

CHAPTER 4

PERCHLORATE SOURCES, SOURCE IDENTIFICATION AND ANALYTICAL METHODS

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4.1 INTRODUCTION

Given the wide range of anthropogenic and natural perchlorate sources, the remediation practitioner should be aware of effective source identification and analytical methods to determine the origin and extent of perchlorate contamination. Characterization issues discussed in this chapter include: (1) anthropogenic and natural sources of perchlorate and their associated co-contaminants; (2) isotopic techniques to distinguish between natural and anthropogenic sources of perchlorate; (3) analytical methods for perchlorate recommended by the U.S. Department of Defense (DoD) and the U.S. Environmental Protection Agency (USEPA) and their limitations; and (4) chemical and geochemical parameters that should be measured during the characterization and treatment of a perchlorate-contaminated site.

4.2 SOURCES OF PERCHLORATE

The use and disposal of rocket propellant in the defense and aerospace industries is the most widely cited source of perchlorate contamination in the environment ([Section 4.2.1.1](#)). However, through monitoring activities mandated by the Unregulated Contaminant Monitoring Rule (USEPA, 1999a), perchlorate has now been detected at low levels (typically less than 50 micrograms per liter [$\mu\text{g/L}$]) in a significant number of areas without apparent military sources (Brandhuber and Clark, 2005).

Widespread, low concentration perchlorate contamination of groundwater can result from a variety of non-military sources, including the use and manufacture of road flares ([Section 4.2.1.2](#)), fireworks displays ([Section 4.2.1.3](#)), blasting agents used in mining and construction ([Section 4.2.1.4](#)), sodium chlorate ([Section 4.2.1.5](#)), sodium hypochlorite (bleach) ([Section 4.2.1.6](#)), and perchloric acid ([Section 4.2.1.7](#)). In addition to these anthropogenic sources, naturally-occurring perchlorate is likely to account for the low levels of contamination found in some regions of the United States ([Section 4.2.2](#)).

4.2.1 Anthropogenic Sources

4.2.1.1 Rocket Propellant

Approximately 90% of perchlorate compounds, primarily ammonium perchlorate, are used in defense activities and the aerospace industry. The widespread manufacture of perchlorate in the United States began in the mid 1940s and, by the 1950s, ammonium perchlorate began replacing potassium perchlorate as the preferred oxidizer for solid propellants in large rocket motors. In the 1960s, solid propellant mixtures of ammonium perchlorate and powdered aluminum replaced liquid propellant systems in intercontinental ballistic missile systems. Other examples of solid rocket motors that use ammonium perchlorate include the space shuttle and commercial satellite vehicles (ITRC, 2005). In the past, munitions manufacturing facilities conducted hydraulic wash out (often referred to as hog-out) of equipment used in solid propellant and munitions production. In some instances, these operations have resulted in the creation of groundwater plumes.

4.2.1.2 Road Flares

Safety flares (or fusées) used in emergency situations for road-side accidents and rail and marine emergencies contain high levels of potassium perchlorate. Although accurate estimates of the number of flares consumed annually are difficult to obtain, it is estimated that between 20 and 40 million flares are produced annually in the United States (Geosyntec, 2005).

A flare generally consists of a waxed cardboard tube casing filled with a burn mixture and a cap at the end to ignite the flare. Based on Material Safety Data Sheets (MSDSs), the burn mixture contains primarily strontium nitrate (75% by weight), potassium perchlorate (<10% by weight), and sulfur (<10% by weight) (Silva, 2003a). Flares from various manufacturers have been found to have perchlorate levels of 5–7% by weight (Geosyntec, 2006). High levels of strontium, nitrate, and possibly sulfur in association with perchlorate in groundwater can be indicative of a road flare source.

Although road flares have high levels of perchlorate, the burning of the flare significantly reduces the potential for perchlorate releases. Silva (2003b) compared perchlorate leaching from unburned flares that had been damaged (i.e., sliced open) to completely burned flares and showed that completely burned flares leached 2,000 times less perchlorate than damaged unburned road flares (i.e., 1.95 milligrams (mg) vs. 3,645 mg perchlorate per flare). An average of 99.8% of perchlorate is consumed upon the complete burning of a flare (Geosyntec, 2006; 2007).

4.2.1.3 Fireworks

Potassium perchlorate is a significant component of fireworks and is used primarily as an oxidizing agent. Because oxidizers must be low in hygroscopicity, potassium salts have been preferred over sodium salts. Potassium perchlorate can be used to produce colored flames, noise, and light when formulated with mixtures of barium (green), strontium (red), copper (blue), aluminum, and magnesium powders (Conkling, 1985). Ammonium perchlorate is also used in some fireworks formulations. Another potential source of perchlorate is the potassium nitrate in the black powder used in the lift charge if the potassium nitrate is of Chilean origin

(Section 4.2.2.2). Large quantities of fireworks are handled and discharged annually in the United States. For example, 220 million pounds (lb) of fireworks were consumed in 2003 (APA, 2004).

Raw perchlorate from fireworks manufacturing facilities and perchlorate residue from launched fireworks have the potential to contaminate surface water and groundwater. For example, perchlorate was detected at a concentration of 270 $\mu\text{g/L}$ in an inactive well near a defunct fireworks site in Rialto, California (CDHS, 2007). Perchlorate derived from fireworks manufacturing also has been detected at a concentration of 122 $\mu\text{g/L}$ in a well near Brookhaven, New York (Grocock, 2002).

Perchlorate contamination linked to fireworks displays was examined by the Massachusetts Department of Environmental Protection (MADEP) at the University of Massachusetts at Dartmouth (UMD). Prior to the 2004 display, soil samples had no detectable levels of perchlorate (MADEP, 2005). Results of soil sampling immediately after the display indicated a maximum perchlorate concentration of 560 micrograms per kilogram ($\mu\text{g/kg}$). Groundwater concentrations were not substantially different after the display than before (MADEP, 2005). Soil sampling conducted following the 2006 display at UMD indicated a maximum perchlorate concentration of 5 milligrams per kilogram (mg/kg) (Geosyntec, 2007). Perchlorate was also reported to increase appreciably in a municipal lake following a fireworks display in 2006, with concentrations increasing from a mean value of 0.043 $\mu\text{g/L}$ just before the display to as high as 44 $\mu\text{g/L}$ after the display (Wilkin et al., 2007). These values decreased to near background within 80 days after the display. Another study to assess the impacts of firework displays at Columbia Lake on the University of Waterloo's campus has recently been completed (<http://www.p2pays.org/ref/22/21726.pdf>).

The presence of elevated levels of potassium and magnesium may indicate the potential for perchlorate contamination from fireworks (Geosyntec, 2007). These metals were generally found at elevated concentrations at both the UMD and Columbia Lake sites following firework displays. As previously noted, other metals commonly associated with fireworks include strontium, copper, cobalt, barium, and aluminum. At many sites, natural background levels of these elements may be too high to distinguish contributions from fireworks.

4.2.1.4 Blasting Agents and Explosives

Sodium and ammonium perchlorate salts are components of some blasting agents and explosives. Approximately 2.7 million tons of blasting agents are used in coal mining, quarrying, metal and non-metal mining and construction annually (Kramer, 2003), but the percentage containing perchlorate is unknown.

