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Validation of Chlorine and Oxygen Isotope Ratio Analysis To Differentiate Perchlorate Sources and To Document Perchlorate Biodegradation

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14. ABSTRACT

Perchlorate in the environment is derived from both synthetic and natural sources. Synthetic perchlorate salts have been widely used as oxidants by the military and aerospace industry. A variety of commercial products also contain synthetic perchlorate. In addition to synthetic sources, natural perchlorate from both Chilean fertilizers and indigenous sources represents a potentially large source of perchlorate in groundwater and drinking water in the U.S. During this ESTCP project, chlorine and oxygen isotope analysis was utilized to both distinguish perchlorate sources and to document perchlorate biodegradation. Chlorine and oxygen isotopic analyses of perchlorate provide the primary direct approach whereby different sources of perchlorate can be distinguished from each other. Other isotopic, chemical, and geochemical techniques that can be applied in conjunction with isotopic analyses of perchlorate to provide supporting data in forensic studies are also described.

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ACRONYMS AND ABBREVIATIONS

‰	per mil
δ, Δ	delta, relative difference of isotope ratios
AFCEE	Air Force Center for Engineering and the Environment
Ag	silver
AgCl	silver chloride
$AgNO_3$	silver nitrate
Al	aluminum
AMS	accelerator mass spectrometry
Ar	argon
Ba	barium
$BaCl_2$	barium chloride
$BaSO_4$	barium sulfate
BOMARC	Boeing and Michigan Aerospace Research Center
Br^-	bromide
BV	bed volumes
°C	degrees Celsius
Ca	calcium
ccSTP	cubic centimeters at Standard Temperature and Pressure
CFC	chlorofluorocarbon
CF-IRMS	continuous-flow isotope ratio mass spectrometry
CH_4	methane
CH_3Cl	methyl chloride
CH_3I	methyl iodide
Cl^-	chloride
Cl	chlorine
^{35}Cl	chlorine-35
^{36}Cl	chlorine-36
^{37}Cl	chlorine-37
ClO_3^-	chlorate
ClO_4^-	perchlorate
cm	centimeters
CO	carbon monoxide
CO_2	carbon dioxide
COC	chain of custody
CsCl	cesium chloride
$CsClO_4$	cesium perchlorate
CsOH	cesium hydroxide
CSIA	compound-specific stable isotope analysis
Cu	copper
D	deuterium or ^2H
DDI	distilled deionized water
DI	deionized water
DI-IRMS	dual-inlet isotope ratio mass spectrometry
DO	dissolved oxygen

DoD	Department of Defense
DTSC	California Department of Toxic Substance Control
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
Fe^{3+}	Iron (III)
$FeCl_3$	iron (III) chloride
$FeCl_4^-$	tetrachloroferrate
$Fe(OH)_3$	iron (III) hydroxide
g	gram
gal	gallon
GC	gas chromatograph
GWMA	Lower Umatilla Basin Groundwater Management Area
^3H	tritium
ha	hectare
HCl	hydrochloric acid
$HClO_4$	perchloric acid
HCO_3	bicarbonate
HDPE	high density polyethylene
He	helium
HNO_3	nitric acid
H_2O	water
H_2O_2	hydrogen peroxide
HPLC-UV	high performance liquid chromatography with ultraviolet detection
hr	hours
IAEA	International Atomic Energy Agency
IC	ion chromatography
ICP-MS	inductively coupled plasma mass spectrometry
ID	inner diameter
IO_3^-	iodate
IRMS	isotope-ratio mass-spectrometry
ITRC	Interstate Technology & Regulatory Council
IUPAC	International Union of Pure and Applied Chemistry
IX	ion exchange
k	one thousand
K	potassium
KCl	potassium chloride
$KClO_4$	potassium perchlorate
kg	kilogram
km^2	square kilometer
KNO_3	potassium nitrate
KOH	potassium hydroxide
L	liter
LC-MS/MS	liquid chromatography-tandem mass spectrometry
μg	microgram
μg/L	microgram per liter
μm	micron

UV	ultraviolet
μmol	micromole
M	molar
m	meter
MΩ	megaohm
MADEP	Massachusetts Department of Environmental Protection
MCL	maximum contaminant level
MDL	method detection limit
Mg	magnesium
mg	milligram
min	minute
mL	milliliter
mm	millimeter
mM	millimolar
MTBE	methyl *tert*-butyl ether
m/z	mass to charge ratio
n	amount of substance
N	nitrogen or normal or number of entities
N_2	nitrogen gas
Na	sodium
NaCl	sodium chloride
$NaClO_4$	sodium perchlorate
NADP	National Atmospheric Deposition Program
NaOCl	sodium hypochlorite (bleach)
NaOH	sodium hydroxide
NASA	National Aeronautics and Space Administration
Ne	neon
ng	nanogram
NH_4ClO_4	ammonium perchlorate
NIST	National Institute of Standards and Technology
N_2O	nitrous oxide
NO_2^-	nitrite
NO_3^-	nitrate
NO_3-N	nitrate as nitrogen
NPT	National pipe thread
O	oxygen
^{16}O	oxygen-16
^{17}O	oxygen-17
^{18}O	oxygen-18
O_2	oxygen gas
O_3	ozone
OD	outer diameter
ORNL	Oak Ridge National Laboratory
ORP	oxidation-reduction potential
per mil (‰)	part per thousand ($\times 10^{-3}$)
ppb	part per billion ($\times 10^{-9}$)

pmc	percent modern carbon
ppm	part per million (× 10^{-6})
PO_4^{2-}	phosphate
PRIME	Purdue Rare Isotope Measurement Laboratory
PVC	polyvinyl chloride
QA/QC	Quality Assurance/Quality Control
RbCl	rubidium chloride
$RbClO_4$	rubidium perchlorate
Re	rhenium
ReO_4^-	perrhenate
S	sulfur
Sb	antimony
SCWA	Suffolk County Water Authority
SERDP	Strategic Environmental Research and Development Program
SF_6	sulfur hexafluoride
SHP	Southern High Plains
SLAP	Standard Light Antarctic Precipitation
SMOC	Standard Mean Ocean Chloride
SO_2	sulfur dioxide
SO_4^{2-}	sulfate
Sr	strontium
TcO_4^-	pertechnetate
TOC	total organic carbon
TU	tritium unit
UIC	University of Illinois at Chicago
UMCD	Umatilla Chemical Depot
UMD	University of Massachusetts, Dartmouth, MA
U.S.	United States
USEPA	United States Environmental Protection Agency
USGS	U.S. Geological Survey
VOCs	volatile organic compounds
VSMOW	Vienna Standard Mean Ocean Water
x	mole fraction
yr	year

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EXECUTIVE SUMMARY

Perchlorate (ClO_4^-) in the environment is derived from both synthetic and natural sources. Synthetic ClO_4^- salts, including ammonium perchlorate (NH_4ClO_4) and potassium perchlorate ($KClO_4$), have been widely used as oxidants by the military and the aerospace industry. A variety of commercial products also contain synthetic ClO_4^- including fireworks, matches, air bags, chlorine bleach, safety flares, perchloric acid, and chlorate herbicides. Historical disposal practices by the military, aerospace industry, and chemical manufacturers have resulted in groundwater and drinking water contamination with ClO_4^- in the U.S. Isolated contamination from fireworks, road flares, explosives, and perchloric acid has also been reported. However, ClO_4^- is also a naturally-occurring anion. It is present with sodium nitrate ($NaNO_3$) in surficial deposits in the Atacama Desert of Chile at an average concentration of around 0.1 % (by mass) of the total soluble salt, and these deposits (sometimes referred to as "Chilean caliche") were widely used in the U.S. during the first half of the 20th century as a source of inorganic nitrogen fertilizer. Natural ClO_4^- that is not associated with Chilean fertilizers has also recently been detected in the vadose zone, groundwaters, and mineral deposits collected from the arid southwestern U.S., including 155,000 km^2 of groundwater in the Southern High Plains (SHP) of Texas and New Mexico. In addition to synthetic sources, natural ClO_4^- from both Chilean fertilizers and indigenous sources represents a potentially large source of ClO_4^- in groundwater and drinking water in the U.S.

Increased health concerns about ClO_4^- during the past decade and subsequent regulatory considerations have generated appreciable interest in source identification. The key objective of the isotopic techniques described in this ESTCP report is to provide evidence concerning the origin of ClO_4^- in soils and groundwater, and more specifically whether that ClO_4^- is synthetic or natural. Chlorine and oxygen isotopic analyses of ClO_4^- provide the primary direct approach whereby different sources of ClO_4^- can be distinguished from each other. These techniques measure the relative abundances of the stable isotopes of chlorine (^{37}Cl and ^{35}Cl) and oxygen (^{18}O, ^{17}O, and ^{16}O) in ClO_4^- using isotope-ratio mass spectrometry (IRMS). In addition, the relative abundance of the radioactive chlorine isotope ^{36}Cl is measured using accelerator mass spectrometry (AMS). Taken together, these measurements provide four independent quantities that can be used to distinguish natural and synthetic ClO_4^- sources, to discriminate different types of natural ClO_4^-, and to detect ClO_4^- biodegradation in the environment. Other isotopic, chemical, and hydrogeologic techniques that can be applied in conjunction with the Cl and O isotopic analyses of ClO_4^- to provide supporting data for forensic studies are also described. The results of forensic studies at four separate sites are presented as is the application of the technique for documenting *in situ* biodegradation at one field location. Moreover, this project has resulted in the description and isotopic characterization of natural ClO_4^- occurring in various regions of the U.S. This information provides a foundation for understanding both the possible mechanisms of formation of natural ClO_4^-, and the processes that may impact its fate and distribution in soils and groundwater.

1.0 INTRODUCTION

1.1 Perchlorate Sources

Perchlorate (ClO_4^-) in the environment is derived from both synthetic and natural sources. The key objective of this ESTCP project was to demonstrate the utility of stable isotope analysis as a method to determine the origin of perchlorate (ClO_4^-) in groundwater, and more specifically whether that ClO_4^- is synthetic or natural. The following introductory sections summarize current information about the sources of synthetic and natural ClO_4^- in the environment and the potential extent of their distribution. Relevant literature is cited to provide sources of additional information about ClO_4^-.

1.1.1 Synthetic Perchlorate

Ammonium perchlorate (NH_4ClO_4) has been used for several decades in the United States (U.S.) as the primary oxidant in a variety of solid rocket propellants and explosives produced for military and aerospace applications. More than 100 varieties of military rocket motors, as well as the solid rocket boosters for the National Aeronautics and Space Administration (NASA) Space Shuttles, contain NH_4ClO_4 (Cunniff et al., 2006). Potassium perchlorate ($KClO_4$) is also used for many military applications, including U.S. Navy underwater munitions. Besides military propellants and explosives, a variety of commercial products contain synthetic ClO_4^- either intentionally or as a manufacturing byproduct, including fireworks, matches, air bags, chlorine bleach, safety flares, perchloric acid, and chlorate herbicides (Trumpholt et al., 2005; Aziz et al., 2006, 2008).

Based on United States Environmental Protection Agency (USEPA) estimates, approximately 4×10^8 kg (400,000 metric tons) of synthetic ClO_4^- has been produced in the U.S. since the 1950's, with an average production rate of 7.1×10^6 kg/yr from 1951-1997 (Dasgupta et al., 2005). Historical testing and disposal practices at some military installations, ClO_4^- production facilities, and aerospace sites have resulted in substantial contamination of soils and groundwater at these locations (Figure 1.1 and Appendix B). Many groundwater ClO_4^- plumes, which are often extensive and have concentrations up to several hundred milligrams per liter of ClO_4^-, have been identified and are subject to site assessment and(or) remediation (e.g., Hatzinger, 2005; ITRC, 2008). However, the contribution of other commercial products as non-point or small point sources of synthetic ClO_4^- is much more difficult to assess and quantify, although road flares, blasting agents, and fireworks have been indicated as sources of ClO_4^- in some groundwaters (e.g., MADEP, 2007; Böhlke et al., 2009; Munster and Hanson, 2009). Further information on synthetic ClO_4^- sources can be found in previously published reviews (Trumpholt et al., 2005; ITRC, 2008; Aziz et al., 2006).

1.1.2 Chilean Nitrate Deposits and Fertilizer

Natural ClO_4^- has long been known to co-occur with sodium nitrate ($NaNO_3$) in surficial deposits in the Atacama Desert of Chile at an average concentration of around 0.1 % (by mass) of the total soluble salt, but with concentrations as high as 6.8 % reported (Schilt, 1979; Ericksen, 1981, 1983; Dasgupta et al., 2005). The NO_3^- deposits, sometimes referred to as "Chilean caliche", were widely used in the U.S. during the first half of the 20th century as a source of inorganic nitrogen fertilizer. According to the California Department of Agriculture, more than 477,000 metric tons of Chilean NO_3^- was used in California as fertilizer between 1923 and 1998 (California Department of Food and Agriculture, 1999). Although man-made nitrogen sources are now used in most fertilizer applications, more than 55,000 metric tons of the Chilean NO_3^- material was shipped to California between 1995 and 2000, primarily for fertilizer application.

The final ClO_4^- concentration of processed Chilean NO_3^- fertilizer prior to 2002 was variable, and likely ranged from, ~ 1,500 to 10,000 mg/kg (i.e., 0.15 to 1 %) based upon analysis of historical samples (Eldridge et al., 2000; Urbansky et al, 2001a, 2001b; Dasgupta et al., 2005). Changes in manufacturing processes after 2002 were reported to reduce the final ClO_4^- concentration to $\leq$ 100 mg/kg (0.01%) (Dasgupta et al., 2005). Thus, apart from synthetic sources, past application of Chilean NO_3^- fertilizer clearly represents a potential source of ClO_4^- in groundwater and drinking water in the U.S. Based on a conservative estimate of 2,000 mg ClO_4^-/kg Chilean fertilizer (0.2%) (Dasgupta et al., 2005), one metric ton of processed Chilean fertilizer likely contained > 2.0 kg of ClO_4^-; enough to contaminate more than 300 million liters of groundwater to above the current California maximum contaminant level (MCL) of 6 μg/L, assuming no losses to biodegradation or other degradative processes. Additional information on Chilean NO_3^- fertilizers as a source of ClO_4^- can be found in previously published papers (Ericksen, 1981, 1983; Dasgupta et al., 2005; Jackson et al., 2006; Böhlke et al., 2009). Some other fertilizer materials, such as kelp, have also been reported to contain ClO_4^-, but the concentrations in these materials, when detected, are generally orders of magnitude lower than those historically present in Chilean NO_3^-, and they are considered unlikely to be of overall environmental significance (Dasgupta et al., 2005; Böhlke et al., 2009).

1.1.3 Indigenous Natural Perchlorate in the U.S.

Natural ClO_4^- that is not associated with fertilizers from the Atacama has also recently been detected in soils, groundwaters, and mineral deposits collected from the arid southwestern U.S., including groundwater underlying an area of 155,000 km^2 in the Southern High Plains (SHP) of Texas and New Mexico (Jackson et al., 2004, 2005, 2006; Rajagopolan et al., 2006). Based on groundwater age dating, some New Mexico samples (with ClO_4^- concentrations ranging from ~ 0.12 to 1.8 μg/L) were recharged many thousands of years before present, indicating pre-anthropogenic (natural) ClO_4^- sources and accumulation processes (Plummer et al., 2006). This "indigenous" natural ClO_4^- is hypothesized to form initially in the stratosphere through photochemical reactions (Murphy and Thomson, 2000; Bao and Gu, 2004; Dasgupta et al., 2005; Sturchio et al., 2009) and subsequently to deposit at the Earth's surface via precipitation or dry deposition. This hypothesis was supported by a recent study reporting the existence of natural ClO_4^- in precipitation from National Atmospheric Deposition Program (NADP) collectors at 26 sites across the contiguous U.S., Puerto Rico, and Alaska over a 3-yr period at concentrations ranging from <5 ng/L to 102 ng/L (n=1578) (Rajagopalan et al., 2009).

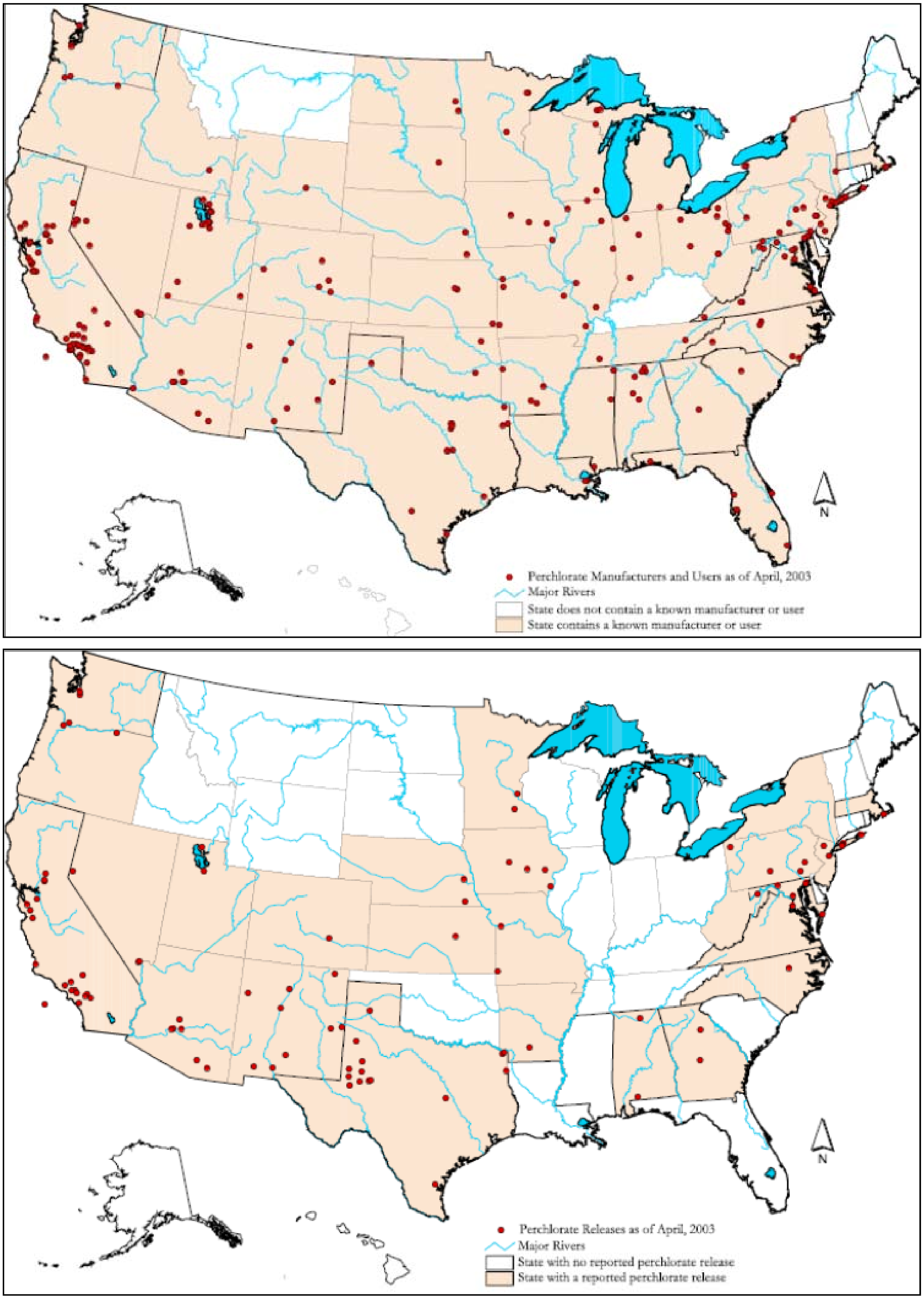
In arid regions, such as parts of the southwestern U.S., ClO_4^- in rainwater and dry deposition is expected to accumulate with time in the vadose zone, along with other deposited salts. This hypothesis was confirmed by Rao et al., (2007), who detected ClO_4^- in the vadose zone at several sites in the southwest with an average accumulated mass per unit area of 408±88 g/ha. The ClO_4^- concentrations were correlated (r=0.59-0.99) to meteoric Cl^- accumulated over the last 6 to 100 kyr, indicating that these anions were deposited together via similar processes. Natural indigenous ClO_4^- has also recently been observed to be associated with natural NO_3^- deposits in Death Valley, California at concentrations ranging from 0.25 to 1.7 mg/kg (Jackson et al., 2010). Further supporting this hypothesis is the discovery of ClO_4^- at concentrations as high as 1,100 μg/kg in the dry valleys of Antarctica (Kounaves et al., 2010; Jackson et al., 2012).

