCL. Data from private domestic wells and wells with less than 15 service connections are not available.

ANALYTICAL INFORMATION			
Approved EPA methods	331.0 (SIM)	331.0 (MRM)	
Detection Limit (µg/L)	0.008	0.005	
Notes	Liquid chromatography electrospray ionization mass spectrometry (LC/ESI/MS; method 331.0) is the state-of-the-art technology for perchlorate analysis in drinking water. Old methods based on gravimetry, spectrophotometry, or atomic absorption lack the selectivity, specificity, and sensitivity for perchlorate that LC/ESI/MS analysis provides. Before 1997, the lon Chromatography (IC) method used for perchlorate detection (Aerojet method) had a method detection limit (MDL) of 100 µg/L. In 1997, the DDW (formerly CDPH) developed and introduced what became the EPA Method 314.0, which has an MDL of 4 µg/L. In 1998, the Dionex AS-11 method was developed by the Air Force Research Laboratory/Operational Toxicology Branch (AFRL/HEST) and reached less than 1 µg/L as MDL. In 2005, EPA published the 331.0 (LC/ESI/MS) method that allows perchlorate detection at the parts per trillion level. The method can use either Selected Ion Monitoring (SIM) or Multiple Reaction Monitoring (MRM) detection. Based on known interferences, MRM detection is recommended.		
Known Limitations to Analytical Methods	Samples must be filtered to remove any native microorganisms since perchlorate is known to be susceptible to microbiological degradation by anaerobic bacteria. Samples are stored with headspace to minimize the chance of developing anaerobic conditions.		
Public Drinking Water Testing Requirements	In October 2007, the DDW established the MCL for perchlorate at 6 µg/L. Testing of all public drinking water sources is required. Perchlorate concentrations in drinking water provided to the public cannot exceed the MCL.		

Perchlorate Occurrence

Anthropogenic Sources

Perchlorate is a manufactured compound that includes perchloric acid and salts such as ammonium, potassium, and sodium perchlorate.

Sources include the manufacturing or testing of solid rocket fuels for the Department of Defense (DOD), and the National Aeronautics and Space Administration (NASA), and the manufacturing of ammonium perchlorate for fireworks and certain types of fertilizers. Perchlorate is present in matches, automotive air bag inflators, nuclear reactors, electronic tubes, and lubricating oils. It is used in leather tanning and finishing chemicals, as a fixer for fabric and dyes, electroplating, aluminum refining, rubber manufacturing, and in the production of paints and enamels.

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. Perchlorate has also been detected at hazardous waste sites.

Natural Sources

Perchlorate also occurs naturally and is reported to be present in sodium-nitrate deposits of Chiles' Atacama Desert that are used to produce nitrate fertilizer. Perchlorate was detected in salts accumulated in thick unsaturated zones in the southwestern USA. Isotopic data suggest an atmospheric origin for the perchlorate in these arid environments, as perchlorate is present in solution precipitation water.

History of Occurrence

In February 1997, perchlorate was first detected in drinking water wells near the Aerojet site in Sacramento County. Aerojet has used perchlorate as a solid rocket propellant. Perchlorate was also detected in drinking water wells in Los Angeles County in April 1997. Since then, several sites have been identified as potential sources of contamination, including Aerojet (Azusa), Whittaker-Bermite (Santa Clarita), and Jet Propulsion Laboratory (Pasadena).

Perchlorate has been detected in drinking water wells associated with a TCE plume at the former operation site of the Lockheed Propulsion Company (San Bernardino and Riverside County), and in several wells located in the Rialto area of San Bernardino County. Potential sources of contamination in Rialto include fireworks manufacturing and landfill sites. In addition, perchlorate has been found in 24 agricultural wells located in San Bernardino County at concentrations ranging from 11 to 221 µg/L. Colorado River water sampling has shown perchlorate concentrations ranging from 5 to 9 µg/L.

The Colorado River is an important source of California's drinking and agricultural irrigation water. These perchlorate detections are associated with contamination from perchlorate manufacturers near Las Vegas, Nevada.

Other locations in California showing groundwater contamination by perchlorate:

- explosives manufacturing facility near Lincoln (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 μ g/L); an agricultural well in the vicinity (34 μ g/L); and a private well (810 μ g/L).

Contaminant Transport Characteristics

Perchlorate is highly soluble and mobile in groundwater and is resistant to degradation. 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 and 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.

Perchlorate treatment technologies may be generally classified into categories of destruction or removal technologies. The optimum treatment technology for a given perchlorate occurrence may depend on several factors, including perchlorate concentration, other water quality parameters (pH, alkalinity, organic matter, total dissolved solids (TDS), metals, etc.), and geochemical parameters (nitrate, sulfate, chloride, dissolved oxygen, redox potential, etc.). The presence of perchlorate-reducing microbes will also influence perchlorate treatment technology effectiveness. For in situ treatment of perchlorate contamination, variables related to the site hydrogeological setting, such as depth to and distribution of contaminants, soil permeability, groundwater flow velocity, etc. are also additionally important.