Unlike explosives, blasting agents require a booster, in addition to a detonator, to initiate. Most water gels and emulsions are classified as blasting agents, as opposed to high explosives, because they are comparatively insensitive materials (i.e., difficult to detonate). This property enhances their ease of handling and safety. However, for certain difficult blasting applications, such as water-saturated construction sites where the explosive is subjected to high static or dynamic pressures, it is desirable to increase the sensitivity by using perchlorate-containing products (IME, 2007; ITRC, 2005). Some water gels and emulsions can contain up to 30% perchlorate (Table 4.1). The inclusion of sodium nitrate of Chilean origin may also introduce perchlorate as discussed in Section 4.2.2.2. Certain seismic explosives can contain 55–72% perchlorate and some non-electric detonators may contain up to 10% perchlorate.

The most common and simplest blasting agent is ammonium nitrate fuel oil (ANFO), which consists of ammonium nitrate (AN) prills soaked with fuel oil (about 5 to 6 weight %). Another popular blasting product consists of a blend of prilled ANFO or AN with AN emulsion in various ratios. Blends containing less than 50% emulsion are sometimes referred to as “heavy ANFO.” Their benefits include reduced mining costs, increased water resistance and increased density/strength (ISEE, 1998). MSDSs for some heavy ANFOs list “inorganic oxidizers”. Further testing is required to determine if these products contain perchlorate.

Table 4.1. Blasting Agents and Explosives Containing Perchlorate (% Composition)*

Type Product	Blasting Agent (1.5) or Explosive (1.1)	NH ₄ NO ₃	NaNO ₃	NaClO ₄
Gel bulk or packaged	Blasting agent	55–85	–	0–4
Packaged gel	Blasting agent	33–40	10–15	–
Package emulsion	Explosive	60–70	0–5	0–15
Package emulsion	Explosive	60–80	0–12	–
Packaged gel	Explosive	<65	<20	<7
Water gel	Blasting agent	<80	–	<5
Water gel	Blasting agent	<75	<5	<5
Water gel	Explosive	<65	<20	<7
Water gel	Explosive	<65	<20	<7
Water gel, presplit	Explosive	<65	<20	<7
Water gel	Blasting agent	10–20	10–20	20–30**

* Data compiled from Material Safety Data Sheets.

** Ammonium perchlorate.

Perchlorate concentrations as high as several hundred µg/L have been measured in groundwater near blasting sites (MADEP, 2005). In response to perchlorate contamination in the Boxborough, Massachusetts area, a ban has been issued by the fire department on the use of perchlorate-based agents for all blasting activities in this area. In addition, the State of Massachusetts is prohibiting its own contractors from using blasting agents that contain perchlorate (Hughes, 2004).

It is theorized that misfires and/or “bad housekeeping” associated with the use of blasting agents are the primary mechanisms that result in groundwater impacts. The DoD Strategic Environmental Research and Development Program (SERDP) is currently funding studies that will attempt to quantify the amount of perchlorate originating from the detonation of blasting agents containing perchlorate (<http://www.p2pays.org/ref/22/21726.pdf>).

4.2.1.5 Sodium Chlorate

Sodium chlorate, widely used in the pulp and paper industry, often contains perchlorate as an impurity. The total annual consumption of sodium chlorate is approximately 1.2 million tons (USDOC, 2003). The pulp and paper industry uses approximately 94% of all sodium chlorate consumed in the United States to produce chlorine dioxide to bleach pulp fibers (OMRI, 2000). In addition, sodium chlorate is used as a non-selective contact herbicide and a defoliant for cotton, sunflowers, sudan grass, safflower, rice, and chili peppers (OMRI, 2000). As a defoliant, approximately 99% of sodium chlorate application is used on cotton plants in California and Arizona (PAN Pesticides Database, 2002).

Sodium chlorate is produced electrochemically by the electrolysis of aqueous sodium chloride according to the following overall equation (Betts and Dluzniewski, 1997):



The formation of perchlorate stems from anodic oxidation of chlorate during the electrochemical reaction in accordance with the following reaction (Betts and Dluzniewski, 1997):



Recent analyses of several sodium chlorate feedstocks being used for large-scale perchlorate manufacturing suggest that perchlorate is present in industrial-grade chlorate products at concentrations ranging from 50 to 230 mg/kg. Twelve samples of laboratory-grade sodium chlorate were procured and found to contain perchlorate at concentrations ranging from 1.5 to 117 mg/kg, with mean and median concentrations of 42 mg/kg and 26 mg/kg, respectively (Geosyntec, 2007).

4.2.1.6 Bleach (Hypochlorite)

Bleach or sodium hypochlorite may contain perchlorate as an impurity. Hypochlorite is widely used as a household bleach and industrial disinfectant and is also routinely used to disinfect groundwater wells. The most common type of hypochlorite/bleach solution is sodium hypochlorite, NaOCl, a greenish-yellow liquid solution. Calcium hypochlorite, a white powder, is often used for swimming pool chlorination.

Bleach is generally produced by the electrolysis of a weak brine (i.e., NaCl) solution at a pH of 10-12 via the following overall reaction:



Sodium hypochlorite solutions are not stable, and decomposition is a well-known industry problem and concern. The most prominent degradation pathway results in the production of chlorate:



This reaction is minimized during production by maintaining basic pH and keeping the temperature low.

In a recent study of bleach under various storage conditions, perchlorate concentrations increased over time in all six bleach brands tested, from a starting average of 19 µg/L to an average of 154 µg/L after six weeks of storage in the dark. When bleach samples were stored in sealed glass vessels while exposed to sunlight, the perchlorate concentrations were much higher, averaging 3,500 µg/L after 6 weeks. These results show that storage conditions, including light exposure and storage duration, significantly influence perchlorate concentrations in bleach (Geosyntec, 2007). Bleach should be stored in the dark and care should be taken to avoid oxygen and sunlight particularly if bleach is to be used to disinfect wells or irrigation equipment.

4.2.1.7 Perchloric Acid

Perchloric acid or hydrogen perchlorate is used in a wide variety of analyses including acid digestions, Kjeldahl digestions, as an oxidizing agent, as a solvent for extracting sulfide ores, and as a dehydrating agent (Geosyntec, 2005). Perchloric acid or hydrogen perchlorate is sold principally as a 72% acid solution. At room temperature, this solution is not an oxidizing agent and can be safely transported and stored. It becomes a powerful oxidizing agent when heated and used in a concentrated form, allowing for chemical reactions and production processes that can be carefully designed and controlled. This property makes perchloric acid unique among the strong acids.

Perchloric acid discharge was implicated in perchlorate detections in the Merrimack River in Massachusetts during 2004–2005. Investigations undertaken by the Town of Billerica eventually identified the source of perchlorate discharge to the municipal sewerage system: a processor of surgical and medical materials that was using approximately 833 L/month (220 gallons/month) of perchloric acid. Although only a small portion of this acid was discharged as rinse water to the sewer system, it equated to an average of 4.5 kg/day (10 lb/day) of perchlorate (MADEP, 2005).

4.2.2 Natural Sources of Perchlorate

Natural sources of perchlorate include its occurrence in Chilean nitrate and in other mineral deposits. Natural perchlorate is believed to be primarily of atmospheric origin, although other reactions may also contribute to its formation.

4.2.2.1 Atmospheric Origin of Perchlorate

A current theory regarding the origin of naturally occurring perchlorate in the environment is that it is generated via atmospheric processes (Bao and Gu, 2004). While the exact mechanism for natural perchlorate formation is unknown, it has been suggested that chloride, possibly in the form of sodium chloride from the sea or land-based chloride compounds, reacts with atmospheric ozone to create perchlorate. This process probably occurs over much of the earth and is analogous to nitrate formation in the atmosphere (Walvoord et al., 2003). In addition, lightning may play a role in the synthesis of some atmospherically-produced perchlorate (Dasgupta et al., 2005).