In undisturbed arid regions, atmospheric ClO_4^- is expected to remain primarily in surficial deposits and soils. However, when such environments become subject to large-scale irrigation, such as in the SHP and other agricultural regions of the western U.S., mobilization of ClO_4^- accumulated in the vadose zone to groundwater is likely. Such agricultural mobilization is hypothesized to account for the high ClO_4^- concentrations observed in groundwater in West Texas, which has been widely irrigated for several decades for production of cotton and other crops (Rajagopalan et al., 2006). Irrigation is also a likely route of transport to groundwater of ClO_4^- applied to crops with Chilean nitrate fertilizers.

1.1.4 USEPA Guidance on Perchlorate Occurrence

The United States Environmental Protection Agency (USEPA) has been evaluating the occurrence of ClO_4^- for more than a decade and recognizes that the chemical is both widespread in the U.S. and has synthetic and natural origins. Figure 1.1 illustrates the location of various ClO_4^- manufactures and known releases in the U.S., and Appendix B provides more detailed information concerning ClO_4^- manufacturers and users (Mayer, 2003). Additional information on ClO_4^- from the USEPA is available online (http://water.epa.gov/drink/contaminants/unregulated/perchlorate.cfm) and in a recent "Fact Sheet" issued by the agency (USEPA, 2009).

Figure 1.1. Perchlorate manufacturers and users (top panel) and releases as of April 2003. Maps from Mayer (2003).



1.2 Objectives of the Demonstration

This ESTCP project is a collaborative effort among scientists at the University of Illinois at Chicago (UIC), the United States Geological Survey in Reston, VA (USGS), Oak Ridge National Laboratory (ORNL) and the Biotechnology Development and Applications Group of Shaw Environmental, Inc. (Shaw). The objectives of this project were: 1) to validate the combined use of Cl and O stable isotope ratio analysis as a forensic tool to distinguish sources of ClO_4^- in groundwater, and 2) to demonstrate the isotopic techniques as a method to verify ClO_4^- biodegradation in the field. The analytical methodology for measuring Cl isotopes in ClO_4^- has proven to be capable of quantifying small differences in ClO_4^- isotope ratios (Ader et al. 2001; Sturchio et al. 2003, 2006). Similar results have now also been observed for O isotopes in ClO_4^- (Bao and Gu, 2004; Bohlke et al., 2005; Sturchio et al., 2006), further strengthening the conclusions that can be drawn from isotopic analysis of ClO_4^- samples. In addition, data gathered during this project reveal that amounts of the radioactive isotope ^{36}Cl in ClO_4^- are also useful for source discrimination (Sturchio et al., 2009). The utility of oxygen and chlorine isotopic analysis in the field were demonstrated during this ESTCP project.

Unlike many ESTCP projects for which a single demonstration site is chosen, this project was conducted at multiple sites across the U.S. Groundwater sampling for ClO_4^- source identification was conducted at several different locations, with the level of effort (i.e., number of wells sampled, supporting parameters obtained, etc.) determined on a site-specific basis. The sites were selected based on several variables, including the possible origin(s) of ClO_4^- in groundwater, the availability and completeness of site data and local expertise, and geographical location. In addition, one site was selected in which active *in situ* ClO_4^- treatment was underway. This site was used to validate the application of isotopic analysis to document *in situ* perchlorate biodegradation. Laboratory studies were also performed early in this ESTCP project to quantify isotopic fractionation of both Cl and O in ClO_4^- by bacterial strains under differing environmental conditions. Data from the laboratory studies were subsequently compared to field data to assess *in situ* biodegradation.

1.3 Regulatory Drivers

There are presently no regulatory drivers for distinguishing natural from anthropogenic ClO_4^-. However, forensic determination of ClO_4^- sources is anticipated to be an important area for determining clean-up liability, particularly at sites where sources are unknown or where a mixture of anthropogenic and natural sources are suspected. The USEPA announced in 2011 that the agency plans to establish a Federal Maximum Contaminant Level (MCL) for ClO_4^- under the Safe Drinking Water Act (http://yosemite.epa.gov/sab/sabproduct.nsf/0/D3BB75D4297CA4698525794300522ACE?OpenDocument). If this Federal MCL is in the low μg/L concentration range, as is the case for current state MCLs in Massachusetts (2 μg/L) and California (6 μg/L), then forensic analysis of ClO_4^- in drinking water supply wells may become more common as public water suppliers evaluate the sources and potential responsible parties for wells with ClO_4^- concentrations exceeding the promulgated standard.

2.0 TECHNOLOGY DESCRIPTION

2.1 Stable Isotope Ratio Analysis

The main approach described in this document, chlorine and oxygen isotopic analysis of ClO_4^-, is the primary direct method whereby different sources of ClO_4^- may be distinguished from each other Isotopes of a given element have the same number of protons and electrons (thus defining the element), but a different numbers of neutrons, the latter of which provide mass but no charge. Some isotopes are subject to nuclear decay, and are termed radioactive, while others are stable. The methods for isotopic analyses of ClO_4^- described herein refer primarily to the stable isotopes of Cl and O; analysis of ^{36}Cl, a long-lived radioactive isotope of Cl, also is included as another promising forensics tool. Because isotopes of a given element differ in mass, they exhibit slight behavioral differences, such that a variety of physical, chemical, and biological processes can alter the relative abundances of isotopes of elements in a given chemical compound, a process termed “isotopic fractionation”.

Isotopic fractionation processes, most of which are mass-dependent (equilibrium and kinetic processes that are based upon mass differences), and some of which are non-mass-dependent (processes that do not occur in proportion to mass differences) commonly cause different samples containing a given element or chemical compound to have distinct isotopic compositions. These different isotope ratios can be indicative of the origin of a molecule, and thus have forensic science applications. In addition, the stable isotope ratios of elements in a parent molecule often change systematically during biodegradation and other degradation processes (e.g., Hunkeler et al., 2008); thus, stable isotope methods can provide unique insights into *in situ* transformation processes and natural attenuation of many constituents in the environment. Additional details and reviews of stable isotope terminology and general principles are provided elsewhere (Clark and Fritz, 1997; Kendall and Caldwell, 1998; Sharp, 2007; Hunkeler et al., 2008; Aelion et al., 2010; Coplen, 2011; Hatzinger et al., 2013).

Measurements of stable isotopic composition are conducted using an isotope-ratio mass spectrometer (IRMS). This instrument is designed to measure precisely the relative differences in the isotope ratios of a given element between different substances, rather than the actual absolute ratios in any given substance, which are more difficult to determine accurately. Relative stable isotope ratios of elements are generally reported as differences from those of internationally recognized measurement standards, so that measurements from different laboratories can be compared. The relative differences of isotope ratios are reported as "delta" (δ) values (Coplen, 2011). The general expression used to report relative abundances of stable isotopes is provided below in Equation 2.1, with Cl isotopes (^{37}Cl and ^{35}Cl) as an example.

[Eq. 2.1] $\delta^{37}\mathrm{Cl}_{\mathrm{P/Q}} = [R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{\mathrm{P}} - R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{\mathrm{Q}}] / R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{\mathrm{Q}}$

R = ratio of the atomic or molar abundances (N, number of entities; alternatively n, amount of substance) of two isotopes of an element, with the isotope of higher atomic mass normally in the numerator, in this case: $R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl}) = N(^{37}\mathrm{Cl})/N(^{35}\mathrm{Cl}) = n(^{37}\mathrm{Cl})/n(^{35}\mathrm{Cl})$

$R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{\mathrm{P}}$ = number ratio of isotopes in substance P

$R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{\mathrm{Q}}$ = number ratio of isotopes in substance Q

The international measurement standard for δ^{37}Cl is "Standard Mean Ocean Chloride" (SMOC), which takes the place of substance Q in Equation 2.1 for reporting the δ^{37}Cl value of a sample (substance P in Equation 2.1), unless stated otherwise. Because delta values (e.g., δ^{37}Cl) typically are small, they commonly are reported in parts per thousand (per mil, with symbol ‰). A positive δ value indicates that the ratio of the heavy/light isotopes in the sample is higher than that of the standard, while a negative δ value indicates that the ratio of the heavy/light isotopes in the sample is lower than that of the standard. For example, if δ^{37}Cl is reported as -18 ‰, this means that $R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})$ in the sample is 18 parts-per-thousand or 1.8 percent lower than $R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})$ in the standard (SMOC), for which the δ^{37}Cl value would be 0 by definition. Absolute isotope ratios (R) are difficult to measure as precisely as relative differences of isotope ratios (δ), so most IRMS equipment and techniques are designed to produce high-precision comparisons of the isotope ratios of samples and standards. The value of $R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})$ in seawater has been reported as 0.31940 ± 0.00007 (Xiao et al., 2002) and found to be homogeneous (to within ±0.1 ‰) in samples of seawater from around the world (Godon et al., 2004). In practice, stable isotope laboratories typically have quantities of secondary isotope reference materials that are used routinely. These secondary reference materials are calibrated against internationally recognized reference materials such as those provided by the National Institute of Standards and Technology or the International Atomic Energy Agency (IAEA). The secondary isotope reference materials must be isotopically homogeneous at the scale of analysis. In addition, it is preferred that isotopic reference materials be similar chemically to the samples being analyzed, and that samples and reference materials are analyzed together using identical procedures (see Werner and Brand, 2001). For oxygen stable isotopes, the international measurement standard is Vienna Mean Ocean Water (VSMOW), for which $\delta^{17}\mathrm{O}$ and $\delta^{18}\mathrm{O}$ are exactly 0 by definition.

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, 2001; Jendrzejewski et al., 1997; Drenzek et al., 2002) have led to new approaches for characterizing the behavior of these compounds in contaminated groundwater aquifers (Sturchio et al., 1998, Dayan et al., 1999; Hunkeler et al., 1999, 2005). Similar evaluations have also been performed with nitrogen isotopes to track the fate of explosives such 2,4,6-trinitrotoluene (TNT) in the environment (Dignazio et al., 1998). Moreover, the development of combined gas chromatography – isotope-ratio mass spectrometry (GC-IRMS) 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 (Hammar et al., 1998), and gasoline oxygenates (Smallwood et al., 2001).

2.2 Isotopes of Chlorine and Oxygen in Perchlorate

Both of the elements comprising the ClO_4^- molecule (i.e., Cl and O) have more than one stable isotope. Oxygen has three stable isotopes (^{16}O, ^{17}O, and ^{18}O), which have molar abundances (mole fractions) of approximately 99.76206 %, 0.03790 %, and 0.20004 %, respectively, in the VSMOW standard (Coplen et al., 2002). Chlorine has two stable isotopes (^{35}Cl and ^{37}Cl), with molar abundances of approximately 75.779 % and 24.221 %, respectively, in the SMOC standard (Coplen et al., 2002). Chlorine also has a long-lived radioactive isotope (^{36}Cl) with a half-life of ~ 301,000 yr, whose relative abundance is small (typically $<10^{-15}$ to 10^{-12} relative to the stable Cl isotopes) but can be useful for studying origins of Cl-bearing compounds (Phillips, 2000). Techniques to determine relative stable isotope ratios of chlorine (^{37}Cl and ^{35}Cl) in the ClO_4^- molecule were first reported by Ader et al., (2001) and Sturchio et al., (2003). Subsequently, methods for analysis of relative isotope ratios of oxygen (^{18}O, ^{17}O, and ^{16}O) in ClO_4^- were described (Bao and Gu, 2004; Böhlke et al., 2005). Methods to collect and purify ClO_4^- from environmental samples, including groundwater, minerals, and soils have been progressing for several years, as have the relevant IRMS techniques for Cl and O isotopic analyses of ClO_4^-. Additional details on stable isotope analysis of O and Cl in ClO_4^- are provided later in this report (Sections 5.2.5 – 5.2.9) and in a guidance document written from the information gained during this ESTCP project (Hatzinger et al., 2011).

2.3 Previous Testing of the Technology

Techniques to quantify the isotope ratio of Cl in the ClO_4^- molecule were developed simultaneously in the laboratories of Dr. Neil Sturchio, presently at the University of Illinois at Chicago (UIC) (Sturchio et al., 2003) and Dr. Max Coleman, presently at Jet Propulsion Laboratories (Ader at al., 2001; Coleman et al., 2003). One of the initial applications of this technique was to determine whether it could be used as a potential monitoring tool to verify ClO_4^- biodegradation. To achieve this end, laboratory studies were conducted using pure cultures of ClO_4^--degrading bacteria isolated by our laboratory (Shaw; Lawrenceville, NJ) and that of Dr. John Coates (University of California, Berkeley, CA). These studies revealed that the Cl isotope ratio (i.e., $^{37}Cl/^{35}Cl$ ratio in the ClO_4^- molecule) increases markedly in the residual ClO_4^- during biodegradation (Sturchio et al.

2003; Coleman et al., 2003) (Figure 2.1). One key objective of this ESTCP project was to verify these findings, augment them with O isotope measurements, and to develop this technique as a tool for field monitoring of perchlorate biodegradation and bioremediation.

A technique to evaluate the isotopic signature of O in ClO_4^- was subsequently developed (Bao and Gu, 2004). This technique was initially applied to evaluate the isotopic signature of O ($\delta^{18}O$ and $\Delta^{17}O$) from a few commercial reagents and from Chilean NO_3^-. Significant differences were observed in O stable isotopes between natural and synthetic ClO_4^-. The O isotope ($^{18}O/^{16}O$) ratio for the natural ClO_4^- was observed to be appreciably higher (~ 10 ‰ average) than for the reagent materials (Figure 2.2). Isotopic analysis of Cl was then applied at UIC to evaluate whether the ClO_4^--Cl in man-made sources (reagent ClO_4^-) differed significantly from that in fertilizer sources (Chilean nitrate-based fertilizer and raw Chilean caliche samples). The data from these initial samples indicated that the Cl isotope ratio in the naturally occurring Chilean ClO_4^- source was much lower (~12 ‰ average) than that in man-made ClO_4^- (Figure 2.2). These data provided some of the first evidence that isotopic analysis of ClO_4^- may be useful as a forensic tool to distinguish natural from man-made ClO_4^-.

One important isotopic difference between synthetic ClO_4^- and natural ClO_4^- from Chile is revealed by analysis of ^{17}O abundances. Based on initial studies, there appeared to be an excess of ^{17}O in natural Chilean-derived ClO_4^-, relative to the abundance that would be consistent with simple mass-dependent isotopic fractionation processes (Bao and Gu, 2004; Böhlke et al., 2005). A similar enrichment was not seen in synthetic ClO_4^-. The generally observed ratio of ^{17}O to ^{18}O for terrestrial materials is $\delta^{17}O = \sim 0.52\ \delta^{18}O$, and natural ClO_4^- (but not synthetic ClO_4^-) shows a significant deviation from this ratio. The excess ^{17}O in natural ClO_4^- is shown in Figure 2.3 as $\Delta^{17}O$, which represents the deviation in ^{17}O from the expected value (terrestrial mass-dependent fractionation line in Figure 2.3). One equation used to derive $\Delta^{17}O$ is as follows:

$$\text{[Eq. 2.2]:}\quad \Delta^{17}O\ (‰) = [[(1 + \delta^{17}O/1000) / (1 + \delta^{18}O/1000)^{0.525}] - 1] \times 1000$$

Synthetic ClO_4^- samples have a $\Delta^{17}O$ value of 0.0 ($\pm$ 0.1 ‰), consistent with ClO_4^- production from brine by electrolysis. In contrast, the mean $\Delta^{17}O$ value of the limited set of Chilean samples analyzed prior to this project had $\Delta^{17}O$ values averaging ~ + 9.6 ‰. The elevated $\Delta^{17}O$ in the Chilean ClO_4^- was hypothesized by Bao and Gu, (2004) to be consistent with atmospheric formation. The data suggest that oxidation of volatile Cl by ozone (O_3) (which is known to have elevated $\Delta^{17}O$ values) in the upper atmosphere is responsible for the initial production of this material (Bao and Gu, 2004).

At the initiation of this ESTCP project, the Cl and O isotopic ratios of natural ClO_4^- derived from the U.S. were unknown. Reports from USGS (Orris et al., 2003) and Texas Tech University (Jackson et al., 2006) indicated that indigenous ClO_4^- was associated with mineral deposits and some unsaturated zone soils in the United States. However, whether the isotopic values ($\delta^{37}Cl$, $\delta^{18}O$ and $\Delta^{17}O$) for this indigenous ClO_4^- resembled that of Chilean-derived ClO_4^-, synthetic ClO_4^-, or were completely different was unknown.

Overall, initial data derived prior to or in the early stages of this ESTCP project indicated that stable isotope ratio analysis could be an important forensic tool for differentiating synthetic and Chilean fertilizer-derived sources of ClO_4^-. The utility of this technique for distinguishing synthetic sources from each other and/or for differentiation of "indigenous" natural ClO_4^- in the U.S. from both Chilean and synthetic ClO_4^- was unknown. The goal of this ESTCP project was to validate the use of Cl and O stable isotope ratio analysis for forensic purposes. Previous laboratory tests also indicated that stable isotope analysis of Cl could be utilized to document biodegradation of ClO_4^- (Sturchio et al., 2003; Coates et al., 2003). A second key objective of this project was to quantify microbial fractionation of Cl and O in ClO_4^- under differing environmental conditions, and to develop this technique as a tool for field monitoring of ClO_4^- biodegradation and bioremediation.

Figure 2.1. Variation in Cl isotope ratio (ln R/Ro) vs. fraction of ClO_4^- remaining in two studies with the ClO_4^--degrading bacterium *Dechlorosoma suillum*. Values for the Cl isotope fractionation factor (α) are provided. F = fraction of ClO_4^- remaining: R_0 = Cl isotope amount ratio ($^{37}Cl/^{35}Cl$) in unreacted ClO_4^- : R = Cl isotope amount ratio in remaining ClO_4^- after reaction (from Sturchio et al., 2003).