Physical Removal Technologies

Ion Exchange

Ion exchange treatment has been successful in reducing perchlorate concentrations in water from 75 μ g/L to less than detectable levels at the San Gabriel Valley Superfund sites. These processes concentrate the perchlorate into brine, which must then be disposed of or treated. Ion exchange is the preferred large-scale treatment method used by most utilities.

Two processes with similar applications of the same ion-exchange technology are:

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

Membrane Techniques

Reverse Osmosis and Nanofiltration (RO and NF) - A semi-permeable membrane is used, allowing the water to pass through it, while retaining perchlorate. RO and NF can be costly due to energy use and the need of subsequent perchlorate disposal. They are typically used on small-scale systems.

Electrodialysis - An electrically driven membrane separation process that separates ions from water. This process is based on the property of ion exchange membranes to selectively reject anions or cations.

Other Treatment Technologies

Biological reduction

Biological fluidized bed reactors (FBR) are an effective and fast-reaction treatment technology that has been successful in minimizing perchlorate concentrations in water at the San Gabriel Valley

Superfund Site and the Aerojet, Sacramento sites. FBRs use naturally occurring microorganisms to convert 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 of the FBR.

Biochemical reduction

This technique uses enzymes to produce a highly effective fast reaction that creates nontoxic byproducts. However, biochemical reduction requires high maintenance efforts and is technically difficult to implement. In addition, the enzymes utilized in the process are costly and lack thorough research.

Chemical reduction

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

Electrochemical reduction

This technique requires large amounts of power to electrolyze the water and produce non-toxic byproducts. It is a well-known, slow, and expensive method that also involves safety concerns.

Other In-Situ treatment methods

Bioremediation, phytoremediation or monitored natural attenuation are also remediation technologies that might be used for perchlorate contaminated sites in specific conditions.

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, DDW (formerly CDPH) informed drinking water utilities that EPA had evaluated the health effects of perchlorate as part of its Superfund activities (EPA, 1992, 1995). EPA used studies on humans to evaluate the health risks of perchlorate and 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. In 2005, the EPA assigned perchlorate a chronic oral reference dose (RfD) of 0.0007 milligrams per kilogram per

day (mg/kg/day), which equates to a Drinking Water Equivalent Level (DWEL) of 24.5 μ g/L. In 2012, the EPA established an Interim Lifetime Drinking Water Health Advisory Level of 15 μ g/L. Perchlorate at this concentration is not expected to cause any adverse effects for a lifetime of exposure. EPA's tap water screening level was calculated at 11 μ g/L in 2013.

In October 2007, the final MCL was set by the DDW at 6 μ g/L. Perchlorate concentrations at or below 6 μ g/L are not considered to pose a health concern for the public, including children and pregnant women, and their developing young. In 2015 OEHHA updated the previous Public Health Goal (PHG) of 6 μ g/L (2004) for perchlorate in drinking water to 1 μ g/L. In response to the revised PHG, DDW will determine if the state MCL should be considered for revision.

Key Resources

- 1. SWRCB Site Assessment & Cleanup Aerojet Rocketdyne <u>https://www.waterboards.ca.gov/centralvalley/water_issues/site_cleanup/aerojet/</u>
- Biological Treatment of Perchlorate-Contaminated Groundwater Using Fluidized Bed Reactors, prepared by Paul B. Hatzinger. <u>http://www.clu-</u> in.org/download/contaminantfocus/perchlorate/Envirogen1.pdf
- 3. California Environmental Protection Agency. Office of Environmental Health Hazard Assessment. Public Health Goal for Perchlorate in Drinking Water <u>http://oehha.ca.gov/media/downloads/water/public-health-</u> <u>goal/perchloratephgfeb2015.pdf</u>
- 4. State Water Resources Control Board. GAMA GIS online tools http://www.waterboards.ca.gov/water_issues/programs/gama/geotracker_gama.shtml
- State Water Resources Control Board. A Compilation of Water Quality Goals, 17th Edition, (SWRCB, 2016). <u>http://www.waterboards.ca.gov/water_issues/programs/water_quality_goals/docs/wq_goals_text.pdf</u>
- 6. State Water Resources Control Board-Division of Drinking Water. Perchlorate in Drinking Water http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Perchlorate.shtml
- 7. U.S. Environmental Protection Agency. Contaminant Focus: Perchlorate (CLU-IN.ORG) http://clu-in.org/contaminantfocus/default.focus/sec/perchlorate/cat/Overview/
- 8. U.S. Environmental Protection Agency, Technical Fact Sheet-Perchlorate, <u>http://www.epa.gov/sites/production/files/2014-</u> 03/documents/ffrrofactsheet_contaminant_perchlorate_january2014_final.pdf
- Urbansky, E.T., Schock, M.R., Issues in managing the risks associated with perchlorate in drinking water, Journal of Environmental Management, (1999) 56,79-95, <u>https://cluin.org/download/contaminantfocus/perchlorate/urbansky1.pdf</u>



Figure 1. Active and standby public drinking water wells that had at least one detection of perchlorate above the MCL, 2007-2017, 230 wells. (Source: Public supply well data in <u>GAMA GIS</u>).