Following atmospheric formation, perchlorate returns to the earth's surface dissolved in precipitation. Dasgupta et al. (2005) analyzed precipitation samples and found perchlorate present in 70% of the samples using preconcentration-preelution ion chromatography/mass spectrometry (IC/MS), with concentrations ranging from below the detection limit to 1.6 µg/L. In arid environments, where the rate of deposition exceeds the rate of dissolution by ongoing precipitation, perchlorate can be incorporated into geologic formations as discussed further in the next two subsections. Recent isotopic studies have suggested that nitrate and perchlorate in the Atacama Desert were formed atmospherically (Böhlke et al., 1997; Michalski et al., 2004). Moreover, perchlorate derived from Atacama nitrate ore has been shown to have significant excess in the ¹⁷O isotope, an indication of atmospheric production involving ozone (Bao and Gu, 2004). Isotopic analyses to distinguish natural sources from man-made sources are discussed in more detail in [Section 4.3](#).

4.2.2.2 Chilean Nitrate

The presence of perchlorate in the caliche deposits of the Atacama Desert region of Chile, one of the most arid regions of the world, has been documented for over 100 years (Michalski et al., 2004; Schilt, 1979). Perchlorate was first discovered in the caliche deposits in 1886. This discovery was followed in 1896 by the confirmation of perchlorate in “Chilean saltpeter” (sodium nitrate) over the widely varying concentration range of 0 to 6.79% (Schilt, 1979). Since the mid 1800s, Chilean nitrate ore has been imported into the United States for use as fertilizer, for saltpeter used in gunpowder, and as a feedstock for making nitric acid, explosives, fireworks, and additional end products (ITRC, 2005). Historical agronomic literature indicates that Chilean nitrate fertilizers were widely used in citrus, cotton, and tobacco farming in the early to mid 1900s (Howard, 1931; Goldenwieser, 1919; Mehring, 1943).

Little attention was paid to the natural occurrence of perchlorate in Chilean nitrate until the emergence of perchlorate as a chemical of concern at military sites. In 2000, a study of perchlorate in agricultural fertilizers conducted by the USEPA concluded that the occurrence of perchlorate in fertilizer was restricted to fertilizer products derived from Chilean nitrate produced by SQM Corporation and that all fertilizers derived partially or completely from Chilean nitrates contained appreciable perchlorate (Urbansky et al., 2001a, 2001b).

Chilean nitrate fertilizer is still produced by SQM Corporation and makes up 0.14% of the total annual fertilizer application in the United States (Urbansky et al., 2001a). It is sold commercially as “Bulldog Soda” and is primarily used in a few niche markets and specialty products. Currently, world production is 900,000 tons/year, of which 75,000 tons are sold to American farmers for use on cotton, tobacco, and fruit crops (Urbansky et al., 2001a; Renner, 1999). SQM reports that the perchlorate concentration in Chilean nitrate fertilizer has been reduced to 0.01% through changes in the refinement processes since 2002 (Urbansky et al., 2001b).

4.2.2.3 Other Natural Mineral Sources

A study of perchlorate in geologic materials from environments with similar characteristics to the Atacama Desert was recently conducted by the U.S. Geological Survey (USGS). Evaporite and evaporite-related minerals and surface crusts of various ages from North and South America were collected and analyzed by Orris et al. (2003). Samples were originally analyzed by IC, which is non-specific for perchlorate, and perchlorate was found in approximately 50% of the mineral samples tested, including several samples of potash ores and playa crusts (Orris et al., 2003). Reanalysis of these original samples plus several new samples by IC-MS-MS has shown that all evaporite samples containing potassium and/or magnesium contain perchlorate, typically in the few to tens of $\mu\text{g/L}$ (Gu and Coates, 2006). The arid environments in which the samples were collected served to concentrate perchlorate and prevent anaerobic conditions that would promote perchlorate biodegradation.

This USGS study highlights the widespread occurrence of natural perchlorate and the importance of evaporative concentration in producing environmentally significant concentrations of perchlorate. This point is illustrated by several recent reports showing the presence of perchlorate in soils and groundwater over more than 104,000 square kilometers (40,000 square miles) of the arid high plains region of northwest Texas (Jackson et al., 2005, 2006; Rajagopalan et al., 2006), in unsaturated soils located throughout the southwestern United States (Rao et al., 2007) and in ancient groundwater from the Rio Grande Basin of New Mexico (Plummer et al., 2006).

4.3 DISTINGUISHING SYNTHETIC FROM NATURAL PERCHLORATE USING STABLE ISOTOPE ANALYSIS

4.3.1 Stable Isotope Analysis

Isotopes of an element have the same number of protons and electrons but a different numbers of neutrons. Stable isotopes (as opposed to radioactive isotopes) are not subject to nuclear decay. The difference in atomic mass among stable isotopes causes these atoms to exhibit slightly different physical and chemical traits. These differences are particularly notable for light elements, including many of geochemical interest such as H, C, N, O, Cl and S. The differing masses of stable isotopes (and the resulting differences in their charge to mass ratio) result in isotopic “fractionation” whereby various physical, chemical, and biological processes alter isotopic ratios. These fractionation processes often provide unique isotopic signatures, which are indicative of the origin and/or geochemical behavior of a compound in the environment (Sharp, 2007; Clark and Fritz, 1997; Kendall and Caldwell, 1998).

Stable isotopes are generally quantified via isotope ratio mass spectrometry (IRMS). This technique utilizes a mass spectrometer that is designed specifically to measure isotopic proportions of a given element, rather than to determine exact molecular quantities. In general, an element must be present as a pure gas (e.g., O₂, CO₂, CO, N₂O) prior to IRMS analysis. A number of different techniques, including combustion, catalytic oxidation and enzymatic conversion, have been developed to convert liquids, solids and gaseous samples of interest into pure gases suitable for IRMS. An overview of IRMS, including sample preparation techniques, is provided by Sharp (2007).

The stable isotope ratios of light elements gained from IRMS are generally reported relative to those of established reference materials as “delta” (δ) values and measured in parts-per-thousand (denoted “‰” = per mil). As an example, the expression used to report relative abundances of Cl isotopes ($^{37}\text{Cl}/^{35}\text{Cl}$) is provided below (Eq. 4.1 and Eq. 4.2).

$$\delta \text{ (in ‰)} = \left[\frac{R_x - R_s}{R_s} \right] \times (1000) \quad (\text{Eq. 4.1})$$

Where: R = ratio heavy/light isotope (e.g., $^{37}\text{Cl}/^{35}\text{Cl}$)

R_x = sample (e.g., $^{37}\text{Cl}/^{35}\text{Cl}$ in environmental sample)

R_s = standard (e.g., $^{37}\text{Cl}/^{35}\text{Cl}$ in “standard mean ocean chloride”)

Thus for Cl isotopes:

$$\delta^{37}\text{Cl}_{\text{sample}} \text{ (in ‰)} = \left[\frac{\left(\frac{^{37}\text{Cl}}{^{35}\text{Cl}} \right)_{\text{sample}} - \left(\frac{^{37}\text{Cl}}{^{35}\text{Cl}} \right)_{\text{standard}}}{\left(\frac{^{37}\text{Cl}}{^{35}\text{Cl}} \right)_{\text{standard}}} \right] \times (1000) \quad (\text{Eq. 4.2})$$

The ratio of the heavy to the light isotope is used by convention, and for the case of Cl, the established international reference material is standard mean ocean chloride (SMOC). A positive delta value indicates that the sample is enriched in the heavy isotope relative to the standard, while a negative delta value shows that the sample contains less of the heavy isotope. For example, if $\delta^{37}\text{Cl}$ is reported as +15‰, this

means that the ratio of $^{37}\text{Cl}/^{35}\text{Cl}$ is 15 parts-per-thousand (or 1.5%) higher in the sample of interest than in SMOC (for which $\delta^{37}\text{Cl}$ is 0.00 ‰).