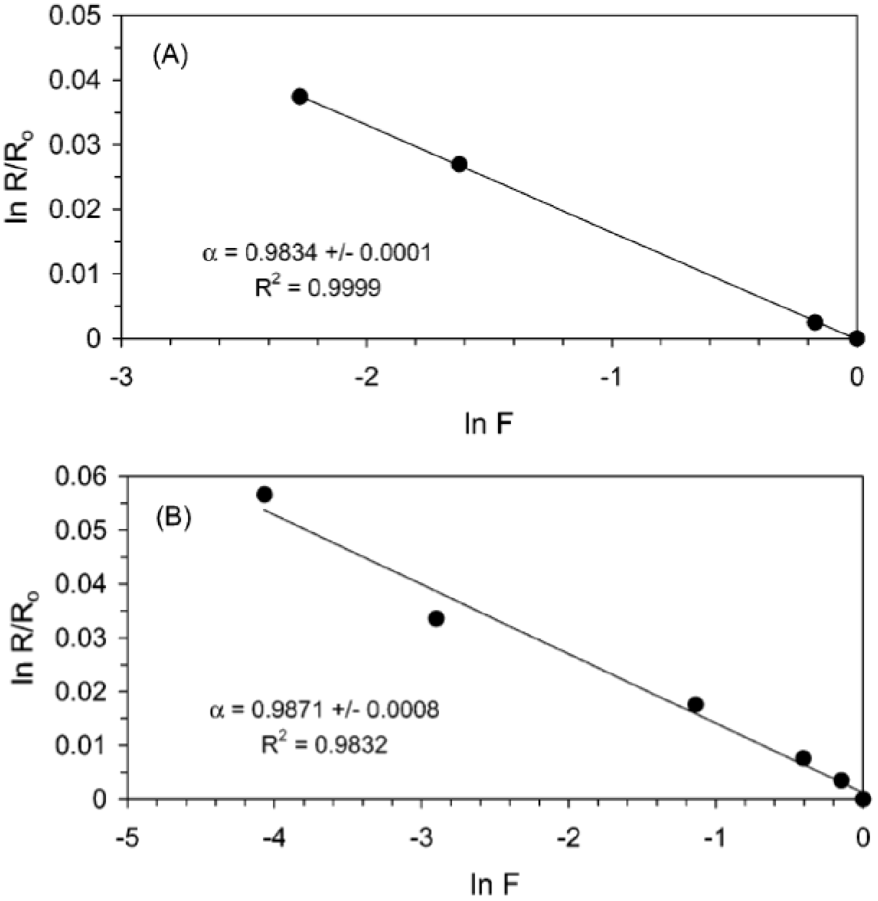


Figure 2.2. Comparison of δ^{37}Cl and δ^{18}O values for anthropogenic and natural ClO_4^-. Figure from Sturchio et al., 2004.

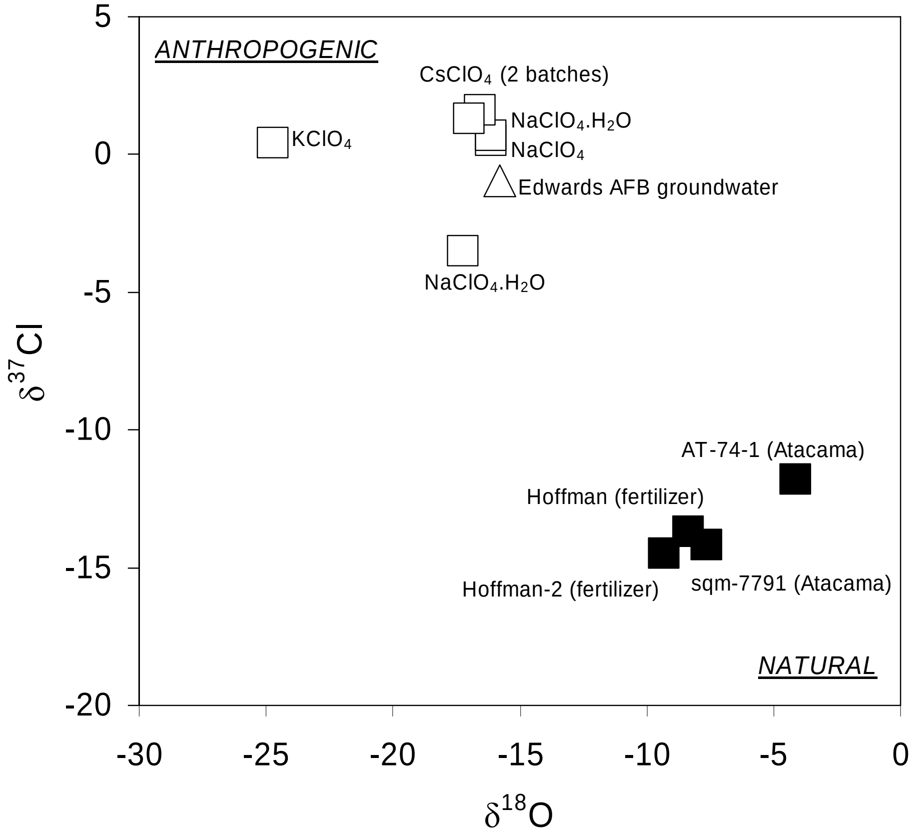
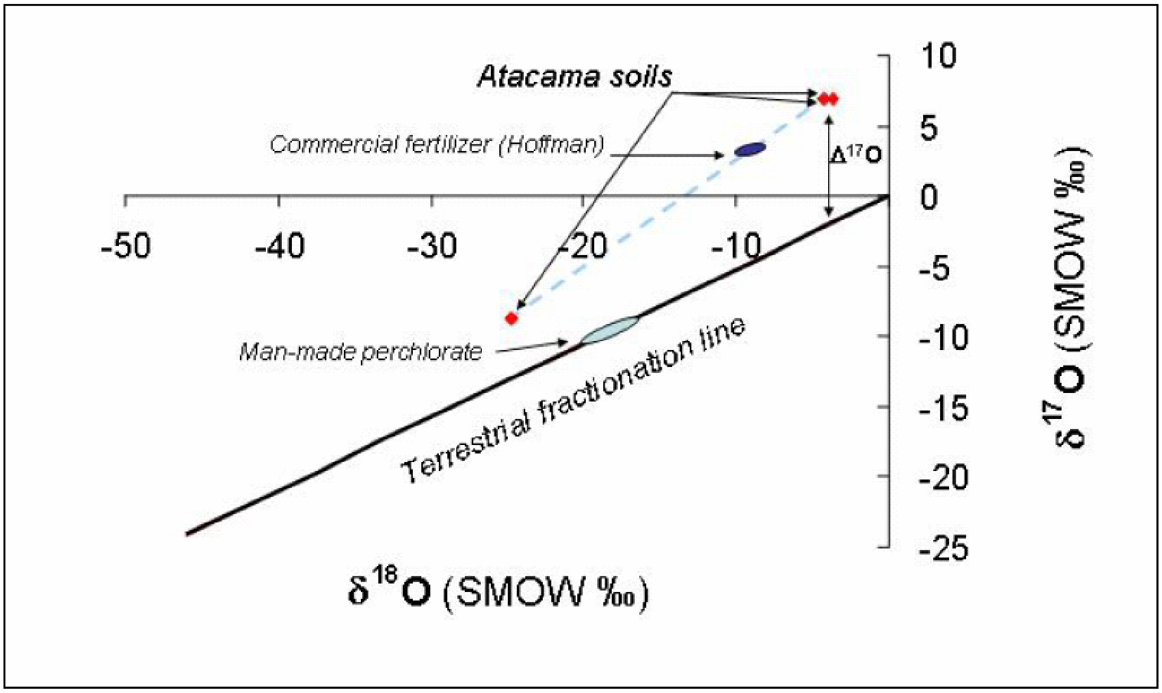


Figure 2.3. Comparison of $\delta^{18}O$ and $\delta^{17}O$ values for man-made and natural ClO_4^-. A ^{17}O excess is apparent for the natural but not the man-made samples. This excess is represented as the elevation of the $\Delta^{17}O$ above the mass-dependent fractionation line. Figure from Bao and Gu, 2004.



2.4 Advantages and Limitations of the Technology

Stable isotope ratio analysis is the only technique presently capable of directly distinguishing between natural ClO_4^- and synthetic ClO_4^-. Taken in context with other site geochemical and hydrogeological data, this is a unique forensic tool. The present limitations in this technology are as follows: (1) sample collection time can be significant for wells with low ClO_4^- concentrations; (2) purification of ClO_4^- for isotopic analysis is time consuming and requires appreciable technical expertise; and (3) only one laboratory presently offers this analysis on a fee-for-service basis.

3.0 PERFORMANCE OBJECTIVES

Performance objectives are provided in Table 3.1.

Table 3.1 Performance Objectives

TYPE OF OBJECTIVE	PRIMARY PERFORMANCE METRICS	EXPECTED PERFORMANCE METRICS	ACTUAL PERFORMANCE OBJECTIVE MET?
Qualitative	Method Implementation	Development of simple procedure to collect perchlorate from low concentration plumes	YES
Qualitative	Method Implementation	Refinement and standardization of procedures for perchlorate extraction, purification, and isotopic analysis	YES
Quantitative	Method implementation	Prepare and characterize analytical reference materials for stable isotope analysis of perchlorate	YES
Quantitative	Analytical data	Precise isotopic analysis of $\delta^{37}C$ and $\delta^{18}O$, and $\Delta^{17}O$ of perchlorate from environmental samples to ± 0.5 ‰	YES*
Quantitative	Forensic application	Develop isotopic database ($\delta^{37}C$,$\delta^{18}O$, and $\Delta^{17}O$) from known man-made and natural perchlorate samples	YES
Qualitative	Forensic application	Develop list of supporting analyses useful for forensic evaluation of perchlorate in groundwater	YES
Quantitative	Biodegradation	Develop fractionation factors for ^{37}Cl and ^{18}O through lab studies and apply to quantify field biodegradation	YES
Qualitative	Application	Transition isotopic methodology to DoD end-users	YES

* Precision of analysis depends on sample characteristics, but this criterion has been met for many samples.

3.1 Performance Metrics

3.1.1 Development of a Simple Procedure for Sample Collection

A simple protocol was developed to extract the required quantities of ClO_4^- from groundwater utilizing small anion exchange columns packed with ClO_4^--specific anion exchange resin (Purolite A530E resin). A separate protocol was developed to extract ClO_4^- from vadose soils and mineral samples. The details of these procedures are provided in Section 5.0 and in the guidance document prepared for this ESTCP project (Hatzinger et al., 2011).

3.1.2 Refinement of Procedures for ClO_4^- Extraction, Purification, and Analysis

Procedures for ClO_4^- extraction, purification, analysis were developed and/or refined during the course of this project. The details of the current protocol for these procedures are provided in Section 5.0. Additional information, including Quality Assurance/Quality Control (QA/QC) recommendations, is provided in Hatzinger et al., 2011.

3.1.3 Prepare and Characterize Analytical Reference Materials

During this ESTCP project, we have developed three reference materials for Cl and O isotopic analysis of ClO_4^- (USGS37, USGS38, and USGS39). USGS37 was prepared from normal commercial reagent $KClO_4$. USGS38 and USGS39 were synthesized by Dr. Kent Richman at the AMPAC facility in Magna, UT (the main producer of commercial ClO_4^- in the U.S) using reagents with widely varying Cl and O isotopic compositions. Two of the reference materials (USGS37 and USGS38) are used routinely by our research group for calibration, and are available for distribution by USGS (Reston, VA). We anticipate that a more detailed description of the preparation and calibration of these reference materials will be published in a peer-reviewed journal. Additional information on the reference materials is provided in Section 5.2.8.

3.1.4 Precise Isotopic Analysis of $\delta^{37}C$ and $\delta^{18}O$, and $\Delta^{17}O$

The precision of stable isotope analysis for $\delta^{37}C$ and $\Delta^{17}O$ using the IRMS techniques developed and refined during this project generally meets the ± 0.5‰ stated objective. The measurement of $\delta^{18}O$ is somewhat more variable, as this parameter is more readily affected by impurities in ClO_4^- samples. In general, the variability in $\delta^{18}O$ analysis is ~ ± 1‰.

3.1.5 Develop Isotopic Database ($\delta^{37}Cl$,$\delta^{18}O$, and $\Delta^{17}O$) from Known Synthetic and Natural ClO_4^- Samples

An isotopic database was developed during this project that includes a wide variety of synthetic sources (military, reagents, fireworks, flares, chlorate herbicides, bleach), natural Chilean perchlorate, and natural perchlorate from Death Valley caliche deposits and groundwater in the Southern High Plains of TX and the Middle Rio Grande Basin of NM. The complete dataset is provided in Appendix A, Table A-1. Detailed discussion on the characteristics of ClO_4^- from these different sources is provided in Section 6, Section 7, and Appendix C.

3.1.6 Develop List of Supporting Analyses Useful for Forensic Evaluation of ClO_4^- in Groundwater

A list of supporting analyses useful in investigations of ClO_4^- sources in groundwater was developed. These analyses are described in Section 5.3.

3.1.7 Develop Fractionation Factors for ^{37}Cl and ^{18}O through Laboratory Studies and Apply to Quantify Field Biodegradation

Fractionation factors for O and Cl were developed using two pure cultures of ClO_4^--reducing bacteria isolated in our laboratory. These data are provided in Section 6.2 and in Sturchio et al., (2007). A field experiment was conducted to evaluate isotopic fractionation of both Cl and O during *in situ* ClO_4^- biodegradation. These data are provided in Section 7.5 and in Hatzinger et al., (2009).

3.1.8 Transition Isotopic Methodology to DoD End-Users

Significant technology transition efforts have been made for this project, including presentation of data at more than 20 national and international scientific meetings, publication of 10 peer-reviewed papers and book chapters, development of training courses for the USEPA, AFCEE, the US Navy, and SERDP/ESTCP, and publication of a guidance document for the technology (Hatzinger et al., 2011). In addition, this technology is currently (2013) being offered on a fee-for-service basis by the Environmental Isotope Geochemistry Laboratory (EIGL) at the University of Illinois at Chicago (UIC). A number of parties have contracted EIGL for ClO_4^- source identification using the techniques developed/refined during this ESTCP project.

4.0 TEST SITE DESCRIPTIONS

A variety of different sites were considered for isotopic sampling of ClO_4^- in groundwater. An attempt was made to collect samples from sites with numerous potential sources including (1) military training, testing, and disposal activities; (2) usage and/or disposal of commercial products, including fireworks, flares, and chlorate herbicides; (3) historical application of Chilean nitrate fertilizers; and (4) natural occurrence in indigenous minerals, soils, and groundwater. The scope of this project did not allow a complete evaluation and differentiation of all potential sources, but rather focused on the most abundant sources and on distinguishing synthetic from natural perchlorate. However, site selection was conducted to maximize the information gained from each location, and an attempt was made to quantify isotopic signatures from as many different sources as possible. The sites selected for sampling are described in Section 4.1.

4.1 Sites Selected for Sampling: History/Characteristics

Sites selected for stable isotope sampling were: (1) Suffolk County, Long Island, NY; (2) Lower Umatilla Basin, OR; (3) Southern High Plains, TX; (4) Stringfellow Superfund Site, Glen Avon, CA; (5) University of Massachusetts, Dartmouth, MA; and (6) the Middle Rio Grande Basin, NM. In addition to these sites, where groundwater samples were collected, sampling of vadose soils was conducted in the Southern High Plains, TX and sampling and analysis of mineral caliche deposits, vadose soil, and groundwater was performed in Death Valley, CA. A description of each of these sites is provided in Section 4.1.1. In addition, to evaluate isotopic signatures during ClO_4^- biodegradation, a field experiment was conducted at a military contractor site in Elkton, MD. Details of this study are provided in Section 4.1.2. Additional information on each site is provided with the sampling results in Section 7.

4.1.1 Sites with Indigenous Natural ClO_4^-.

The following subsections provide details for the locations selected for sampling and characterizing natural ClO_4^- indigenous to the US.

4.1.1.1 Southern High Plains, West Texas

As described in Section 1.1.3, natural ClO_4^- has been detected over a broad area of the

Southern High Plains of West Texas (SHP). A large scale sampling program was conducted by Texas Tech University (TTU) to determine the distribution of ClO_4^- in this region. An area exceeding 155,000 km^2 sq. and comprising 54 counties in Texas and two counties in New Mexico was sampled (Jackson et al., 2004, 2005). The wells sampled were screened in five different aquifer systems, including the Edwards-Trinity (Plateau), Cenozoic Pecos Alluvium, Dockum, Seymour, and Ogallala. Among the public wells sampled in Texas, 256 (46%) contained ClO_4^- (>0.5 μg/L), and 18% of these contained ClO_4^- equal to or greater than 4 μg/L. Of the private wells tested, 47% had detectable ClO_4^-, and 30% had ClO_4^- concentrations at or above 4 μg/L. Extensive sampling of vadose and surface soils was also performed.

As part of this ESTCP effort, we worked with Dr. W. Andrew Jackson at TTU, the Principal Investigator of SERDP Project ER-1435, to select wells for sampling and isotopic analysis. Nested wells installed in Bailey, Gaines, and Martin Counties, TX were sampled as was a well at the Muleshoe Wildlife Refuge on the SHP. Besides isotopic sampling, a suite of other geochemical and isotopic analyses was performed on groundwater extracted from these wells, including groundwater dating, NO_3^- isotopic analysis, anion and cation analysis, and measurement of dissolved gases. These supporting methods are described in additional detail in Section 5.3. Finally, vadose zone soil collected from an undisturbed range area near Lubbock, TX was extracted and analyzed for ClO_4^- isotopes. These samples were analyzed to determine the stable isotope characteristics of natural "indigenous" ClO_4^- in this region.

4.1.1.2 Middle Rio Grande Basin, NM

Perchlorate was reported in groundwater from remote locations of the Middle Rio Grande Basin (MRGB) of New Mexico at concentrations ranging from 0.1 to 1.8 μg/L (Plummer et al., 2006). Based on radiocarbon dating, many of the water samples containing ClO_4^- recharged the aquifer between 10,000 and 28,000 years ago, obviously predating anthropogenic production or importation of the anion to the U.S. in fertilizer Thus, this material represents ClO_4^- formed naturally in this region of the country, perhaps by mechanisms similar to those proposed for West Texas.

Because ClO_4^- concentrations were extremely low, the wells were generally remote, and much of the groundwater was deep (> 100 m bgs), collecting ClO_4^- for isotopic analysis from this region was a challenge. However, obtaining an isotopic signature of this ClO_4^- was a crucial to understanding the sources of this anion in the U.S. Thus, our research team has worked with local personnel from the USGS in New Mexico to sample two remote wells for stable isotope analysis. Details and results are provided in section 6.1.2.2.

4.1.1.3 Death Valley, CA

Perchlorate was obtained from near-surface caliche-type salt deposits at four locations in the Death Valley region of the Mojave Desert, CA. These caliche salts have attracted previous study because of their unusually high concentrations of NO_3^-, which resemble those in the Atacama Desert (Böhlke et al., 1997; Erickson et al., 1988; Noble, 1931; Noble et al., 1922). The caliche samples were collected from the select locations using picks and shovels (Figure 4.1). ClO_4^- concentrations were measured in the mineral samples and then the ClO_4^- was extracted for stable isotope ratio analysis. Results and additional details are provided in Section 6.1.2.2.

4.1.2 Forensic Evaluations of ClO_4^- in Groundwater

Several sites were selected and samples to test the efficacy of the ClO_4^- stable isotope method for identification of probable sources of the anion in groundwater. These sites are listed below.