Stable isotope ratio analysis has been used for several decades by earth scientists to better understand natural geological, geochemical and hydrogeological processes (e.g., Sharp, 2007; Clark and Fritz, 1997). More recently, stable isotope ratio analysis has been applied as an analytical tool to assess the origin and disposition of common industrial and military pollutants. For example, advances in the measurement and application of the stable isotope ratios of carbon and chlorine in chlorinated solvents (Holt et al., 1997; Holt et al., 2001; Drenzek et al., 2002; Jendrzewski et al., 1997) have led to new approaches for characterizing the behavior of these compounds in contaminated groundwater aquifers (Sturchio et al., 1998; Dayan et al., 1999; Song et al., 2002; Hunkeler et al., 1999; Hunkeler et al., 2005). Similar evaluations also have been performed with nitrogen isotopes to track the fate of explosives such as cyclotrimethylenetrinitramine (also termed **Royal Demolition eXplosive** or RDX) and 2,4,5-trinitrotoluene (TNT) in the environment (Dignazio et al., 1998). Moreover, the development of combined gas chromatography-isotope ratio mass spectrometry (GCIRMS) now provides a technique to gain isotopic ratios of individual chemicals from complex mixtures (Philip, 2002). This approach has been used to determine the origin of various hydrocarbons, including crude oils (Mansuy et al., 1997), gasoline components (Kelly et al., 1997), polycyclic aromatic hydrocarbons (Hammer et al., 1998) and gasoline oxygenates (Smallwood et al., 2001).

4.3.2 Stable Isotope Methods for Perchlorate

Both of the atoms composing a perchlorate molecule (Cl and O) have multiple isotopes. Chlorine has three naturally occurring isotopes, one of which is a long-lived radioactive species (^{36}Cl) and two of which are stable (^{35}Cl and ^{37}Cl , occurring at abundances of 75.77% and 24.23% of naturally occurring chlorine, respectively) (USGS, 2006a). Oxygen has three stable isotopes, ^{16}O , ^{17}O and ^{18}O . These occur in the following percentages in nature: ^{16}O (99.63%), ^{17}O (0.0375%) and ^{18}O (0.1995%) (USGS, 2006b). Techniques to quantify the stable isotope ratio of chlorine ($^{37}\text{Cl}/^{35}\text{Cl}$) in the perchlorate molecule were reported by Ader et al. (2001) and Sturchio et al. (2003). Subsequently, methods for analysis of $^{18}\text{O}/^{16}\text{O}$ and $^{17}\text{O}/^{16}\text{O}$ in perchlorate were described (Bao and Gu, 2004; Böhlke et al., 2005).

4.3.2.1 Sample Preparation and Analysis

For determination of $\delta^{37}\text{Cl}$ from pure perchlorate salts, the sample is combusted to produce Cl_2 , which is then dissolved and re-precipitated as AgCl . The AgCl is subsequently reacted with CH_3I to produce CH_3Cl , which is further purified and analyzed by IRMS for determination of $\delta^{37}\text{Cl}$ (Sturchio et al., 2003; Böhlke et al., 2005). The average precision of this technique is reported as approximately 0.03 ‰. For determination of $\delta^{18}\text{O}$, the perchlorate salt is initially reacted with glassy carbon at high temperature to produce CO , which is then purified by GC and analyzed by IRMS (Böhlke et al., 2005). Measurement of ^{17}O (which is generally reported as $\Delta^{17}\text{O}$; see [Section 4.3.2.2](#)) is performed by combusting the perchlorate salt to produce O_2 , which is subsequently analyzed by IRMS. The average variability for measurements of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$, are 0.2 ‰ and 0.1 ‰, respectively (Böhlke et al., 2005).

In order to analyze perchlorate from environmental samples, the anion must first be collected in sufficient quantity (~10 mg), then extracted and purified. For soil samples, the perchlorate is initially extracted with water, and then the extract is passed through small columns of perchlorate-specific anion exchange resin to remove it from solution (Bao and Gu, 2004). A similar approach has been used to collect dilute perchlorate from groundwater. In this case however, the groundwater is pumped from a well (or collected in a secondary container), and then passed through the ion exchange column in the volume required for ~10 mg of perchlorate to be trapped on the resin (Sturchio et al., 2006; Böhlke et al., 2005). Once sufficient perchlorate has been collected on a resin column (from water or extracts), an aqueous solution containing tetrachloroferrate is passed through the column. This ion is preferentially bound and displaces the perchlorate ions from the resin (Gu et al., 2001). The perchlorate-bearing solution is subsequently subjected to a series of purification steps which ultimately result in a pure precipitate of either KClO_4 or CsClO_4 , both of which are relatively insoluble. After verification of the purity of this material, the salts can be prepared and analyzed by IRMS for determination of $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and/or $\Delta^{17}\text{O}$, as described previously. It is critical to ensure that pure perchlorate salts are analyzed as small quantities of oxygen or chlorine-containing impurities can alter the isotopic ratios for these elements.

4.3.2.2 Isotopic Results to Date

Isotopic ratios of Cl and O were recently reported for a variety of different perchlorate salts of laboratory, commercial and military origin as well as for several natural perchlorate samples and fertilizers derived from the Atacama Desert of Chile (Sturchio et al., 2006; Böhlke et al., 2005). Additional samples obtained from road flares, fireworks, chlorate herbicides, bleach, propellants, and other materials are presently being collected and analyzed as part of a DoD Environmental Security Technology Certification Program (ESTCP) project (Hatzinger et al., 2008). Current data from isotopic analyses reveal that the $^{37}\text{Cl}/^{35}\text{Cl}$ isotope ratio in naturally occurring perchlorate is consistently and significantly lower than that of man-made perchlorate (Figure 4.1). Based on analyses to date, the mean $\delta^{37}\text{Cl}$ value (\pm standard deviation) for synthetic perchlorate is 0.6 ± 1.0 ‰ ($n = 18$) compared to -12.6 ± 2.0 ‰ for natural perchlorate ($n = 6$) (Sturchio et al., 2006; unpublished data from Hatzinger et al., 2008). The values for synthetic perchlorate which range from -3.1 to ± 1.6 ‰, are reasonably close to that of standard ocean chloride (0.00 ‰), reflecting the fact that synthetic perchlorate is synthesized electrochemically from NaCl by a process that is efficient and yields little isotopic fractionation (Sturchio et al., 2006). By comparison, the consistently low $\delta^{37}\text{Cl}$ values for Chilean-derived natural perchlorate confirm a different mode of formation of this material, which, based on the corresponding $\Delta^{17}\text{O}$ values (see Figure 4.3 and supporting text) suggests oxidation of volatile chlorine by ozone (which is known to have elevated ^{17}O values) in the upper atmosphere (Bao and Gu, 2004; Dasgupta et al., 2005).