4.1.2.1 Suffolk County, Long Island, NY

Perchlorate has been detected in groundwater at several locations in Suffolk County, Long Island, NY at μg/L concentrations (Groocock, 2002). Some of these regions represent historical farming areas, and it is possible that past application of Chilean nitrate fertilizer accounts for the ClO_4^- contamination. The use of marine kelp as fertilizer on organic vineyards and farms has also been cited as a possible source of ClO_4^- in this region (Abbene, 2006). With a few exceptions, however, ClO_4^- sources in Suffolk County are unknown and other anthropogenic sources, such as road flares and blasting explosives cannot be ruled out.

In collaboration with an ongoing USGS project in the region, we collected groundwater samples from six ClO_4^--contaminated wells in Suffolk County. The sampling effort included three wells on the North Fork of Long Island, which is agricultural, two public supply wells near Northport in a suburban setting, and two wells from a former BOMARC missile site in Westhampton which is currently used for training by the Suffolk County Police Department. Results from this study are provided in Section 7.1 and in Böhlke et al., 2009.

4.1.2.2 Stringfellow Superfund Site, CA

Perchlorate was collected from two groundwater wells and two water treatment facilities in the vicinity of the Stringfellow Superfund Site in Glen Avon, CA. The sampling was conducted in conjunction with Kleinfelder Consultants and the California Department of Toxic Substance Control (DTSC). The core objective of this isotopic sampling and analysis was to determine if any sources other than synthetic ClO_4^- (which is known to emanate from a landfill at the site) contribute to groundwater contamination in this region. Results are presented in Section 7.2.

4.1.2.3 Lower Umatilla Basin, OR

The Lower Umatilla Basin, OR was subject to a large-scale groundwater study in 1992 to define sources of area-wide NO_3^- contamination (Oregon DEQ, 2006). This study, which focused on 352,000 acres in northern portions of Umatilla and Morrow counties (defined by as the Lower Umatilla Basin Groundwater Management Area; GWMA) was repeated in 2003 to determine whether NO_3^- concentrations had changed in the region over the previous decade. In addition to NO_3^- and various geochemical parameters, analysis of ClO_4^- was also conducted during the 2003 sampling event. ClO_4^- was detected (1 to 25 μg/L) in 72 of the 133 wells for which groundwater data were collected. Moreover, ClO_4^- was observed over a wide area and in both alluvial wells (64/119) and basalt wells (6/11).

The source(s) of ClO_4^- in the Lower Umatilla Basin were unknown prior to this study. The study region is highly agricultural, but also includes military installations and a former Boeing facility. Proposed ClO_4^- sources include natural geological deposits, Chilean nitrate fertilizer, demolition of ordnance in the Umatilla Chemical Depot's Ammunition Demolition Area, training activities at the Boardman Bombing Range and the Cold Springs Bombing Range, activities performed at the former Boeing Jet Engine Plant, and bleach used to treat large-scale drip irrigation systems (Oregon DEQ, 2006). Road flares and fireworks should also not be ruled out as contributing factors.

Umatilla was an ideal site to conduct forensic studies under this ESTCP project, as ClO_4^- is distributed over a wide area, and sources may include military, agricultural and natural ClO_4^-. We worked with the Oregon DEQ and the USEPA to select wells for sampling and isotopic analysis. Eight wells were sampled for ClO_4^- isotope analysis and supporting parameters. The results from this site are presented in Section 7.4

4.1.2.4 University of Massachusetts, Dartmouth, MA

A study was conducted by the Massachusetts Department of Environmental Protection (MADEP) in conjunction with the University of Massachusetts, Dartmouth (UMD) to determine whether a typical fireworks display results in significant environmental contamination with perchlorate (MADEP, 2007). A site was selected on the UMD campus in which fireworks had been launched for approximately 10 yrs. A total of 8 monitoring wells (UMD-1 to UMD-8) were installed by MADEP in the vicinity of the display area. Groundwater samples were collected from each well and analyzed for ClO_4^- beginning in June 2004 (prior to the July 04, 2004 display). Several sampling events were conducted between June, 2004 and May, 2006, before and after fireworks displays. Perchlorate concentrations ranging from < 1 μg/L to 62 μg/L were detected during the 2-year study (MADEP, 2007).

Groundwater samples were collected from the UMD site in July, 2006 as part of this ESTCP project in order to assess whether ClO_4^- derived from fireworks exhibits a unique isotopic signature. This work was done in conjunction with SERDP Project ER-1429 (Evan Cox, PI; Geosyntec Consultants), whose objective was to assess ClO_4^- contamination in soils and groundwater resulting from a fireworks display, and to determine if there were correlations between ClO_4^- and other elements/metals commonly associated with fireworks, including aluminum, antimony, barium, calcium, magnesium, potassium, sodium, and strontium. Based on groundwater concentrations during the 2005 final sampling event at the site, ClO_4^- samples were collected for isotopic analysis from two wells, UMD-7 and UMD-8 (duplicate columns taken). The ClO_4^- concentrations in these wells were in excess of 20 μg/L as of February, 2005. Analysis of ClO_4^- concentrations, geochemical parameters, anions, and trace elements were performed for all eight wells. In addition, two small samples of unexploded fireworks and two road flares were found at the site. Enough ClO_4^- was obtained from these samples for isotopic analysis. These data were compared to groundwater data. Results are provided in Section 7.3.

4.2 ClO_4^- Isotope Fractionation Evaluation: Biobarrier Site, Elkton, MD

A DoD Contractor facility in Elkton, MD, that previously tested and manufactured solid propellant rockets, was selected for an evaluation of Cl and O isotope fractionation during *in situ* ClO_4^- biodegradation. A small area on the property served as a pilot test site for an ESTCP-funded demonstration of *in situ* perchlorate treatment using an emulsified oil biobarrier (Zawtocki et al., 2004; ESTCP, 2006; Borden, 2007). During this demonstration, EOS edible oil substrate was injected in a shallow ClO_4^--contaminated aquifer to form a 15 m long biobarrier. The aquifer was previously impacted by ClO_4^- and solvents released from a small surface impoundment. Over a 2.5-year monitoring period, the emulsified oil promoted the biological degradation of perchlorate and 1,1,1,-trichloroethane in the demonstration plot. Perchlorate levels as high as 13 mg/L were degraded to below detection (<4 μg/L) during this time. Additional details concerning the project are available in Borden, (2007) and in the ESTCP Final Report entitled "Edible Oil Barriers for Treatment of Perchlorate-Contaminated Groundwater" (ESTCP, 2006).

A study of *in situ* isotopic fractionation of perchlorate was performed at the facility during June, 2006. An *in situ* test was performed in which 400 L of ClO_4^--contaminated groundwater was collected from upgradient of the barrier and re-injected directly into the oil biobarrier. The water was then slowly pumped back out of the well (after different residence times in the barrier) over a two day period, and samples were obtained for ClO_4^- isotopic analysis. The required residence time for the test was determined based on a preliminary test performed in May, 2006 in which ClO_4^- and NO_3^- degradation were monitored with time after injection (i.e., isotope samples were not collected). The data from this study provide information on levels of *in situ* biological fractionation of both ClO_4^- and NO_3^- isotopes. These data were compared to results obtained during pre-demonstration laboratory studies (Section 6.2.1 and Sturchio et al., 2007). Study results are summarized in Section 7.4. Complete results are provided in Hatzinger et al., 2009, which is provided in Appendix C.

Figure 4.1. Collection of surface caliche mineral samples for determination of perchlorate concentrations and isotope values

5.0 TEST DESIGN

5.1 Conceptual Experimental Design

The primary objectives of this project were to: 1) validate the combined use of chlorine and oxygen stable isotope ratio analysis as a forensic tool to distinguish sources of ClO_4^- in groundwater, and 2) to demonstrate the isotopic techniques as a method to verify ClO_4^- biodegradation in the field. In order to achieve these objectives, initial tasks were conducted to develop the database necessary for evaluating ClO_4^- sources in natural samples and for improving the stable isotope sampling and analysis method. More specifically, these tasks were as follows: (1) an expanded database of Cl and O isotope values for synthetic and natural ClO_4^- source samples was developed; (2) methods for collecting field samples for isotope analysis, purifying ClO_4^- from those samples, and performing stable isotope analysis of Cl and O, as well as $^{36}Cl/Cl$ analysis were developed and/or refined; (3) new isotope standards were prepared and characterized; (4) laboratory studies were conducted to determine isotope fractionation factors (ε values) for O and Cl by pure cultures of ClO_4^--degrading bacteria; and (5) experiments were performed to assess the potential for isotope exchange between ClO_4^- and H_2O, and to assess various factors that may influence isotope results, such as the presence of trace levels of contaminating anions in samples. Ultimately, the results from these tasks were important for both developing a reliable method for forensic analysis of ClO_4^- collected from field samples, and interpreting the field results for both forensics and biodegradation. The isotope method was then used to evaluate ClO_4^- sources at a number of different sites and to assess the utility of the technique for documenting *in situ* ClO_4^- biodegradation based on isotopic fractionation. The details of conducting stable isotope analysis, and the results of laboratory and field studies conducted during this project are described in the subsequent sections.

5.2 Isotopic Analysis of Cl and O in ClO_4^-: Technology Application

The isotopic analysis of Cl and O in ClO_4^- consists of several steps. A complete description of these steps is provided in an ESTCP Guidance Document that was published in advance of this Final Report (Hatzinger et al., 2011). These methods were developed, refined, and/or used during this project. A brief summary of the steps/procedures is provided in this section. Methods for determining the isotopic composition of ClO_4^- consist of six basic steps:

(1) Sampling perchlorate in groundwater using ion exchange (IX) columns
(2) Extraction and purification of ClO_4^- from IX columns
(3) Verification of sample purity
(4) Analysis of stable O isotopes in ClO_4^- by IRMS
(5) Analysis of stable Cl isotopes in ClO_4^- by IRMS
(6) Analysis of ^{36}Cl by AMS

Abbreviated descriptions of the fundamental methods utilized for this procedure have been published in several peer-reviewed papers and book chapters, most of which were generated during this project, including Sturchio et al., (2006, 2007, 2009, 2011); Böhlke et al., (2005, 2009); Hatzinger et al., (2009); Jackson et al., (2010); Gu et al., (2011), and Bao and Gu, (2004).

5.2.1 Sampling Groundwater Using Ion Exchange (IX) Columns

Approximately 20 µmol of pure ClO_4^- salt (as $CsClO_4$ or $KClO_4$, prepared as described in Section 5.2.4) is normally sufficient to obtain duplicate stable isotope ratio measurements by IRMS for both O and Cl in the ClO_4^- ion. However, because of potential losses during sample purification (Section 5.2.4), and allowing sufficient sample for ^{36}Cl and replicate analyses, it is desirable to collect samples containing at least 100 µmol (i.e. 10 mg) of ClO_4^- from each source. The following sections focus on sample collection from a groundwater source, which is the most typical application of this method. Section 5.2.2 provides a brief description of sampling techniques for soils. For groundwaters with low ClO_4^- concentrations (i.e., < 5 µg/L), collecting 10 mg of ClO_4^- can be challenging. For example, if the ClO_4^- concentration in a well is 5 µg/L, then 2000 L (~530 gal) of water is required to obtain the necessary 10 mg. Shipping this volume of water is impractical. Rather, small columns containing about 100 mL (~ 60 g dry wt) of Purolite A-530E ClO_4^--specific anion exchange resin (IX resin) were developed and deployed for field use. Water is passed through these columns, and the ClO_4^- is trapped by the IX resin. Although many hours may be required for sample collection in some cases (flow rates up to 2 liters per minute (L/min) are recommended), the columns are capable of trapping 10 mg of ClO_4^- on a small volume of resin. Water bodies with ClO_4^- concentrations as low as 0.05 µg/L have been sampled successfully with cumulative pumping times of days to weeks. The ClO_4^- is then extracted from the resin and purified prior to IRMS analyses, as described in Section 5.2.4.

5.2.1.1 Sampling Column Construction

The sampling columns used to collect ClO_4^- in the field are custom made. They are simple to construct, and various design modifications are possible based on the specific application. The design and materials for a typical 100-mL sampling column are provided in Figure 5.1. This basic column design was used in the field for ClO_4^- sample collection at numerous sites during this effort (Sections 4 and 7; Böhlke et al., 2005, 2009; Jackson et al., 2010; Hatzinger et al., 2009). Complete details of column construction are provided in Hatzinger et al., (2011). It should be noted that early in this ESTCP project, several different column designs were evaluated, including small glass chromatography columns and larger stainless steel columns. Sites where alternative columns were used are noted in the results for each site (Section 7).

5.2.1.2 Collection of Perchlorate Samples from Groundwater

A groundwater well can be sampled for ClO_4^- using either a submersible pump (e.g., Grundfos “Redi-flo" or equivalent) or by sampling a sidestream from a municipal supply well or a household well that already has a submersible or external pump in place. Both techniques were used during this demonstration. Bladder pumps, bailers, and inertia pumps are generally not suitable for ClO_4^- sampling with IX columns because the pressures and/or volumes are not usually adequate for sample collection. In those instances in which ClO_4^- concentrations in groundwater are relatively high such that bulk water samples can be collected and transported to the laboratory (e.g., a 5-L volume of water from a well with

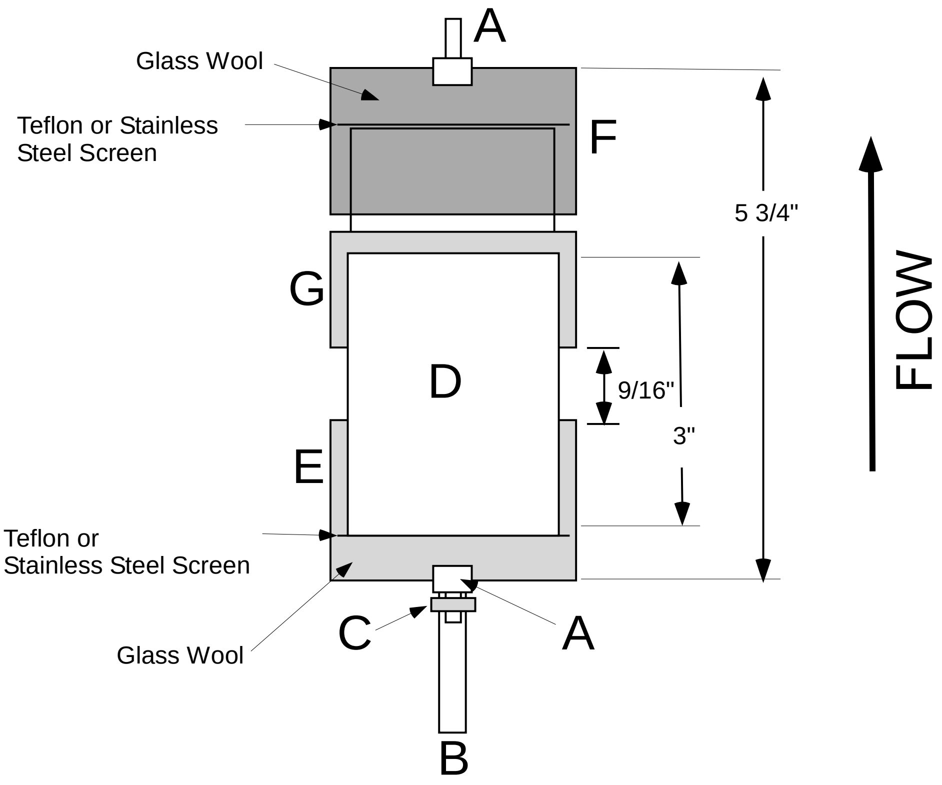
ClO_4^- concentration of 2 mg/L), the aforementioned pumps can be used for groundwater sampling. Typically, however, groundwater with ClO_4^- of unknown origin has concentrations that are far below that necessary to collect bulk water samples.

During this demonstration, “low-flow” groundwater sampling principles were generally applied (Puls and Barcelona, 1996). In general, water was pumped thorough a multi-meter with a flow cell (e.g., YSI 600 XL, YSI Inc., Yellow Springs, OH), and key field parameters such as pH, oxidation-reduction potential, turbidity, and dissolved oxygen were measured. When the field parameters stabilized, water samples were collected for measurement of supporting parameters, and then IX columns were connected to the pump for collection of ClO_4^- for stable isotope analysis. The flow rates employed by the “low-flow” approach were often increased compared to typical guidance (i.e., to 2 L/min in some instances). However, even at these slightly elevated flow rates, the groundwater that passed through the column was considered to be representative of that entering the screened interval of the well.

During sampling, water was pumped directly from a well or, in some instances from a tap or faucet, to the inlet port of the column using tubing and metal and/or plastic fittings and connections. Because ClO_4^- has a low affinity for most tubing materials, the tubing selected for sampling was not considered critical. Because well water commonly has some turbidity due to suspended sediments or other precipitates, cartridge pre-filters were often placed in-line before the IX column to prevent fouling of the IX resin and a consequent increase in pressure across the column. A typical column setup for a groundwater well is provided in Figure 5.3. For household sampling, a barbed hose fitting and tubing was generally used to connect directly between an outside house faucet and the IX column using polyethylene, Tygon, or other tubing. A cartridge pre-filter generally was not required for this application.

Columns were usually operated in an upflow direction (vertical orientation). For the typical 100-mL column set-up as shown in Figs 5.1-5.3, flow rates were generally set not exceed ~ 2 L/min to allow adequate residence time for ClO_4^- adsorption in the IX resin within the column. Prior to initiating groundwater flow through the IX column, and periodically thereafter (with intervals determined by expected sampling time), groundwater samples generally were collected prior to the IX column (influent) and after the column (effluent) for analysis of ClO_4^- concentration. The flow rate of water through the column also checked periodically, and the flow rates adjusted accordingly.

Figure 5.1. Schematic diagram of typical ion exchange (IX) column used to collect ClO_4^- from groundwater.



A = 1/4" x 1/8" polypropylene or brass hose fitting (2)
B = Tygon tubing (2 ft) 1/4"x3/8"
C = Hose clamp (1)
D = 1 1/4" clear PVC pipe, sch 80 (2 3/4")
E = 1 1/4" PVC sch 40 end cap (1) F = 1 1/4" PVC sch 80 threaded cap (1)
G = 1 1/4" PVC sch 40 male adaptor NPT x socket weld (1)

Figure 5.2. Photograph of (A) IX column used to collect ClO_4^- from groundwater and (b) column attached to well during sample collection.

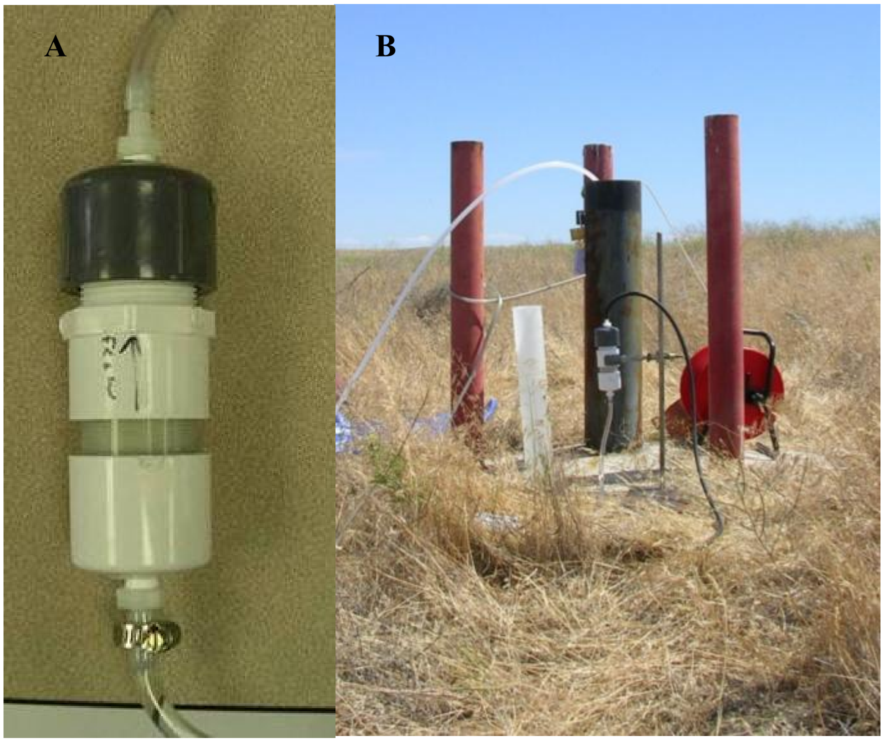
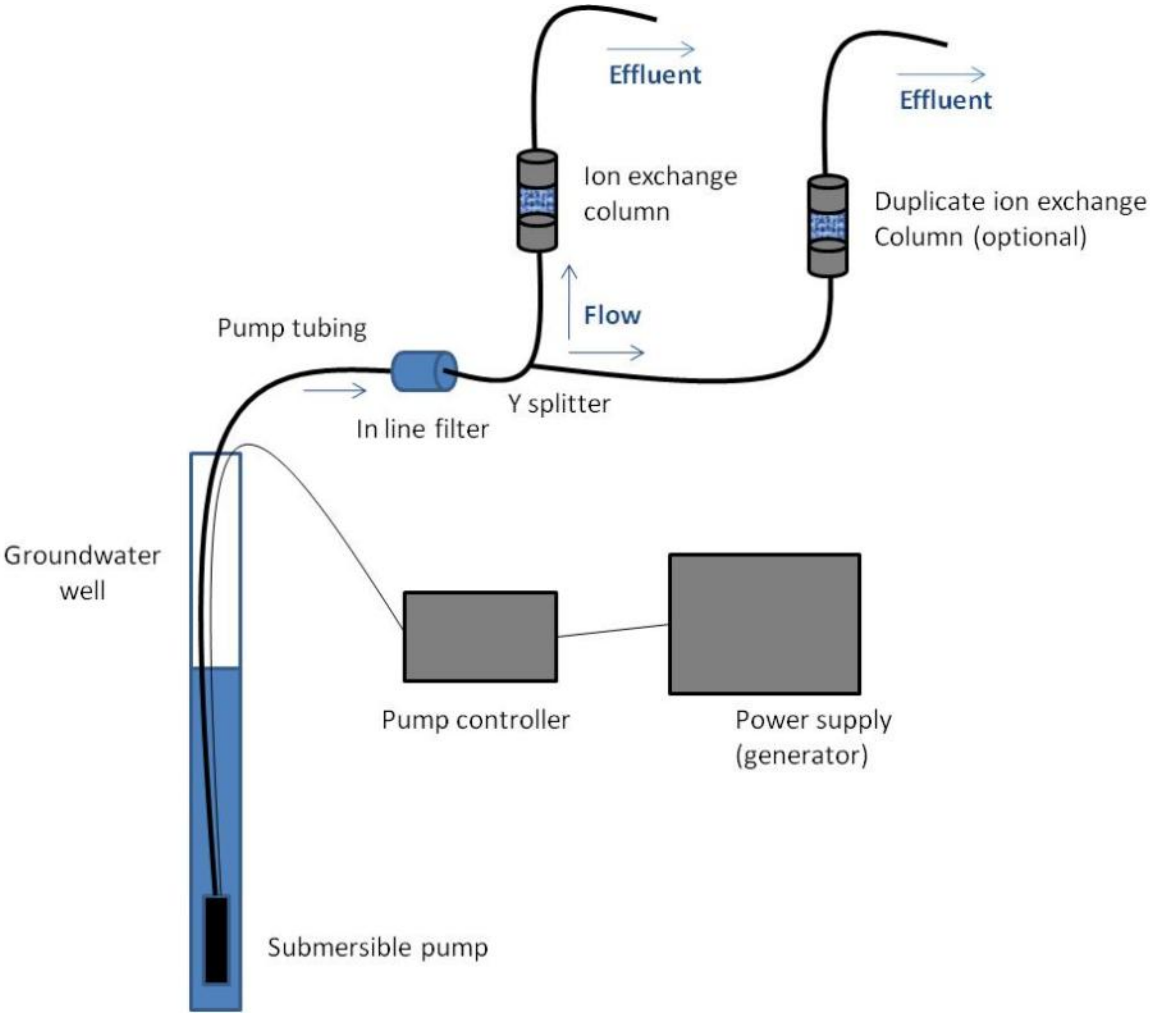


Figure 5.3. Typical set-up of ClO_4^- sampling equipment at a groundwater well. A duplicate column is recommended but optional.



5.2.1.3 Sample Preservation and Shipment

Once the desired amount of water was passed through the IX column to collect ClO_4^- (generally 5-10 mg adsorbed to the resin) the column was disconnected from the pump, drained of standing water, and sealed by attaching a small piece of tubing from one end to the other (i.e., attached to the hose barbs on each end with a hose clamp). The columns were then placed in double Ziploc style storage bags and stored/shipped at 4°C for preservation prior to processing. In most instances, ClO_4^- will be stable on the column under these conditions because air is present in the column, and ClO_4^- biodegradation does not occur under aerobic conditions (Coates and Achenbach, 2004). Adsorption of the ClO_4^- onto the resin is also expected to inhibit biodegradation. However, in instances where samples were collected from anoxic groundwater and(or) water with high total organic carbon content (e.g., during *in situ* tests of perchlorate fractionation during biodegradation; Section 7.5; Hatzinger et al., 2009), the potential for ClO_4^- biodegradation on the column exists. In these instances, dilute HCl was used to preserve the column prior to processing. To preserve with HCl, the column was drained of groundwater, and then the resin was saturated with a solution of 0.05 N HCl, which will reduce the pH to < 2 (Hatzinger et al., 2009). No loss of ClO_4^- is expected during this step. The ends were then sealed with a single piece of tubing using hose clamps as described previously, and the column was placed in double Ziploc style storage bags. The preserved columns were stored/shipped at 4 °C prior to processing. At present, columns do not have a maximum "hold time" prior to extraction and analysis. Additional groundwater sampling details and relevant QA/QC procedures are described in the accompanying ESTCP Guidance Document (Hatzinger et al., 2011).

5.2.2 Soil Sampling

Perchlorate for isotopic analysis was extracted from solid samples of surficial salt deposits, and vadose zone soils during this project. The basic procedure for collection was described recently by Jackson et al., (2010) (See Appendix C). Initially, the concentration of ClO_4^- in the bulk material was determined by collecting several solid samples, extracting soluble salts from the samples with ClO_4^--free water, and then measuring the ClO_4^- concentration. The total amount of solid material that must be extracted (leached) to collect the required mg quantities of ClO_4^- for purification and isotopic analysis was then determined. Because

ClO_4^- is highly soluble in water, it can be removed readily from dispersed solids by aqueous leaching. During soil sampling, the vadose-zone material containing ClO_4^- was initially collected using a backhoe and placed on a tarp to isolate it from surrounding soils, and then extracted with ClO_4^--free water (Jackson et al., 2010). It is important to remove any ClO_4^- from the water source used for solid extraction, which can be accomplished by initially passing that water through a large column of Purolite A530E resin prior to use, as described in Jackson et al., (2010).

Extraction of ClO_4^- from vadose soil was conducted in small batches by adding solid material (40 to 60 kg) and water (~ 80 L) in a clean cement mixer, mixing the slurry for ~10 min, then decanting the liquid into a large polyethylene drum (Figure 5.4). After sediments settled in the drums, the overlying water (with dissolved ClO_4^-) was pumped to a clean container, then passed through a sediment pre-filter (50-µM pore-size; General Electric Co., Trevose, PA) and an IX resin column in sequence, as described previously for groundwater sampling (see Figures 5.3 and 5.4). It should be noted that for ClO_4^- at low µg/kg concentrations in solid material, extraction of several thousand kg of solids is required to obtain sufficient ClO_4^- for Cl and O isotopic analyses.

5.2.3 Collection and Purification of Perchlorate in Samples with Elevated Chlorate

5.2.3.1 Bacterial Degradation of Chlorate

A specialized method was developed to remove chlorate (ClO_3^-) from two samples of chlorate defoliants (Defol 5 and Poly-foliant 5), so that the stable isotope ratio of Cl and O in ClO_4^- present within those samples could be accurately measured. This method utilized a chlorate-reducing bacterium, *Pseudomonas* sp. PDA, provided by the laboratory of Dr. Bruce Logan at Penn State University (Xu et al., 2004). Strain PDA reduces ClO_3^-, but not NO_3^- or ClO_4^-. This bacterial strain was grown in a basal salts medium (BSM; Hareland et al., 1975), amended with acetate as a carbon source to approximately 3,000 mg/L and with one of the two defoliants to a maximum ClO_3^- concentration of ~ 4000 mg/L. In order to collect enough ClO_4^- for stable isotope analysis from the samples, 60 to 90 L of culture was grown on the defoliants in poly drums. The Defol 5 contained 423,000 mg/L of ClO_3^- and 26 mg/L of ClO_4^-, and the Poly-Foliant 5 contained 450,000 mg/L of ClO_3^- and 16 mg/L of

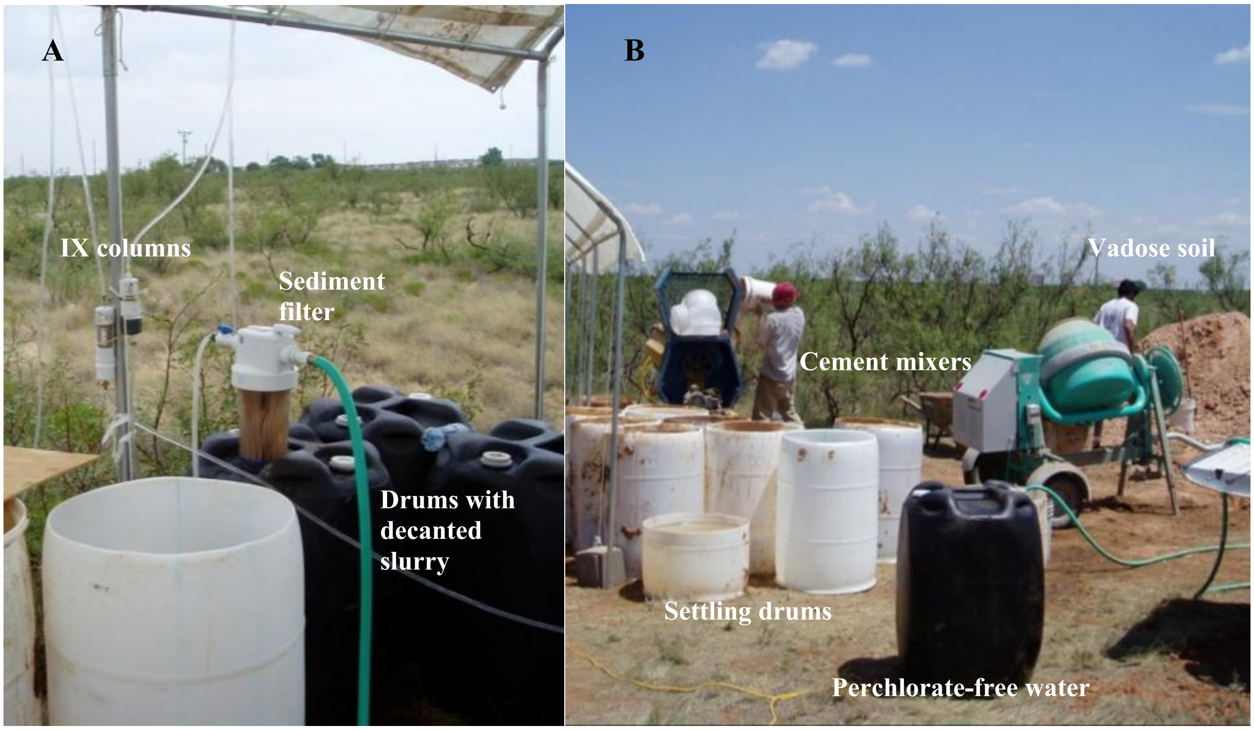
ClO_4^-. The drums were sparged with nitrogen gas to maintain anoxic conditions. Subsamples were collected periodically, filtered to remove cells, and analyzed for acetate, ClO_3^-, and ClO_4^-. Acetate was re-added when concentrations declined to below detection via analysis of volatile fatty acids by EPA Method 300m. When ClO_3^- concentrations were below detection by ion chromatography (< 0.2 mg/L; EPA Method 300), the volumes in the drums were centrifuged using a continuous centrifuge (Carl Padberg, West Germany), and the effluent was passed through a ClO_4^- ion exchange column, as described for soils and groundwater, and shipped on ice to ORNL for ClO_4^- extraction and purification as described in subsequent sections.

5.2.3.2 Degradation of Chlorate using Hydrogen Gas and a Nickel Catalyst

Previous studies conducted in Shaw's laboratory by Dr. Charles Schaefer revealed that, in the presence of a zero-valent nickel (Ni) catalyst, hydrogen gas could be used to abiotically degrade ClO_3^- and NO_3^-, but that ClO_4^- was unaffected (*Schaefer, unpublished data*). This catalytic process was utilized for some commercial bleach samples to remove residual ClO_3^- from samples prior to processing for ClO_4^- analysis. The bacterial method described previously in Section 5.2.3.1 could not be used in this case because the residual hypochlorite (OCl^-) was likely to kill *Pseudomonas* sp. PDA. In addition, the abiotic technique does not require the addition of growth substrate (acetate) and inorganic nutrients to the samples for microbial growth, so ultimately this technique is a preferred method to remove ClO_3^- or NO_3^- from samples where required.

In order to remove ClO_3^- from the bleach samples, each sample was placed in a glass carboy with a vented rubber stopper. The samples received ~ 5 g/L of Ni (65% wt on silica alumina catalyst; Sigma-Aldrich, St. Louis, MO) and were purged with hydrogen gas at a flow rate of ~ 25 mL/min through a steel sparge stone. All samples received a stir bar and were placed on a stir plate during incubation at room temperature. Subsamples were taken with time and analyzed for ClO_4^- and ClO_3^-. When the ClO_3^- concentration was below detection by ion chromatography (EPA Method 300), then the effluent was passed through a ClO_4^- ion exchange column, as described for soils and groundwater, and shipped on ice to ORNL for ClO_4^- extraction and purification as described in subsequent sections.

Figure 5.4. Extraction of ClO_4^- from vadose-zone sediment in West Texas. (A) Collection of ClO_4^- from decanted soil extracts on IX columns after passing through a sediment filter. (B) Extraction of ClO_4^- from soil by slurrying in cement mixers. (see Appendix C; Jackson et al. 2010 for further details).



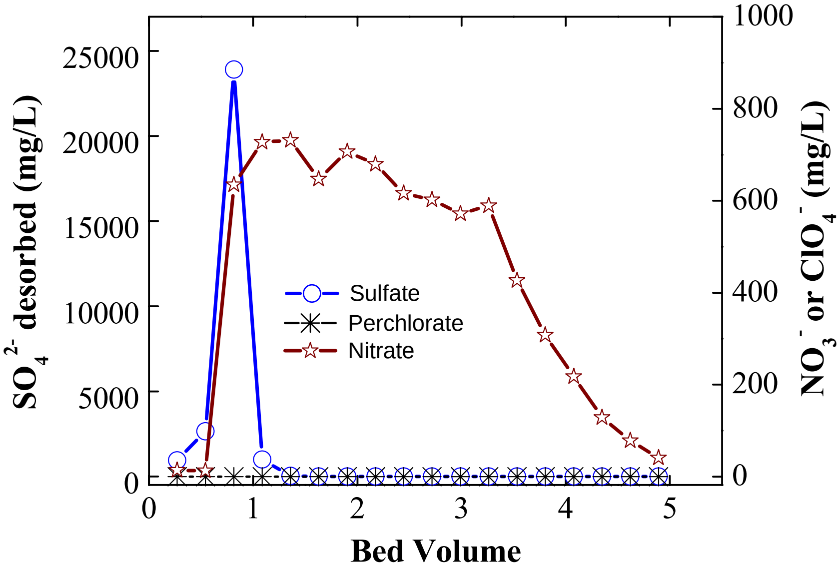
5.2.4 Extraction and Purification of Perchlorate on IX Columns

The second step after collection of ClO_4^- in the field is extraction of the adsorbed ClO_4^- from the IX resin and separation of the ClO_4^- from other compounds that also have some affinity to the IX resin, including NO_3^-, sulfate (SO_4^{2-}), bicarbonate, (HCO_3^-), and a range of humic and(or) other organic compounds and clays. Depending on the environmental source and location of the sample, other compounds, including perrhenate (ReO_4^-) and ClO_3^- may also be present on the resin, and in urban areas, surfactants and detergents commonly are adsorbed. A simple process utilizing ferric chloride ($FeCl_3$) and hydrochloric acid (HCl) has been developed to remove ClO_4^- from the bifunctional anion exchange resin, primarily by generating tetrachloroferrate ($FeCl_4^-$), which effectively displaces ClO_4^- on adsorption sites (Gu et al., 2001, 2007; Gu and Brown, 2006). However, the subsequent steps required to purify the extracted ClO_4^- from the complex mixture of residual $FeCl_3$, anions, and organic compounds removed from the resin, are both labor intensive and somewhat variable in nature depending on the anions and other chemicals in the extract. This phase of the process, which includes various precipitation, selective adsorption, and filtration steps has been the subject of significant research and development over the course of this project. These purification methods and relevant QA/QC procedures are described in detail in Hatzinger et al., (2011). Please refer to this document for additional details. A summary of methods is provided in subsequent sections.

5.2.4.1 Resin Removal from IX Columns and Resin Pre-Wash

To remove other anions from the IX resin columns, the resin was generally packed into a glass preparatory column and then washed with several bed volumes (BV) of 4 M HCl. The HCl solution removes much of the adsorbed SO_4^{2-}, NO_3^-, HCO_3^-, and some of the humics, but does not desorb ClO_4^- which is more strongly held by the bifunctional resin than most other anions or organics. A typical elution profile from a preparative column packed with resin is provided in Figure 5.5. The 4 M HCl also removes a significant fraction of the organics and carbonates when they are present on the resin. Although it is difficult to monitor for organics in the effluent solution, a “brownish” color of the initial solution eluting from the column is evidence of their presence in the HCl. Carbonates will be removed primarily as CO_2 gas evolution from the acidic solution.

Figure 5.5. Elution profiles of SO_4^{2-}, NO_3^-, and ClO_4^- from IX columns using 4 M HCl as an extractant. The number of bed volumes of HCl is given on the x-axis.