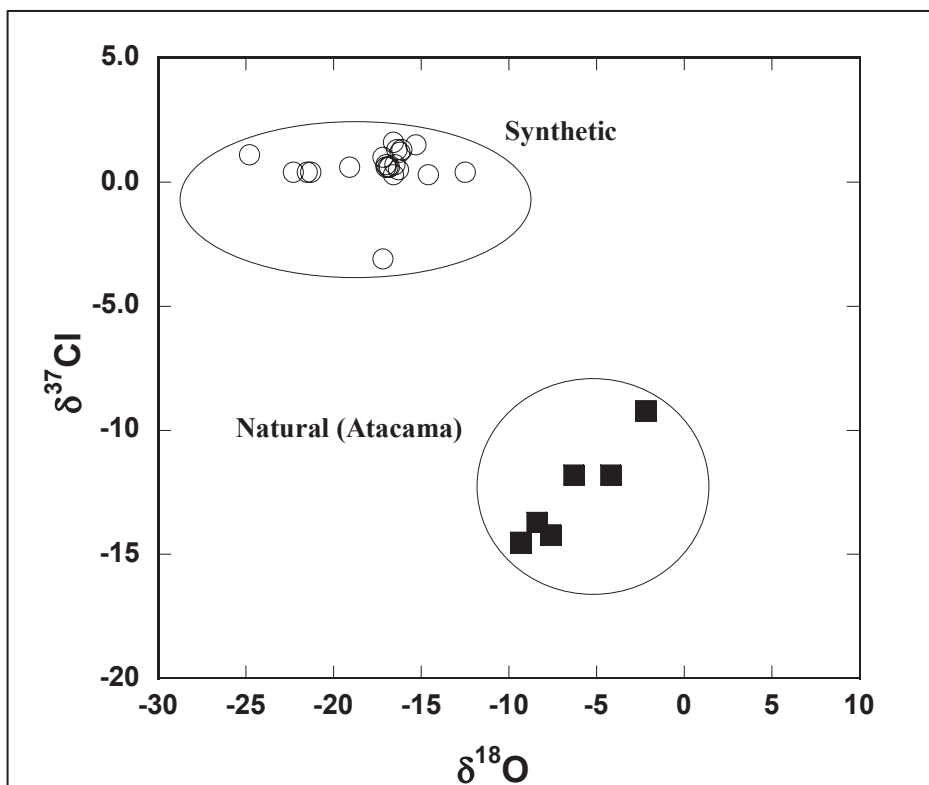


Figure 4.1. Comparison of $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ for various sources of synthetic perchlorate and for natural perchlorate derived from the Atacama Desert of Chile (from Sturchio et al., 2006 and unpublished data from Hatzinger et al., 2008)

In contrast to the $^{37}\text{Cl}/^{35}\text{Cl}$ data, the $^{18}\text{O}/^{16}\text{O}$ isotope ratio in natural perchlorate is appreciably higher than in the synthetic materials. The average $\delta^{18}\text{O}$ for natural perchlorate in six samples analyzed to date is -6.3 ± 2.7 ‰ compared to -17.8 ± 3.2 ‰ for 18 samples of synthetic perchlorate. The $\delta^{18}\text{O}$ values in the synthetic samples vary from -12.5 to -24.8 ‰, which is a significantly broader range than that for $\delta^{37}\text{Cl}$. Interestingly, however, the $\delta^{18}\text{O}$ values from different samples produced by the same manufacturer (e.g., KClO_4 and NaClO_4 from the same facility) group very tightly together (Figure 4.2). The oxygen in the perchlorate molecule is derived from H_2O during the electrochemical formation of perchlorate. This process is less efficient than for chloride, and a 7 ‰ isotopic enrichment of oxygen in the perchlorate molecule compared to the source water has been reported (Sturchio et al., 2006). However, the limited information gathered so far (i.e., data presented in Figure 4.2) suggest that $\delta^{18}\text{O}$ data may be useful for distinguishing synthetic perchlorate sources.

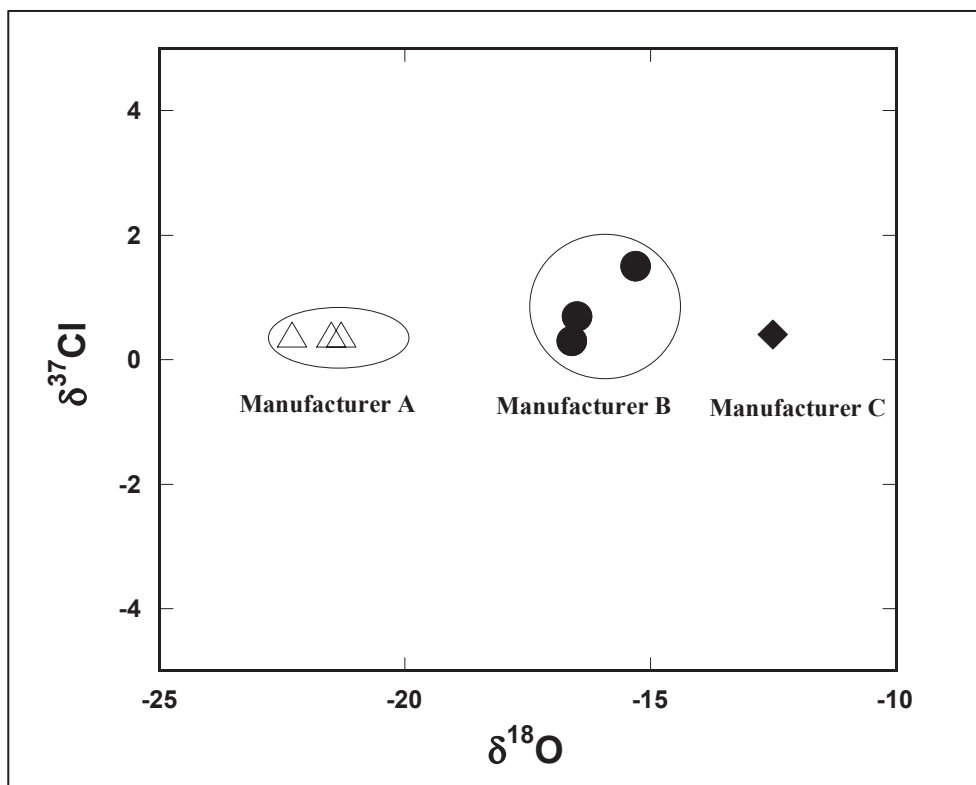


Figure 4.2. Comparison of $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ for three sources of synthetic perchlorate. Analytical error is approximately ± 0.3 per mil (modified from Sturchio et al., 2006)

Perhaps the most important isotopic difference between natural perchlorate derived from Chile and synthetic perchlorate comes from analysis of ^{17}O . There appears to be a consistent and reproducible excess of ^{17}O in natural perchlorate, relative to the abundance that would be consistent with simple mass-dependent isotopic fractionation processes (Bao and Gu, 2004; Böhlke et al., 2005; Sturchio et al., 2006). A similar enrichment is not seen in synthetic perchlorate. More simply, there is an expected ratio of ^{17}O to ^{18}O for terrestrial materials ($\delta^{17}\text{O} = 0.525 \delta^{18}\text{O}$) and natural perchlorate (but not synthetic perchlorate) shows a significant deviation from this ratio. The excess ^{17}O in natural perchlorate is shown in Figure 4.3 as $\Delta^{17}\text{O}$, which represents the deviation in ^{17}O from the expected value. The equation used to derive $\Delta^{17}\text{O}$ is as follows:

$$\Delta^{17}\text{O} (\text{‰}) = \left[\left(\frac{1 + \delta^{17}\text{O}/1000}{(1 + \delta^{18}\text{O}/1000)^{0.525}} \right) - 1 \right] \times 1000 \quad (\text{Eq. 4.3})$$

As shown in Figure 4.3, synthetic samples analyzed to date have a $\Delta^{17}\text{O}$ value in the vicinity of 0 ($0.02 \pm 0.05 \text{‰}$), which is as expected for man-made materials. In contrast, the mean $\Delta^{17}\text{O}$ of natural samples averages $+9.6 \text{‰}$. As previously noted, the elevated $\Delta^{17}\text{O}$ in the Chilean perchlorate is consistent with atmospheric formation (Bao and Gu, 2004; Dasgupta et al., 2005).

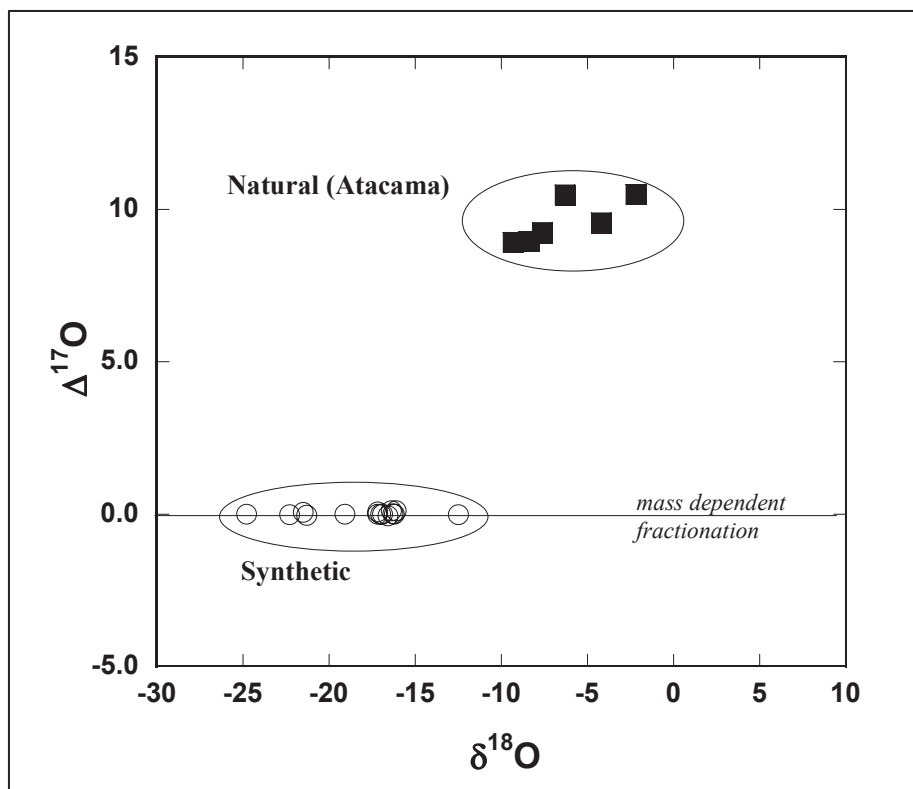


Figure 4.3. Comparison of $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ for synthetic perchlorate and natural perchlorate derived from the Atacama Desert of Chile (from Sturchio et al., 2006 and unpublished data from Hatzinger et al., 2008)

Current data suggest that stable isotope analysis of Cl and O represents a practical forensic tool to distinguish natural perchlorate of Chilean origin from synthetic perchlorate. A recent study also shows that isotopic fractionation due to biodegradation of perchlorate is unlikely to cause isotopic signatures of synthetic and Chilean-derived perchlorate to overlap (Sturchio et al., 2007). The potential utility of stable isotopes to distinguish perchlorate from different synthetic sources is less clear. It appears that $\delta^{37}\text{Cl}$ values are too similar among different samples to be of use, but that $\delta^{18}\text{O}$ may differ enough in some instances to distinguish source materials. Additional studies are required to quantify the variability in $\delta^{18}\text{O}$ values between batches of perchlorate from a single manufacturing plant, and to further quantify differences in $\delta^{18}\text{O}$ among different production plants in the United States and abroad. Natural perchlorate also has been detected in evaporites and mineral deposits in the United States and Canada (see Section 4.2.2) as well as in surface soils throughout the southwestern United States (Rajagopalan et al., 2006; Rao et al., 2007). The isotopic values for Cl and O in natural perchlorate collected from evaporites in the Mojave Desert and other locations are presently under investigation, but results are not yet available (Hatzinger et al., 2008). Thus, it is currently unknown whether perchlorate derived from these materials is isotopically distinct from either synthetic material or Chilean-derived perchlorate.

4.4 ANALYTICAL METHODS FOR PERCHLORATE ANALYSIS

A variety of methods exist for the analysis of perchlorate in groundwater. The DoD Perchlorate Handbook (DoD EDQW, 2007) discusses perchlorate sampling and analysis. The following sections discuss the DoD-approved analytical methods for perchlorate, other widely used USEPA methods, and their respective detection limits and limitations.

4.4.1 DoD-Approved Analytical Methods

According to recent DoD perchlorate policy, only methods employing MS are to be used for environmental restoration/cleanup or range assessment projects. Methods employing IC with conductivity detection alone (e.g., USEPA Methods 314.0 and 314.1) are not appropriate for these purposes. A summary of each of the DoD-recommended perchlorate methods, their applicability, limitations and target reporting limits are provided in Table 4.2 (DoD EDQW, 2007). Of the methods listed in Table 4.2, only USEPA Methods 6850 and 6860 have been approved by the DoD for groundwater analysis. The DoD has approved methods 331.0 and 332.0 for analysis of drinking water. These methods are briefly described as follows:

4.4.1.1 USEPA Methods 6850 (HPLC/ESI/MS) and 6860 (IC/ESI/MS)

The USEPA Office of Solid Waste (OSW) has developed and validated two new methods for the determination of perchlorate in various environmental media, including soil, sludge, wastewater and high salt water. Method 6850 uses high performance liquid chromatography/electrospray ionization/mass spectrometry (HPLC/ESI/MS) and Method 6860 uses ion chromatography/electrospray ionization/mass spectrometry (IC/ESI/MS). The Methods 6850 and 6860 were published in January 2007 and are available on the USEPA OSW Methods Web Site (<http://www.epa.gov/epaoswer/hazwaste/test/new-meth.htm#6850>).

4.4.1.2 USEPA Method 331.0—Liquid Chromatography Electrospray Ionization Mass Spectrometry

Method 331.0 is a liquid chromatography/electrospray ionization/mass spectrometry (LC/ESI/MS) method for the determination of perchlorate in raw and finished drinking water (USEPA, 2005a). In this method, water samples are collected in the field using a sterile filtration technique. Prior to analysis, isotopically enriched perchlorate is added to the sample as an internal standard. The sample is injected without cleanup or concentration onto a chromatographic column, which separates perchlorate from other anions and background interferences. Perchlorate is subsequently detected by negative electrospray ionization mass spectrometry and is quantified using the internal standard technique. The reporting limit in water is 0.02 µg/L (USEPA, 2005a).