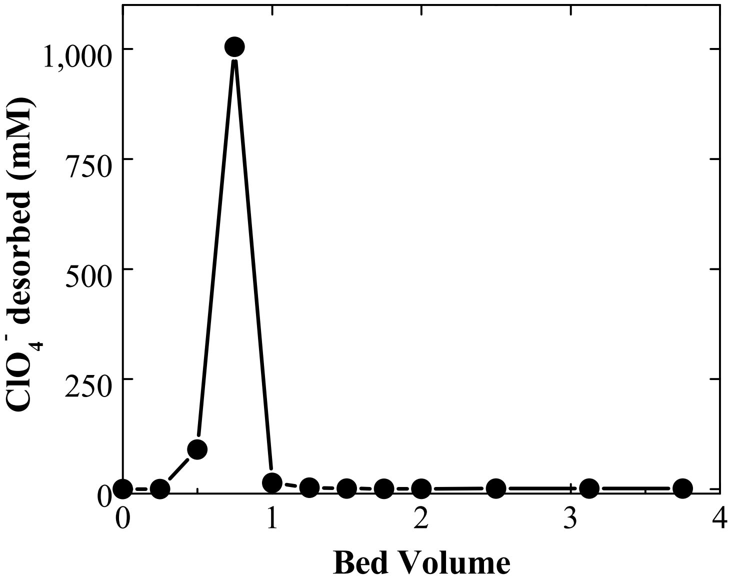
5.2.4.2 *Perchlorate Elution and Analysis*

The preparative column (Section 5.2.4.1) was next eluted with a combination of 1 M $FeCl_3$ and 4 M HCl to remove adsorbed ClO_4^- (Gu et al., 2001, 2007, 2011). When the $FeCl_3$ is mixed into an excess of Cl^-, tetrachloroferrate ($FeCl_4^-$) ions form at equilibrium according to Equation 5.1:

[Eq. 5.1] $$FeCl_3(aq) + Cl^- \rightleftharpoons FeCl_4^-$$

The $FeCl_4^-$ ion is chemically similar to ClO_4^-, each being large, poorly hydrated, tetrahedral anions. Because of their physicochemical similarities, $FeCl_4^-$ effectively displaces ClO_4^- from the bifunctional IX resin, and only a small number of bed volumes of the solution are required to completely desorb the resin-bound ClO_4^- (Fig 5.6). In general, the effluent was collected in fractions, and the ClO_4^- concentration in each fraction was analyzed using EPA Method 314.0 or an alternative accepted method (USEPA, 2009). The total amount of eluted ClO_4^- was then determined using the concentration and volume of each fraction. The effluent fractions containing ClO_4^- were then combined into a single sample.

Figure 5.6. Elution of ClO_4^- from IX resin using $FeCl_4^-$ solution. The number of bed volumes of extractant is given on the x-axis.



5.2.4.3 Effluent Clean-up and Concentration of ClO_4^-

Two somewhat different approaches were developed to recover ClO_4^- from the HCl-$FeCl_3$ eluent solution (Section 5.2.4.2). These alternative approaches, the first of which was developed at ORNL and the second at UIC, utilize different techniques to remove abundant quantities of Fe (from the $FeCl_3$-HCl eluent) from solution. The approach developed at ORNL, which was used to process most of the samples collected during this project, is summarized herein. A comparison of the two techniques is provided in Hatzinger et al., (2011).

The raw eluent solution containing ClO_4^- also contains a high concentration of Fe, as well as a mixture of other anions and organics. A pure ClO_4^- salt must be obtained from this mixture. The ORNL approach to remove Fe and other impurities entails initial neutralization of the acidic eluent with sodium hydroxide (NaOH) in a glass beaker to achieve a pH between 9 and 10. At this alkaline pH, the Fe in solution precipitates primarily as $Fe(OH)_3$ (red-brown precipitate) with the ClO_4^- remaining in the clear solution. The $Fe(OH)_3$ precipitates usually were separated by centrifugation, washed once with deionized (DI) water, re-centrifuged, and the clear supernatant solution (with ClO_4^-) was collected. The resulting clear supernatant solution with ClO_4^- was then concentrated using a vacuum concentration system. The evaporative process continued until the estimated ClO_4^- concentration in solution (based on estimates in the $FeCl_3$-HCl eluent) was in excess of 3 mg/mL.

5.2.4.4 Perchlorate Crystallization and Recovery

The final step in sample processing is crystallization of ClO_4^- as a salt. Prior to this step, it is important to check that no other precipitates are present in the final concentrated extract (> 3 mg/mL ClO_4^-). If precipitates are observed, they should be removed via filtration. The concentrated ClO_4^- in the solution can be crystallized as rubidium perchlorate ($RbClO_4$) by adding RbCl, as cesium perchlorate ($CsClO_4$) by addition of CsCl or CsOH, or as potassium perchlorate ($KClO_4$) by addition of KOH or KCl. Most of the samples prepared for this project were precipitated as $CsClO_4$ (See Appendix A, Table A-1). After crystallization of the ClO_4 salt was observed, the crystals were collected by filtration, and the liquid saved and analyzed for residual ClO_4^-. The crystals were next rinsed with a few drops of 90 % methanol (by volume, in water) to ensure that surface of the crystallized ClO_4^- salt was free from other salts. The salts were then carefully collected and placed in a clean glass vial for assessment of purity as described in the next section.

5.2.4.5 Assessing Purity of Recovered Perchlorate Crystals

To ensure that the recovered $CsClO_4$ (or $KClO_4$) was of the highest purity for IRMS, the recovered ClO_4^- salts were examined using one of two techniques: (1) non-destructive Raman spectroscopy or (2) dissolution and analysis by ion chromatography (IC) using USEPA Method 300.0 (USEPA, 1993) or equivalent. Additional details for these two techniques are given in Hatzinger et al., 2011. Raman spectroscopy was used for most of the samples analyzed for this project. Among the most common potential contaminants containing O are NO_3^- and SO_4^{2-}. ReO_4^- has also been identified in a subset of samples (Gu et al., 2011). It is desirable that impurities in the ClO_4^- salt comprise no more than 1 % of the total O in the sample on a molar basis (i.e., the mole fraction of O in the sample that is not attributable to ClO_4^- should be less than 0.01) in order to minimize any effects on O isotopic analysis. On a mass basis, this would correspond to approximately 0.02 mg of NO_3^- or 0.03 mg of SO_4^{2-} per mg of ClO_4^-. Organic compounds also are sometimes residual contaminants in purified samples if purification steps are not 100 % effective. These compounds can potentially react with O_2 released during ClO_4^- decomposition, generating CO_2 and causing O isotopic fractionation. The CO_2 peak was generally monitored when analyzing O_2 produced by ClO_4^- decomposition during IRMS to determine the level of contamination with organic C, as described in more detail in Section 5.2.5 and in Hatzinger et al., (2011).

5.2.4.6 Reprocessing Impure Samples

If impurities were identified in a purified sample of $CsClO_4$ (or $KClO_4$) by Raman spectroscopy and(or) IC at concentrations appreciably greater than 1 % of the total O in the sample on a molar basis, the sample was often re-purified by dissolving in ClO_4^--free distilled deionized water (DDI), re-precipitating by evaporation, and rinsing with a small amount (e.g., 1 drop) of methanol or H_2O_2 solution, until satisfactory purity was achieved. In some instances, depending on the type of contaminant, the aqueous solution with ClO_4^- was passed through a small (e.g., 5-mL volume) glass preparative column with A530E resin so that the ClO_4^- was selectively adsorbed in the resin. The resin was then re-processed by washing with HCl to remove impurities as described previously. When impurities are detected at concentrations corresponding to < 0.01 for the mole fraction of O in the sample by Raman spectroscopy and(or) IC, the sample was then ready for O and Cl isotopic analyses (or re-analysis) by IRMS as described in subsequent Sections 5.2.5 and 5.2.6, respectively.

5.2.5 Analysis of Oxygen Isotopes in Perchlorate by IRMS

After the $CsClO_4$, $RbClO_4$, or $KClO_4$ was purified according to the procedures described in the previous section, it was analyzed for O and Cl isotopic composition by IRMS according to the procedures described in this section for O and in Section 5.2.6 for Cl. Analysis of O isotopes in ClO_4^- can be conducted by two different methods, both of which are described in the following sections. The first method entails conversion of alkali ClO_4^- salts to alkali

Cl salts plus O_2 gas. The values of $\delta^{18}O$ and $\delta^{17}O$ can each be measured by decomposing $CsClO_4$ (or $RbClO_4$ or $KClO_4$) to yield a stoichiometric quantity of O_2 according to Eq 5.2:

[Eq. 5.2] $$CsClO_4 \rightarrow CsCl + 2O_2$$

The O_2 gas is then admitted to a magnetic-sector type, dual-inlet isotope-ratio mass spectrometer (DI-IRMS) and analyzed by monitoring *m/z* 32 ($^{16}O^{16}O$), 33 ($^{17}O^{16}O$), and 34 ($^{18}O^{16}O$, plus an insignificant contribution from $^{17}O^{17}O$). Yields of O (as O_2) by this method are typically within ±5 % for pure ClO_4^- salts. Analysis of $\delta^{18}O$ (but not $\delta^{17}O$) also can be done by reacting the ClO_4^- salt with glassy C to produce CO, which is then transferred in a He carrier through a molecular-sieve to a continuous-flow IRMS (CF-IRMS) and analyzed by monitoring peaks at *m/z* 28 ($^{12}C^{16}O$) and 30 ($^{12}C^{18}O$, plus an insignificant contribution from $^{13}C^{17}O$). Yields of O (as CO) typically are 100 ±2 % for pure ClO_4^- reagents and samples.

5.2.5.1 Terminology and Standards for Oxygen Stable Isotopic Analysis

As described in Section 2.1, stable isotopic compositions are measured and reported as relative differences of isotope ratios (in either moles or numbers of atoms) between two substances, one of which may be an international measurement standard. For oxygen:

[Eq. 5.3] $$\delta^{18}O = R(^{18}O/^{16}O)_{sample}/R(^{18}O/^{16}O)_{standard} - 1$$

[Eq. 5.4] $$\delta^{17}O = R(^{17}O/^{16}O)_{sample}/R(^{17}O/^{16}O)_{standard} - 1,$$

where the standard in both equations is Vienna Standard Mean Ocean Water (VSMOW). Values of $\delta^{18}O$ and $\delta^{17}O$ typically are reported in parts per thousand (per mil, or ‰). By international convention, the $\delta^{18}O$ scale is defined by two standards, with VSMOW at 0 and Standard Light Antarctic Precipitation (SLAP) at a value of -55.5 ‰ (Gonfiantini, 1978; Coplen, 1994).

Variations in $R(^{17}O/^{16}O)$ and $R(^{18}O/^{16}O)$ caused by most physical-chemical fractionation processes on Earth are related systematically by the relative differences in the masses of the isotopes. Such "mass-dependent" variations can vary slightly for different processes and they can be described in various ways (e.g., Thiemens, 1999; Miller, 2002; Angert et al., 2004; Assonov and Brenninkmeijer, 2005). For this project:

$$\text{[Eq. 5.5]} \qquad (1 + \delta^{17}\mathrm{O}) = (1 + \delta^{18}\mathrm{O})^{\lambda},$$

with $\lambda \approx 0.525$ (Miller, 2002; Böhlke et al., 2005). Departures from mass-dependent O-isotope variation are important features of some materials, including some natural ClO_4^-. Departures from mass-dependent O-isotope variation in ClO_4^- are described in this report as deviations from the relation given in Equation 5.5:

$$\text{[Eq. 5.6]} \qquad \Delta^{17}\mathrm{O} = [(1 + \delta^{17}\mathrm{O}) / (1 + \delta^{18}\mathrm{O})^{0.525}] - 1.$$

Values of Δ^{17}O typically are reported in parts per thousand (per mil, or ‰).

Because water (H_2O) samples may not be compatible with analytical techniques used for other compounds such as ClO_4^-, Equations 5.3 and 5.4 are expanded to permit routine calibration of ClO_4^- analyses using a pair of ClO_4^- isotopic reference materials developed during this project (USGS37 and USGS38) (see description in Section 5.2.8) with contrasting isotopic compositions on the VSMOW-SLAP scale, a process commonly referred to as "normalization":

$$\text{[Eq. 5.7]} \qquad \delta^{18}\mathrm{O}_{\mathrm{i/VSMOW}} = \delta^{18}\mathrm{O}_{\mathrm{37/VSMOW}} + [\delta^{18}\mathrm{O}_{\mathrm{i/rg}} - \delta^{18}\mathrm{O}_{\mathrm{37/rg}}]_{\mathrm{meas.}} \cdot [\delta^{18}\mathrm{O}_{\mathrm{38/VSMOW}} - \delta^{18}\mathrm{O}_{\mathrm{37/VSMOW}}] / [\delta^{18}\mathrm{O}_{\mathrm{38/rg}} - \delta^{18}\mathrm{O}_{\mathrm{37/rg}}]_{\mathrm{meas}}.$$

$$\text{[Eq. 5.8]} \qquad \delta^{17}\mathrm{O}_{\mathrm{i/VSMOW}} = \delta^{17}\mathrm{O}_{\mathrm{37/VSMOW}} + [\delta^{17}\mathrm{O}_{\mathrm{i/rg}} - \delta^{17}\mathrm{O}_{\mathrm{37/rg}}]_{\mathrm{meas.}} \cdot [\delta^{17}\mathrm{O}_{\mathrm{38/VSMOW}} - \delta^{17}\mathrm{O}_{\mathrm{37/VSMOW}}] / [\delta^{17}\mathrm{O}_{\mathrm{38/rg}} - \delta^{17}\mathrm{O}_{\mathrm{37/rg}}]_{\mathrm{meas}}.,$$

where 37 and 38 refer to the ClO_4^- reference materials USGS37 and USG38, and rg is an internal laboratory reference gas (either CO or O_2, see below) against which all samples and reference materials are analyzed in the mass spectrometer during a single batch of analyses.

The isotopic reference materials consist of reagent-grade $KClO_4$ salts that were prepared specifically for calibration of ClO_4^- isotopic analyses as part of this ESTCP Project (see Section 5.2.8). The $\delta^{18}O$ scale is based on CO-CF-IRMS analyses (see below) of the ClO_4^- isotopic reference materials against international H_2O, NO_3^-, and SO_4^{2-} isotopic reference materials as described by Böhlke et al., (2003), and all data are referenced to the conventional VSMOW-SLAP scale (Gonfiantini, 1978; Coplen, 1994). For $\delta^{18}O$, the secondary calibration values used to generate provisional ClO_4^- data with respect to VSMOW are -27.9 ‰ for USGS34 (KNO_3), +25.6 ‰ for IAEA-N3 (KNO_3), +57.5 ‰ for USGS35 ($NaNO_3$), and +8.6 ‰ for NBS 127 ($BaSO_4$) (Böhlke et al., 2003). The $\delta^{17}O$ scale for ClO_4^- is provisionally based on the assumption that the normal reagent $KClO_4$ reference material (USGS37) has $R(^{17}O/^{16}O)$ and $R(^{18}O/^{16}O)$ values that are related to those of VSMOW by mass-dependent processes ($\Delta^{17}O = 0$, as defined by Equation 2.6; Böhlke et al., 2005).

International efforts to reconcile $\delta^{18}O$ calibration scales for different reference materials are ongoing in the scientific community (e.g., Brand et al., 2009), as are efforts to define and calibrate mass-dependent variations in $\delta^{18}O$ and $\delta^{17}O$ for different chemical systems and processes. The current project is contributing to these efforts, while providing an interim basis for reporting and comparing O isotope data for environmental samples of ClO_4^-. Because the calibration data are provisional and could change, reported data are accompanied by descriptions of the reference materials and calibration values that were used during the analyses, and by the equations that were used to evaluate mass dependence, to permit subsequent re-evaluation and comparison with other data.

5.2.5.2 Analysis of $\delta^{18}O$ and $\delta^{17}O$ by Off-Line Conversion to O_2, with Dual-Inlet Isotope-Ratio Mass Spectrometry (O2-DI-IRMS)

To perform DI-IRMS on O_2 derived from ClO_4^-, aliquots of pure $CsClO_4$, $RbClO_4$, or $KClO_4$, including reagents and environmental samples derived from the sampling and purification methods described previously in this document, are weighed into quartz glass tubes (mass equivalent to 2.5 µmol of ClO_4^- per tube). The tubes are evacuated and sealed with a torch and baked at 650 °C for 20 min to produce O_2 gas from the ClO_4^-. Alternatively, samples are weighed into Pyrex glass tubes (mass equivalent to 2.5 µmol of ClO_4^- per tube), which are evacuated and sealed with a torch, and baked at 600 °C for 30 min to produce O_2 gas. The tubes are broken manually in an evacuated glass tube cracker, the O_2 is expanded into a liquid N_2 cold trap for 1 min to remove traces of condensable gases (except when being tested for other decomposition products such as CO_2), then admitted to an IRMS and analyzed in dual-inlet mode against an O_2 reference gas from a tank by monitoring *m/z* 32 ($^{16}O^{16}O$), 33 ($^{17}O^{16}O$), and 34 ($^{18}O^{16}O$, plus an insignificant contribution from $^{17}O^{17}O$). Typical reproducibility of $\delta^{18}O$ measurements by O2-DI-IRMS on multiple aliquots (typically three to four) in a given batch generally are around ±0.2‰ or better for USGS37 and ±0.5‰ or better for USGS38 (Hatzinger et al., 2011).

5.2.5.3 Analysis of $\delta^{18}O$ by On-Line Conversion to CO, with Continuous-Flow Isotope-Ratio Mass Spectrometry (CO-CF-IRMS)

To perform CF-IRMS on CO derived from ClO_4^-, aliquots of pure $CsClO_4$, $RbClO_4$, or $KClO_4$, including reagents and environmental samples derived from the sampling and purification methods detailed previously in this document, are weighed into silver foil cups (mass equivalent to 2 µmol of ClO_4^- per cup). The loaded cups are dropped automatically from a He-flushed carousel into a graphite crucible in a glassy carbon reactor at a nominal (gauge) temperature of 1325°C to produce CO gas from the ClO_4^-. The CO is transferred in He carrier gas through a molecular-sieve gas chromatograph to an IRMS and analyzed in continuous-flow mode by monitoring peaks at *m/z* 28 ($^{12}C^{16}O$) and 30 ($^{12}C^{18}O$, plus an insignificant contribution from $^{13}C^{17}O$). Typical reproducibility of $\delta^{18}O$ measurements by CO-CF-IRMS on multiple aliquots (typically four to eight) in a given batch generally are around ±0.2‰ or better for USGS37 and ±0.2‰ or better for USGS38 (Hatzinger et al., 2011).

5.2.6 Analysis of Chlorine Isotopes in Perchlorate by Isotope-Ratio Mass Spectrometry

The analysis of Cl stable isotopes is conducted on the Cl^- produced by decomposition of alkali ClO_4^- salts as described in Section 5.2.5 for production of O_2. The Cl^- derived from ClO_4^- initially is converted to methyl chloride (CH_3Cl) gas by reaction of AgCl with CH_3I

(Eggenkamp, 1994; Holt et al., 1997), which is then analyzed by IRMS according to the procedures described in this section. The methods and calibrations of Cl isotopic analyses from ClO_4^- have been summarized previously in several papers and book chapters as described previously, and additional details on method procedures and QA/QC are found in Hatzinger et al., 2011. Typical reproducibility of δ^{37}Cl measurements on multiple aliquots in a given batch generally are around ±0.2‰ or better for USGS37 and ±0.3‰ or better for USGS38 (Hatzinger et al., 2011).

5.2.6.1 Terminology and Standards for Chlorine Stable Isotopic Analysis

As described previously, stable isotopic compositions are measured and reported as relative differences of isotope ratios (in either moles or numbers of atoms) between two substances, one of which may be an international measurement standard . For chlorine:

[Eq. 5.9] $$\delta^{37}\mathrm{Cl} = R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{\mathrm{sample}} / R(^{37}\mathrm{Cl}/^{35}\mathrm{Cl})_{\mathrm{standard}} - 1$$

where the international measurement standard is Standard Mean Ocean Chloride (SMOC). Values of δ^{37}Cl typically are reported in parts per thousand (per mil, or ‰). The most widely-used Cl isotope reference material is chloride prepared from seawater which has uniform δ^{37}Cl to within ± 0.08 ‰ (Godon et al., 2004).

Routine calibration of ClO_4^- isotopic analyses can be done by using the pair of ClO_4^- isotopic reference materials developed during this project (USGS37 and USGS38) with contrasting isotopic compositions, a process commonly referred to as "normalization":

[Eq. 5.10] $$\delta^{37}\mathrm{Cl}_{\mathrm{i/SMOC}} = \delta^{37}\mathrm{Cl}_{\mathrm{37/SMOC}} + [\delta^{37}\mathrm{Cl}_{\mathrm{i/rg}} - \delta^{37}\mathrm{Cl}_{\mathrm{37/rg}}]_{\mathrm{meas.}} \cdot [\delta^{37}\mathrm{Cl}_{\mathrm{38/SMOC}} - \delta^{37}\mathrm{Cl}_{\mathrm{37/SMOC}}] / [\delta^{37}\mathrm{Cl}_{\mathrm{38/rg}} - \delta^{37}\mathrm{Cl}_{\mathrm{37/rg}}]_{\mathrm{meas.}}$$

where 37 and 38 refer to the perchlorate isotopic reference materials USGS37 and USG38, and rg is an internal laboratory reference gas (CH_3Cl) against which all samples and reference materials are analyzed in the mass spectrometer during a single batch of analyses.

Isotopic reference materials consist of reagent-grade $KClO_4$ salts that were prepared specifically for calibration of ClO_4^- isotopic analyses as described in Section 5.2.8. The $\delta^{37}Cl$ scale is based on isotopic analyses of the USGS ClO_4^- isotopic reference materials against SMOC. As noted for O isotopes in ClO_4^-, the current ClO_4^- isotope project is providing an interim basis for reporting and comparing Cl isotope data for environmental samples of ClO_4^-. Because the calibration data are provisional and could change, reported data are accompanied by statements describing the normalization equations and values that were used during the analyses to permit subsequent re-evaluation.

5.2.6.2 Analysis of $\delta^{37}Cl$ by Off-Line Conversion to Methyl Chloride, with Dual-Inlet Isotope-Ratio Mass Spectrometry (CH_3Cl-DI-IRMS)

Chlorine isotopic analyses are performed on samples of alkali halide (CsCl, RbCl, or KCl) residues from decomposition of ClO_4^- salts as described above for preparation of O_2 for isotopic analysis (Section 5.2.5). Alkali halide residue in a decomposition tube is dissolved using 10 mL of warm 18.2 MΩ deionized water. The dissolved alkali halide residue is transferred into a 50-mL polypropylene conical tube. Sodium phosphate/citric acid buffer (0.004 M phosphate, 0.098 M citric acid) and potassium nitrate (0.4 M KNO_3) are added to optimize crystallization of AgCl in the subsequent step. This solution is then heated to 80 °C and an excess of silver nitrate ($AgNO_3$) is added as described in Eggenkamp, (1994). Silver chloride (AgCl) precipitates are then allowed to ripen in the dark for ~ 24 hr. The AgCl solids are then centrifuged, the supernatant is removed, and dilute 0.03 M nitric acid (HNO_3) is used to rinse the solids three times. Solids are then transferred into a Pyrex combustion tube (20 cm x 9 mm) and dried in a darkened vacuum oven at 80 °C. After the sample is dry, the combustion tube is evacuated and methyl iodide (CH_3I) is cryogenically transferred into the tube which is then sealed and baked for 2 h at 300 °C as described in Holt et al. (1997). The resulting CH_3Cl is purified using gas chromatography, cryo-concentrated, and then admitted to an IRMS and analyzed in dual-inlet mode by monitoring peaks at *m/z* 52 ($^{12}C^1H_3{}^{37}Cl$) and 50 ($^{12}C^1H_3{}^{35}Cl$). Samples smaller than 5 μmol of Cl (0.5 mg ClO_4^-) can be analyzed by CF-IRMS, as described below in Section 5.2.6.3.

5.2.6.3 Analysis of $\delta^{37}Cl$ by On-Line Separation of Methyl Chloride, with Continuous-Flow Isotope-Ratio Mass Spectrometry (CH_3Cl-CF-IRMS)

Small samples (< 5 μmol of Cl in CH_3Cl) can be analyzed for Cl isotopic composition by CF-IRMS rather than DI-IRMS (Section 5.2.6.2). The same general sample preparation techniques are used as described in Section 5.2.6.2 until the final steps. The reacted CH_3Cl/CH_3I mixture is transferred in a He carrier-gas through a molecular-sieve gas chromatograph to separate CH_3Cl from CH_3I, then the He carrier-gas is admitted to an IRMS and the Cl isotope ratio analyzed in continuous-flow mode by monitoring peaks at *m/z* 52 ($^{12}C^{1}H_3{}^{37}Cl$) and 50 ($^{12}C^{1}H_3{}^{35}Cl$).

5.2.7 Analysis of ^{36}Cl from Perchlorate

Chlorine-36 (^{36}Cl) is a long-lived radioactive isotope of Cl with a half-life of ~ 301,000 yr. The abundance of ^{36}Cl in a sample traditionally is expressed as ^{36}Cl/Cl, which is equivalent to the atom fraction or mole fraction of ^{36}Cl, $x(^{36}Cl)$, or $N(^{36}Cl)/N(\Sigma Cl)$. Meteoric water has an average natural ^{36}Cl/Cl value of approximately 700×10^{-15} (Bentley et al., 1986; Phillips, 2000; Davis et al., 2003). ^{36}Cl is formed primarily in the stratosphere through the cosmic ray spallation of ^{40}Ar (Lehmann et al., 1993). Thermonuclear bomb tests in the Pacific Ocean (1952-1958) also contributed ^{36}Cl to the atmosphere over a short time, although the potential for production of ClO_4^- via such tests is unclear (Sturchio et al., 2009). This radioactive isotope is of interest for forensic analysis of ClO_4^- because recent data indicate that it is significantly enriched in natural indigenous ClO_4^- samples collected from the southwestern U.S. (^{36}Cl/Cl values ranging from 3130×10^{-15} to $28,800 \times 10^{-15}$) compared to either synthetic samples (^{36}Cl/Cl values ranging from 0×10^{-15} to 40×10^{-15}) or natural Chilean samples (^{36}Cl/Cl values ranging from 22×10^{-15} to 590×10^{-15}) (Sturchio et al., 2009, 2011; Jackson et al., 2010). Age dating of some of the Southwest US samples rules out bomb-pulse ^{36}Cl as a contributing factor (Sturchio et al., 2009). In other instances, where surface caliche deposits were collected or young groundwater was analyzed the input of bomb-pulse ^{36}Cl in ClO_4^- can not be excluded. Additional details on ^{36}Cl are provided in Sections 6.1.3, 7.2 and 7.3 and in Sturchio et al., 2009. The current data indicate that analysis of ^{36}Cl can provide important evidence concerning the origin of ClO_4^- in environmental samples. Therefore, the basic method for analysis is provided herein.

Analysis of ^{36}Cl in ClO_4^- is performed by accelerator mass spectrometry (AMS) using Cl^- derived from ClO_4^-. There are a limited number of AMS facilities in the U.S., and the ^{36}Cl analyses on ClO_4^- reported to date have been performed at the Purdue Rare Isotope Measurement Laboratory (PRIME) at Purdue University (www.physics.purdue.edu/ primelab). The basic procedure used to produce Cl^- for AMS is as described in Section 5.2.6 of this document to the point of AgCl precipitation, washing, and drying of crystals (i.e., prior to the reaction with CH_3I). Generally, a portion of the sample prepared to this step for Cl stable isotopic analysis is saved for ^{36}Cl analysis. The AgCl is subsequently re-dissolved and the Cl^- is purified twice by anion chromatography (using a method developed by the PRIME Lab at Purdue University; http://www.physics.purdue.edu/primelab/ AMSQAQC/chemProc004.pdf) to ensure removal of trace amounts of S that might cause isobaric interference at mass 36. Purified Cl^- is then re-precipitated as AgCl for AMS measurement. Analysis of seawater Cl^- provides a reference datum of $^{36}Cl/Cl = 0.5 \times 10^-$ (Argento et al., 2010).

5.2.8. Development of Isotopic Reference Materials

Development of isotopic reference materials and calibration procedures is an important step in the application of isotopic measurements to perchlorate isotope forensics. Reference materials are needed to ensure that isotopic analyses by different laboratories are comparable (Gonfiantini, 1978; Coplen et al., 1983; Coplen, 1988). Researchers at the USGS Reston Stable Isotope Laboratory have worked previously with the National Institute of Standards and Technology (NIST), the International Atomic Energy Agency (IAEA), and the International Union of Pure and Applied Chemistry (IUPAC) in the development and calibration of isotopic reference materials for H, C, N, O, and S isotope measurements (Brand et al., 2009). This work typically begins with the production of chemically pure, isotopically homogeneous materials with widely varying isotopic compositions that can be divided up for distribution to laboratories worldwide. Calibrations are done by using state-of-the-art techniques and commonly involve multiple techniques and(or) multiple laboratories whose efforts are coordinated. Supplies of such materials commonly are limited and distribution may be controlled to insure availability over a long period of time.

During this ESTCP project, we developed three reference materials for Cl and O isotopic analysis of ClO_4^- (USGS37, USGS38, and USGS39). One of these materials (USGS37) was a normal commercial $KClO_4$ reagent, which was homogenized, split, and characterized. The other two were synthesized by Dr. Kent Richman at the AMPAC facility in Magna, UT (the main producer of commercial perchlorate in the U.S). Dr. Richman constructed a laboratory-scale electrolytic cell, similar to commercial-scale cells used to manufacture ClO_4^- from NaCl and water, to produce small batches of ClO_4^- with isotope ratios that differ substantially from those of normal ClO_4^- commercial products. Approximately 500 g quantities of isotopically distinct $KClO_4^-$ were synthesized with this cell for potential use as isotopic reference materials. The starting materials for the synthesis of USGS38 were 250 g of NaCl enriched in ^{35}Cl and 2 L of water enriched in ^{18}O and ^{17}O, with substantial excess ^{17}O in comparison to mass-dependent O isotopic variation. The starting materials for USGS39 were NaCl with normal Cl isotope ratio and water enriched in ^{18}O and ^{17}O, but with no excess ^{17}O with respect to mass dependent variation. The provisionally determined isotopic compositions of USGS37 and USGS38 are as follows: USGS37: $\delta^{37}Cl = +0.6$ ‰; $\delta^{18}O = -17.0$ ‰; $\Delta^{17}O = 0.0$ ‰; USGS38: $\delta^{37}Cl = += -87.2$ ‰; $\delta^{18}O = +52.4$ ‰; $\Delta^{17}O = +73.3$ ‰; with $\Delta^{17}O$ calculated according to Eq. 5.6. USGS39 is currently being calibrated. The large range of isotope ratios in the reference materials makes them useful for normalizing isotopic analyses of environmental samples and detecting problems with analytical techniques. Provisional values of $\delta^{18}O$, $\Delta^{17}O$, and $\delta^{37}Cl$ were determined at USGS and UIC, and reported in peer-reviewed publications describing results from several environmental studies (Sturchio et al., 2007; Böhlke et al., 2009; Jackson et al., 2010). A separate publication describing in more detail the reference materials and calibrations is being prepared for publication in a peer-reviewed journal. Aliquots of USGS37 and USGS38 have been sent to several other laboratories engaged in ClO_4^- isotope studies.

5.2.9 Summary of Sampling, Purification and Analysis of Chlorine and Oxygen Isotopes in Perchlorate

A summary of the general procedures involved in the collection, purification, and analysis of ClO_4^- samples for Cl and O isotopes is provided in Figure 5.7. The procedures, which are provided in detail in the previous sections, are summarized as follows:

1. ClO_4^- (~ 10 mg) is collected directly from groundwater using IX resin columns or collected from mineral deposits and(or) soils by extraction of solids with ClO_4^--free water and collection of dissolved ClO_4^- from the extract using IX resin columns. Columns can be preserved with 0.05 N HCl.

2. The ClO_4^- is then eluted from the IX column after an initial wash with 4 M HCl to remove impurities. Elution is done using a solution of 4M HCl and 1M $FeCl_3$. Fractions are collected during the elution phase to minimize total volume of the ClO_4^- bearing eluent.

3. The ClO_4^- in the eluant subsequently is purified by a series of steps, and then the ClO_4^- is recovered by precipitation as cesium perchlorate ($CsClO_4$), potassium perchlorate ($KClO_4$), or rubidium perchlorate ($RbClO_4$).

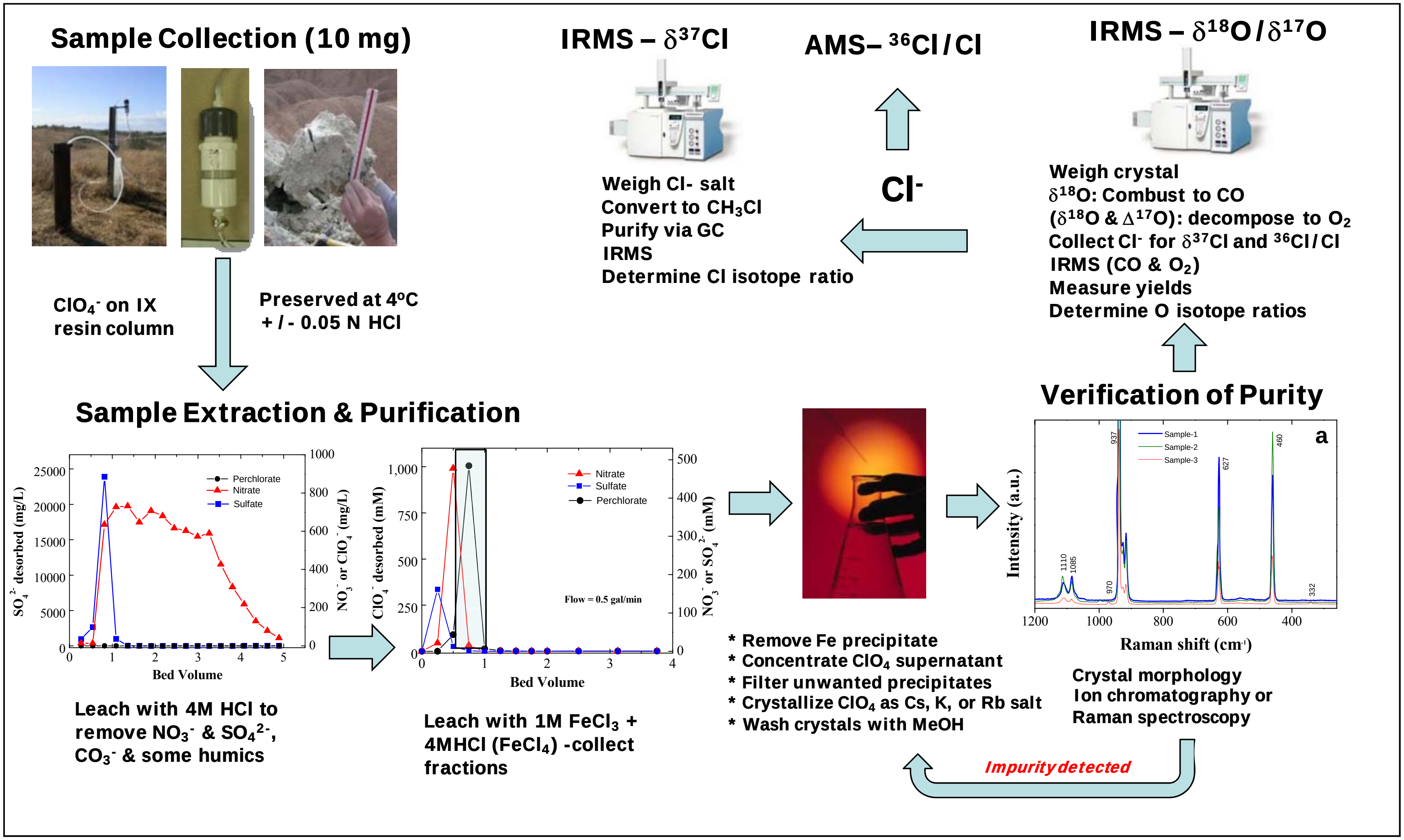
4. The crystals are collected via filtration or evaporation and washed with methanol, after which the purity is determined by crystal morphology, Raman spectroscopy, and(or) ion chromatography. If impurities are detected at concentrations greater than 1 % for the mole fraction of O in the ClO_4^- sample, the sample is re-purified.

5. After crystals are determined to be pure, $\delta^{18}O$ is measured by on-line conversion to CO with CF-IRMS and $\delta^{18}O$ and $\Delta^{17}O$ are measured by off-line conversion to O_2 with DI-IRMS.

6. Aliquots of alkali halide (CsCl, RbCl, or KCl) remaining after the decomposition of ClO_4^- salts for O isotopic analyses (Step 5) are collected, converted to AgCl, then to CH_3Cl, and then analyzed for $\delta^{37}Cl$ using either DI-IRMS or CF-IRMS depending on sample size.

7. Additional aliquots of alkali halide from Step 5 are converted to AgCl and analyzed for $^{36}Cl/Cl$ by AMS.

Figure 5.7. Overview of the procedures involved in the collection, purification, and analysis of ClO_4^- samples for Cl and O isotopic composition.



Sample Collection (10 mg)

ClO_4^- on IX resin column

Preserved at 4ºC +/- 0.05 N HCl

Sample Extraction & Purification

Leach with 4M HCl to remove NO_3^- & SO_4^{2-}, CO_3^- & some humics

Leach with 1M $FeCl_3$ + 4MHCl ($FeCl_4$) -collect fractions

- * Remove Fe precipitate
- * Concentrate ClO_4 supernatant
- * Filter unwanted precipitates
- * Crystallize ClO_4 as Cs, K, or Rb salt
- * Wash crystals with MeOH

Verification of Purity

Crystal morphology
Ion chromatography or
Raman spectroscopy

Impurity detected

IRMS – $\delta^{18}O/\delta^{17}O$

Weigh crystal
$\delta^{18}O$: Combust to CO
($\delta^{18}O$ & $\Delta^{17}O$): decompose to O_2
Collect Cl^- for $\delta^{37}Cl$ and $^{36}Cl/Cl$
IRMS (CO & O_2)
Measure yields
Determine O isotope ratios

Cl^-

AMS– $^{36}Cl/Cl$

IRMS – $\delta^{37}Cl$

Weigh Cl- salt
Convert to CH_3Cl
Purify via GC
IRMS
Determine Cl isotope ratio

5.3 Supporting Information for Perchlorate Forensic Studies

There are a variety of analytical techniques that can potentially provide important supporting information concerning the origin of ClO_4^- in groundwater (e.g., Clark and Fritz, 1997; Cook and Herczeg, 2000). Examples of relevant methods and basic sample collection procedures are provided in Table 5.1. Numerous laboratories conduct various combinations of these different types of analyses, including facilities at USGS, national laboratories, universities, and commercial facilities. The supporting methods are described briefly in the sections below. Not all of these techniques were performed at the sites for which groundwater samples were collected for isotopic analysis during this ESTCP project. Rather, a subset of these analyses was performed on a site-specific basis depending on the information available and the objective for testing at each site. Results for these techniques are provided with the isotope results from each specific site tested (Sections 6 and 7).