4.4.1.3 USEPA Method 332.0—Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry

This IC/MS method is an ion chromatography method with an MS and electrospray interface (USEPA, 2005b). The method requires the use of a suppressor to avoid inorganic salt buildup and uses a conductivity meter to check its efficiency. It uses m/z 99 and 101 ions for peak identification of perchlorate. The advantages of IC/MS are increased sensitivity and increased specificity. One should be aware that high sulfate content (~1000 mg/L) will elevate the baseline at m/z 99 because it elutes prior to perchlorate. However, even with a sulfate concentration of 1000 mg/L, 0.1 µg/L perchlorate can still be detected. If the baseline is elevated, there is a mandatory cleanup step to remove the sulfate prior to sample injection. The quantitation limit in water is reported to be 0.1 µg/L (USEPA, 2005b; ITRC, 2005).

Table 4.2. DoD Recommended Methods for Perchlorate Analysis*

Method (Technique)	Applicability	Limitations	Target Reporting Limits
USEPA Method 6850 (LC/ESI/MS)	<ul style="list-style-type: none"> Environmental Restoration Operational Ranges Wastewater Aqueous samples including those with high TDS Soil and sludge samples 	<ul style="list-style-type: none"> Requires a proprietary column 	<ul style="list-style-type: none"> Drinking Water and Groundwater: 0.2 µg/L Soil: 2 µg/kg Wastewater: <1 µg/L
USEPA Method 6860 (IC/ESI/MS) (IC/ESI/MS/MS)	<ul style="list-style-type: none"> Environmental Restoration Operational Ranges Wastewater Aqueous samples including those with high TDS Soil and sludge samples 	<ul style="list-style-type: none"> Pretreatment recommended for samples with high concentrations of sulfate 	<ul style="list-style-type: none"> Drinking Water and Groundwater: 0.2 µg/L Soil: 2 µg/kg Wastewater: <1 µg/L
USEPA 331.0 (LC/MS) (LC/MS/MS)	<ul style="list-style-type: none"> DoD-Owned Drinking Water Systems (proposed for UCMR 2) Applicable to drinking water samples, including those with high TDS 	<ul style="list-style-type: none"> Pretreatment recommended for samples with high concentrations of sulfate (proposed for UCMR 2) Validated for drinking water samples only 	<ul style="list-style-type: none"> Drinking Water: 0.1 µg/L (LC/MS) 0.02 µg/L (LC/MS/MS)
USEPA 332.0 (IC/MS) (IC/MS/MS)	<ul style="list-style-type: none"> DoD-Owned Drinking Water Systems (proposed for UCMR 2) Applicable to drinking water samples, including those with high TDS 	<ul style="list-style-type: none"> Pretreatment recommended for samples with high concentrations of sulfate (proposed for UCMR 2) Validated for drinking water samples only 	<ul style="list-style-type: none"> Drinking Water: 0.1 µg/L (IC/MS) 0.02 µg/L (IC/MS/MS)

TDS = Total dissolved solids

UCMR = Unregulated Contaminant Monitoring Rule

* Adapted from DoD Environmental Data Quality Workgroup *DoD Perchlorate Handbook*, August 2007 (DoD EDQW, 2007).

4.4.2 Other Analytical Methods for Perchlorate

Table 4.3 provides information about other widely used perchlorate methods that are not recommended for groundwater analysis in accordance with the DoD Perchlorate Policy (DoD EDQW, 2007). These methods include USEPA Method 314.0 (IC), USEPA Method 314.1, and USEPA Method 9058 (IC). The methods are discussed briefly below.

Table 4.3. Other Available Methods for Perchlorate Analysis*

Method (Technique)	Applicability	Limitations	Target Reporting Limits
USEPA 314.0 (IC)	<ul style="list-style-type: none"> Mandatory for Drinking Water samples reported under UCMR 1 Aqueous samples with low dissolved solids (conductivity <1 milliSiemens per centimeter [mS/cm] TDS) and chloride, sulfate, and carbonate concentrations < 100 mg/L each Not proposed for UCMR 2 	<ul style="list-style-type: none"> Subject to false positives due to lack of specificity of the conductivity detector Validated for drinking water samples only Inappropriate for use in samples with high TDS 	Drinking Water 4 µg/L
USEPA 314.1 (IC)	<ul style="list-style-type: none"> Drinking Water samples Proposed option for UCMR 2 	<ul style="list-style-type: none"> Reduces but does not eliminate the potential for false positives Validated for drinking water samples only Long analytical run time Limited commercial availability Requires confirmation of perchlorate results above reporting limit when used for UCMR 2 	Drinking Water 0.13 µg/L
USEPA Method 9058 (IC)	<ul style="list-style-type: none"> Aqueous samples with low dissolved solids (conductivity <1 mS/cm TDS) and chloride, sulfate, and carbonate concentrations <100 mg/L each 	<ul style="list-style-type: none"> Subject to false positives due to lack of specificity of the conductivity detector Inadequate quality control criteria Method is expected to undergo significant revision prior to publication 	Low TDS Groundwater 4 µg/L

* Reproduced from DoD Environmental Data Quality Workgroup *DoD Perchlorate Handbook*, August 2007 (DoD EDQW, 2007).

4.4.2.1 USEPA Method 314.0—Ion Chromatography

USEPA Method 314.0 (USEPA, 1999b), an ion chromatography method, has been the most-widely used method to date. Aqueous samples are introduced into an ion chromatograph and the perchlorate ion is separated from other ions based on its affinity for the chromatographic column. A conductivity detector is used to differentiate the perchlorate ion based solely on retention times.

The use of Method 314.0 involves many sources of uncertainty including (1) non-specificity for perchlorate, (2) possible interferences, (3) a relatively high method reporting limit (MRL) of 4 µg/L and (4) absence of systematic validation in matrices other than potable water (DoD EDQW, 2007). It should be emphasized that USEPA Method 314.0 was developed for perchlorate detection in drinking water, not other matrices. In most instances this method provides reliable results when applied to drinking water, and it is by far the least expensive and most widely available commercial analytical method for this purpose. However, because no other method for perchlorate detection was available until a few years ago, USEPA Method 314.0 has been applied to many different matrices for which it was not designed, including soil extracts, saline waters and industrial and residential wastewaters. Even in these cases, the method has generally provided dependable results, although as noted below, specific interferences have been observed. Most of these interferences would not typically be associated with drinking water, but rather are an artifact of application of the method to other types of samples.

Sample matrices with high concentrations of common anions, such as chloride, sulfate and carbonate, can destabilize the baseline in the retention time window for perchlorate and also increase or suppress the response of the detector to perchlorate. The concentration of these anions can be indirectly assessed by monitoring the conductivity of the matrix. The laboratory must determine its instrument-specific matrix conductivity threshold (MCT), and all sample matrices must be monitored for conductivity prior to analysis. When the MCT is exceeded, sample dilution and/or pretreatment must be performed. However, sample dilution leads to elevated reporting limits, and pretreatment to remove potential interfering ions at low concentrations has the potential to reduce the actual perchlorate content of the sample (USEPA, 1999b).

There is evidence of cases where Method 314.0 has resulted in the reporting of false positives, falsely elevated concentrations and false negatives when applied to non-drinking water matrices. For example, investigation of polluted groundwater at an industrial site in the Henderson, Nevada, area showed that the compound p-chlorobenzenesulfonate (p-CBS) co-elutes with perchlorate during analysis using USEPA Method 314.0, causing falsely elevated perchlorate concentrations (Johnson et al., 2003). In addition, data from a study comparing perchlorate analytical methods for analysis of groundwater at 13 locations from the United States and Canada using USEPA 314.0 compared to analysis by IC/MS (Geosyntec, 2007). Six samples were polluted groundwater collected near residential or public septic systems, two were from a plume near a dichlorodiphenyltrichloroethane (DDT) manufacturing facility, one was from a landfill and one was from a site where groundwater was known to contain surfactants. The interfering compounds were not positively identified in any of the cases of false positives in groundwater near septic systems, but this study suggests that Method 314.0 is not appropriate for analysis of sewage or surfactant impacted water. p-CBS was identified by the MS analyses in four of the other samples that had falsely high detects. p-CBS is a by-product of DDT manufacturing and is used as a solvent in some paints (Johnson et al., 2003).

4.4.2.2 USEPA Method 314.1—Inline Column Concentration/Matrix Elimination Ion Chromatography with Suppressed Conductivity Detection

USEPA Method 314.1 is intended to increase sensitivity, tolerance of TDS and selectivity through the use of a confirmation column and in-line concentration (USEPA, 2005c). Water samples are collected in the field using a sterile filtration technique. The sample, without cleanup, is concentrated onto the concentrator/trap column, which is placed in the sample loop position and binds perchlorate more strongly than other matrix anions. The sample matrix anions are rinsed from the concentrator column with 1 mL of 10 millimolar (mM) NaOH. This weak rinse solution allows the concentrator to retain the perchlorate while eluting the majority of the matrix anions, which are directed to waste. The concentrator column is switched in-line and the perchlorate is eluted from the concentrator column with a 0.50 mM NaOH solution. Following elution from the concentrator, the perchlorate is refocused onto the front of the guard column. The eluent strength is then increased to 65 mM NaOH, which elutes the perchlorate from the guard column and onto the analytical column where perchlorate is separated from other anions and remaining background interferences. Perchlorate is subsequently detected using suppressed conductivity and is quantified using an external standard technique. Confirmation of any perchlorate concentration reported at or above the MRL on the primary column is accomplished with a second analytical column that has a dissimilar separation mechanism (USEPA, 2005c).

4.4.2.3 USEPA Method 9058—Ion Chromatography with Chemical Suppression Conductivity Detection

USEPA Method 9058 is the USEPA's OSW IC method and is essentially the same as Method 314.0, with the exception of the MCT requirement. The method is stated to perform adequately on water samples with conductivities up to 1000 microsiemens per centimeter ($\mu\text{S}/\text{cm}$) and is potentially applicable to surface water, mixed domestic water, and industrial wastewaters. The limitations described above for Method 314.0 apply similarly to Method 9058. OSW is in the process of revising the November 2000 version of Method 9058 given the known interferences and the high probability of false positive and false negative results. Optimization of the method may include an extraction procedure for solids, making the method applicable for high TDS aqueous samples, lowering the detection limit to sub- $\mu\text{g}/\text{L}$ levels, better separation, and minimization of false positive and negative results. After the revised method is drafted, an interlaboratory validation study will be conducted (USEPA, 2000; ITRC, 2005).

4.5 SITE CHARACTERIZATION FOR PERCHLORATE TREATMENT

In addition to characterizing the concentration and distribution of perchlorate, several other chemical and geochemical parameters should be assessed during evaluation of a perchlorate-contaminated site as they may play a role in the effectiveness of perchlorate treatment. Table 4.4 presents a list of chemical and geochemical indicators and the importance of their measurement for either bioremediation or ion exchange, the two most widely used *ex situ* treatment technologies for perchlorate-contaminated water. A more detailed discussion of groundwater characterization and monitoring during *in situ* bioremediation is provided in Chapter 3, Principles of Perchlorate Treatment.

Table 4.4. Additional Chemical and Geochemical Parameters to Measure during Site Characterization

Parameter	Rationale
Oxidation-Reduction Potential (ORP)	Low ORP or anaerobic groundwater required for bioremediation. Addition of sufficient electron donor to stimulate bioremediation without achieving highly reduced, sulfate reducing conditions.
pH	pH outside range of 5 to 8.5 is inhibitory to perchlorate-degrading bacteria.
Specific Conductance	High values indicative of high TDS, which can interfere with effectiveness of ion exchange.
Ferrous Iron and Manganese	Measured during bioremediation. Minimize mobilization through control of ORP and amount of electron donor added.
Nitrate	High nitrate levels will require additional electron donor for reduction during bioremediation and may interfere with removal of perchlorate via ion exchange.
Sulfate, Chloride	High sulfate and chloride levels may compete with perchlorate treatment via ion exchange.
Total Dissolved Solids (TDS)	Gross measure of anions such as sulfate, chloride etc. High levels may compete with perchlorate treatment via ion exchange.
Bicarbonate, Carbonate	High bicarbonate and carbonate levels may compete with perchlorate treatment via ion exchange.
Bromide	High bromide levels may compete with perchlorate treatment via ion exchange.

The most common co-contaminant found at perchlorate-contaminated sites is nitrate. Nitrate concentrations are generally far greater than those of perchlorate; however, nitrate is commonly removed along with perchlorate during *in situ* or *ex situ* bioremediation because most perchlorate-reducing bacteria are denitrifiers as well (Logan, 2001; Coates and Achenbach, 2004). Other anions, such as sulfate and carbonate, generally do not adversely impact perchlorate biodegradation, as perchlorate is generally reduced before sulfate. The anions sulfate, nitrate, bicarbonate, carbonate, and bromide compete with perchlorate during the ion exchange process (ITRC, 2005). Ion exchange resins have differing affinities for each of these anions, so levels of each must be considered when selecting resins and determining system operating parameters. Additional information on ion exchange for perchlorate treatment is provided in Boodoo (2003) and Gu and Coates (2006).

4.6 SUMMARY

Over the past several years, various sources of perchlorate in groundwater have been identified. These include various natural sources (e.g., Chilean nitrate, other evaporite deposits, and precipitation) as well as a host of anthropogenic sources such as fireworks, road flares, sodium chlorate, bleach, and perchloric acid. SERDP Project ER-1429 is attempting to identify key co-contaminants to aid in source identification. In addition, current data suggest that stable isotope analysis of Cl and O represents a practical forensic tool to distinguish natural perchlorate of Chilean origin from synthetic perchlorate. The potential utility of stable isotopes to distinguish perchlorate from different synthetic sources is less clear as it appears that $\delta^{37}\text{Cl}$ values are too similar among different samples to be of use. However, $\delta^{18}\text{O}$ may differ enough in some instances to distinguish source materials.

Several analytical methods are available to analyze perchlorate in environmental media. However, the DoD Environmental Data Quality Workgroup specifically recommends the use of IC/MS or LC/MS methods (e.g., USEPA Methods 6850 and 6860) for contaminated groundwater because of the potential for false positives with ion chromatography methods that were initially developed for drinking water. For example, the presence of sulfate, carbonate, chloride, and p-CBS have the potential to interfere with IC methods. Depending on the proposed groundwater treatment technology, other anions, such as sulfate, nitrate, bicarbonate, carbonate, and bromide, also should be measured, as the presence of these anions can potentially adversely impact treatment performance.

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