5.3.1 Field Parameters

Typical geochemical parameters should be collected at each well during ClO_4^- sampling using a field meter (e.g., YSI 6000 XL multi-parameter meter; YSI Inc., Yellow Springs, OH). The parameters, which provide a basic geochemical baseline for each well, include temperature, dissolved oxygen, oxidation-reduction potential, conductivity, and pH. The stabilization of these parameters with time is used in low-flow sampling applications to determine when to collect field samples, as described in Section 5.2 of this document. In addition, these parameters can be useful for assessing relations between water masses and geochemical conditions that could affect the stability of ClO_4^- through biodegradation.

5.3.2 Groundwater Dating

The age of groundwater (time since infiltration or recharge) is an important forensic tool for ClO_4^- that may be either natural or anthropogenic in origin, particularly given that much of the known synthetic ClO_4^- contamination in the U.S. occurred after the 1940s. Measurable groundwater ages in aquifers commonly range from years to millennia and therefore can be used to relate ClO_4^- occurrences to land-use history, as was done in Long Island, New York, in support of isotopic data showing that Chilean nitrate fertilizers account for some of the groundwater ClO_4^- in this region (see Section 7.1 and Böhlke et al., 2009 in Appendix C). Groundwater ages between about 0 and 60 yr can be determined by analyses of atmospheric environmental tracers including tritium (^3H), sulfur hexafluoride (SF_6), and chlorofluorocarbons (CFCs), all of which have been incorporated in groundwater in varying concentrations since the middle of the 20th century (similar to synthetic ClO_4^-). Analyses of ^3He, the decay product of ^3H, provide additional estimates of groundwater age. Analysis of dissolved neon (Ne) also is conducted during tritium-helium dating to evaluate degassing or the presence of excess air in samples. Groundwater ages on the order of 10^3 to 10^4 yr can be estimated from concentrations of ^{14}C, as was done in the southwestern U.S. to document the occurrence of natural (pre-anthropogenic) ClO_4^- (Plummer et al., 2006; Jackson et al., 2010 in Appendix C). Descriptions of collection and interpretation of groundwater-age data are described in several publications (Cook and Herczeg, 2000; Busenberg and Plummer, 1992, 2000), with additional details in the following sources and references therein (Thatcher et al., 1976; USGS, 2011a).

5.3.3 Stable Hydrogen and Oxygen Isotopes in Water

The stable H and O isotopic composition of H_2O is used commonly to distinguish sources of water, effects of evaporation, and in some cases relative ages of groundwater (Coplen et al., 2000; Clark and Fritz, 1997), all of which may be useful in some situations for distinguishing sources of ClO_4^-. Analyses of H and O isotopes in water can be performed by equilibration with H_2 and CO_2, respectively, for mass spectrometry (Coplen et al., 1991; Révész and Coplen, 2011; USGS, 2011b).

5.3.4 Stable Nitrogen and Oxygen Isotopes in NO_3^-

NO_3^- commonly occurs with ClO_4^- because both are produced naturally in the atmosphere, both may be introduced by agricultural practices, and both have similar transport properties and similar susceptibility to biodegradation. Therefore, stable isotopic and other evidence for the origin and fate of NO_3^- (Heaton, 1986; Kendall and Aravena, 2000; Böhlke, 2002; Böhlke et al., 1997; Michalski et al., 2004; McMahon and Böhlke, 2006) can provide important information concerning the origin and behavior of coexisting ClO_4^- in some situations (e.g., Plummer et al., 2006; Jackson et al., 2010). The stable isotopes of N and O in NO_3^- can be analyzed by various methods including bacterial conversion to N_2O and continuous-flow mass spectrometry (Sigman et al., 2001; Casciotti et al., 2002; Coplen et al., 2004; Révész and Coplen, 2011; USGS, 2011b).

5.3.5 Stable Sulfur and Oxygen Isotopes in Sulfate

Sulfate (SO_4^{2-}) is another oxyanion that may be associated with ClO_4^- as a result of atmospheric deposition or anthropogenic applications, and it may indicate changes in redox conditions that affect ClO_4^- transport. Stable isotopic analyses of SO_4^{2-} can be useful in evaluating sources and fate of SO_4^{2-} (Krouse and Grinenko, 1991; Krouse and Mayer, 2000), which may provide information about ClO_4^- distribution in aquifers. The stable isotopes of sulfur and oxygen in SO_4^{2-} can be analyzed by high-temperature conversion of $BaSO_4$ to SO_2 and CO, respectively, for mass spectrometry (Carmody et al., 1998; Révész and Coplen, 2011; USGS, 2011b).

5.3.6 Dissolved Gas Concentrations

Concentrations of dissolved gases provide important information about groundwater recharge temperatures (Ar, N_2, Ne Kr, Xe) and subsurface redox reactions (O_2, CH_4, N_2). Recharge temperatures are important for the estimation of groundwater ages from atmospheric environmental tracers (Section 5.3.2) and they may be useful for distinguishing water masses from different sources and ages (Cook and Herczeg, 2000). In addition, past and current redox conditions are critical for understanding the potential for ClO_4^- biodegradation in aquifers (e.g., Coates and Achenbach, 2004). Dissolved N_2 concentrations can be used to assess whether a sample has experienced denitrification (e.g., Böhlke et al., 2002), which typically precedes ClO_4^- reduction as conditions become reducing. Major dissolved gases can be analyzed by gas chromatography on equilibrated headspace (USGS, 2011a). Neon analyses typically are done as part of the ^3H-^3He groundwater dating method (USGS, 2011a).

5.3.7 Trace Element Concentrations

Trace element analysis may be helpful, for example where fireworks are a potential source of ClO_4^-. Elements commonly associated with fireworks include aluminum (Al), antimony (Sb), barium (Ba), calcium (Ca), magnesium (Mg), potassium (K), sodium (Na), and strontium (Sr), (Conklin, 1985) and correlations between ClO_4^- and these elements are possible if fireworks are a source (Geosyntec, 2010). A common method for analysis of trace elements is Inductively Coupled Plasma Mass Spectrometry (ICP-MS) according to modified EPA Method 200.8 (USEPA, 1994).

5.3.8 Anion Concentrations

Typical groundwater anions, including NO_3^-, Cl^-, Br^-, and SO_4^{2-} can be measured, in addition to ClO_4^-, to provide geochemical background information for each well. It may also be useful to measure iodate (IO_3^-), which can form atmospherically and has been observed to co-occur with natural ClO_4^- in groundwater beneath the Southern High Plains (SHP) of West Texas and New Mexico (Dasgupta et al., 2005). Samples can be filtered (preferably with pore size 0.2 μm or smaller) in the field to minimize the possibility of biodegradation of some anions during storage, particularly if groundwater is anoxic. The anions, except IO_3^-, can be analyzed by ion chromatography according to EPA Method 300.0. IO_3^- can be measured using high performance liquid chromatography with UV detection (HPLC-UV), as described in Dasgupta et al. (2005) or by liquid chromatography−tandem mass spectrometry (LC−MS/MS) (Snyder et al., 2005).

Table 5.1 Examples of Supporting Analytical Methods and Sampling Requirements

Field Measurement		**Equipment**			
Temperature		Field meter			
Specific conductivity		Field meter			
pH		Field meter			
Dissolved O_2		Field meter			
Reduction potential		Field meter			
Sample	**#**	**Container**	**Filter**	**Treatment**	**Analytical Lab**
Water H and O isotopes*	2	60-mL glass, Polyseal cap	No	small headspace, ship cool	USGS
Tritium* (groundwater dating)	2	500-mL glass, Polyseal cap	No	small headspace, ship cool	USGS
Major gases*	3	serum bottle, pre-weighed butyl stopper, crimper-top	No	no bubbles, 1 KOH pellet, cap underwater, 4 °C	USGS
He and Ne isotopes* (groundwater dating)	3	Cu tube, crimped	No	no bubbles, backpressure, crimp while flowing	USGS
CFC* Groundwater dating)	5	CFC bottle, Al-lined cap	No	no bubbles, cap underwater, tape on cap, 4 °C	USGS
SF_6* (groundwater dating)	2	2.5-L glass, Polyseal cap	No	no bubbles	USGS
Trace elements	2	125-mL HDPE, acid-rinsed	0.2 µm	In-line filter, 1 mL clean HNO_3	USGS
Anions	2	50-mL sterile poly tube	0.2 µm	Sterile syringe filter – aerobic headspace - 4 °C	Shaw Environmental
NO_3^- N and O isotopes	1	1-L HDPE, Polyseal cap	0.2 µm	KOH pellets (pH > 11)	USGS
SO_4^{2-} S and O isotopes (>20 mg/L)*	1	- L HDPE, Polyseal cap	0.2 µm	None – ship cool	USGS
SO_4^{2-} S and O isotopes (<20 mg/L)*	1	resin cartridge, HCl, $BaCl_2$, bucket	in cartridge	None – ship cool	USGS
Perchlorate (ClO_4^-)	1	50-mL sterile poly tube	0.2 µm	Sterile syringe filter – aerobic headspace - 4 °C	Shaw Environmental
Iodate (IO_3^-)	1	50-mL sterile poly tube	0.2 µm	Sterile syringe filter – aerobic headspace - 4 °C	Texas Tech University

Methods and laboratories commonly used for field studies conducted for ESTCP-ER200509; other procedures and laboratories are also available.

* For additional details, see the following websites: http://isotopes.usgs.gov/; http://water.usgs.gov/lab/cfc/.

6.0 RESULTS PART I: ISOTOPIC CHARACTERISTICS OF SYNTHETIC AND NATURAL PERCHLORATE

This section includes results from several different laboratory tasks and/or experiments conducted during the course of this project as described in the Section 5.1. These tasks include: (1) compilation of an isotopic database; (2) development of isotopic reference materials; (3) assessment of isotopic exchange between ClO_4^- and H_2O, and (4) quantification of biological fractionation of O and Cl isotopes in ClO_4^- by pure bacterial cultures. Details and results for these tasks are provided below.

6.1 Compilation of an Isotopic Database

The first objective of this project was to conclusively demonstrate that isotopic assessment could be used as a forensic tool to distinguish sources of ClO_4^- contamination, particularly fertilizer and natural mineral sources vs. military and commercial sources. Previous analyses by members of our team of a limited number of fertilizer and synthetic sources of ClO_4^- (primarily reagent salts) showed that these two materials have inherently different isotopic signatures for both chlorine and oxygen (Section 2.3; Bao and Gu, 2004; Bohlke et al., 2005). During this task, that database was expanded to include important samples of ClO_4^- from numerous military, commercial, and mineral sources. In addition to the military items, the isotopic signatures of ClO_4^- present in commercial products, including roadside flares, gunpowder, explosives, and fireworks were analyzed as were samples of the source ClO_4^- that is used in the manufacture of some of these items. The isotopic signatures of ClO_4^- present in chlorate herbicides and hypochlorite bleach were analyzed as well. Isotopic ratios of O and Cl in ClO_4^- were tested/confirmed in Chilean caliche, in commercial fertilizer sources prepared from this material, and in evaporite minerals observed to contain ClO_4^- in the Southwestern U.S. The complete isotopic values for these samples are provided in Appendix A: Table A-1. The stable isotope methods used to analyze these samples are as described previously in Section 5 and in more detail in Hatzinger et al., (2011).

6.1.1 Stable Isotope Ratios of Cl and O in Synthetic Perchlorate

Synthetic ClO_4^- is synthesized electrochemically using NaCl and H_2O (Schumacher, 1960). Samples from a variety of different synthetic sources, including laboratory reagents, commercial manufacturers, and ClO_4^- derived from road flares, fireworks, Pyrodex gunpowder, and chlorate herbicides, were analyzed for Cl and O stable isotope ratios. Additional details on these samples are provided in Bao and Gu, (2004), Böhlke et al., (2005), and Sturchio et al., (2006, 2011). Data for samples of synthetic ClO_4^- in which both $\delta^{18}O$ and $\delta^{37}Cl$ values were measured are shown in Figure 6.1, and specific samples grouped by manufacturer (source) are shown in Figure 6.2. In addition, the complete dataset is provided in Appendix A, Table A-1.

The $\delta^{37}Cl$ values of all synthetic ClO_4^- samples presented in Figure 6.1 group within a range from -3.1 ‰ to + 2.3 ‰ and have a mean value of ~ + 0.6 ‰. This value is near that reported for common industrial sources of NaCl, such as halite from Phanerozoic bedded evaporates, which has reported $\delta^{37}Cl$ values of 0.0 ± 0.9 ‰ (Eastoe et al., 2007). The electrochemical synthesis of ClO_4^- is nearly stoichiometric for Cl^- (i.e., nearly all of the added Cl^- is converted to ClO_4^-), so it is not surprising that the Cl isotope values in the resulting ClO_4^- are similar to those in the starting NaCl. The current $\delta^{18}O$ values of synthetic ClO_4^- vary over a wider range than for $\delta^{37}Cl$, from -24.8 ‰ to -12.5 ‰ (Figure 6.1). It has been hypothesized that the $\delta^{18}O$ values of the synthetic ClO_4^- samples reflect the $\delta^{18}O$ in the H_2O used for production, and that some O isotopic fractionation occurs during ClO_4^- synthesis (Sturchio et al., 2006). In one set of samples in which $\delta^{18}O$ was measured in both the produced ClO_4^- and the local meteoric H_2O used in the synthesis, the observed difference was ~ 7 ‰ (Sturchio et al., 2006). In contrast to $\delta^{18}O$, $\Delta^{17}O$ values of all synthetic ClO_4^- samples analyzed to date are 0.0 ± 0.1 ‰ (when calibrated by assuming the USGS37 standard has $\Delta^{17}O = 0$; See Section 5.2.8 for more details on the reference standards), indicating that there is negligible mass-independent isotopic fractionation of O during ClO_4^- synthesis (Sturchio et al., 2006, 2011).

When multiple samples of ClO_4^- from individual manufacturers were analyzed, the $\delta^{18}O$ and $\delta^{37}Cl$ values grouped closely together (Figure 6.2). For example, the $\delta^{18}O$ values of three salts produced by Manufacturer A ($KClO_4^-$, $NaClO_4^-$, and $NH_4ClO_4^-$, respectively) ranged from -21.3 to -22.3 ‰ (-21.7 ± 0.5 ‰) and the δ^{37}Cl value for all three samples was +0.4 ‰ (from Sturchio et al., 2006). The δ^{18}O for ClO_4^- salts from Manufacturer B ranged from -15.6 to -16.3 ‰ (-16.1 ± 0.5 ‰) and the δ^{37}Cl values averaged +0.8 ± 0.6 ‰. In this specific instance, the δ^{18}O values of ClO_4^- produced by the two manufacturers would permit the two sources to be distinguished (i.e., the values between manufacturers are statistically different). However, use of stable isotopes to distinguish synthetic sources of ClO_4^- in the field may be limited by uncertainties about undocumented sources. Substantial isotopic differences among synthetic ClO_4^- sources mainly occur in δ^{18}O and, in contrast to the specific example provided in Fig 6.2, there is substantial overlap in the δ^{18}O values of different products tested to date, as is apparent from the data in Figure 6.1. In addition, differences in δ^{18}O values for ClO_4^- produced by a single manufacturer in different batches and(or) over long time periods were not studied.

In addition to electrochemical synthesis, ClO_4^- is known to be produced over time (to concentrations of the order of mg/L) in hypochlorite solutions (e.g., household or commercial bleach) by disproportionation reactions (Kang et al., 2006; Trumpolt et al., 2005). ClO_4^- formation in bleach can be accelerated by exposure to sunlight via photochemical reactions (Kang et al., 2006). For example, in one experiment conducted during this project, a fresh bleach solution (~6.25% NaOCl; Clorox serial number E68194 21 MD2) was placed in quartz tubes and exposed to sunlight over a period of several days. Hours of exposure were recorded and subsamples were collected periodically and analyzed for ClO_4^- by EPA Method 314.0. The results revealed that the ClO_4^- concentration in the bleach increased from ~ 1,000 μg /L to > 7,600 μg/L during the first 9.5 hrs of sunlight exposure (Figure 6.3). The ClO_4^- concentration in the bleach reached nearly 11,000 μg/L after 25 hrs of sunlight exposure, and stabilized thereafter.

Based on this result, a study was conducted to produce ClO_4^- from bleach in quantities large enough to conduct stable isotope analysis of Cl and O. In this case, ~ 17 L of Clorox bleach (~6.25% NaOCl) was placed in a Nalgene High density polyethylene carboy. The bleach was recirculated via peristaltic pump using ¼" ID Tygon tubing through a quartz tube (180 mL volume) and back into the Nalgene container. The flow rate was 350 mL/min resulting in complete recirculation of bleach through the quartz tube every 49 min. The entire apparatus was placed in sunlight during recirculation to promote the UV-mediated formation of ClO_4^- in the bleach solution. Hours of sunlight exposure were recorded, and samples were collected periodically to analyze for total ClO_4^- concentration. After 63, 300, and 400 hrs of exposure, samples were collected (3L at 63 hrs, 4L at 300 hrs, and 8L at 400 hrs) and placed in the dark at 4^oC. The formation of ClO_4^- in these samples is shown in Figure 6.4. At the conclusion of the experiment, ClO_4^- was removed from two of the subsamples (collected at 300 and 400 hrs) using the Ni-catalyst approach described in Section 5.2.3.2, and the samples were passed through ion exchange columns and sent to ORNL for extraction and purification. At the completion of this report, isotopic analysis of these samples is not yet complete. These data will be reported in the Final Report for SERDP Project ER-1435.

Two samples of ClO_4^- derived from bleach that had been stored for long periods were processed and analyzed for ClO_4^- isotopes during this project. In each case, the bleach was in the original bottle and was not presumably exposed to sunlight to allow UV-mediated formation of ClO_4^-, rather the formation of ClO_4^- presumably occurred through a slower dark reaction. The first sample was 6.25% household bleach provided by Peter Philbrook of the USEPA that was estimated to be 3 yrs old at the time of sampling and contained ~ 37 mg/L ClO_4^-, and the second sample was a commercial bleach solution provided by Greg Harvey of the USAF, which has ~ 20 mg/L of ClO_4^-. The concentration of hypochlorite in this bleach sample is unknown. Interestingly, both samples had unusually low values of $\delta^{18}O$ (< -50 ‰) and high values of $\delta^{37}Cl$ (> +9 ‰) (Figure 5.4). If similar values are found as more samples are analyzed, $\delta^{18}O$ and $\delta^{37}Cl$ values may be useful for distinguishing ClO_4^- derived from bleach from that produced by electrochemical synthesis.

Figure 6.1 Values of δ^{37}Cl versus δ^{18}O for samples of synthetic ClO_4^- from different sources. Analytical uncertainty is ~ ±0.3 ‰. Dashed line is δ^{37}Cl reference value of 0 for SMOC.

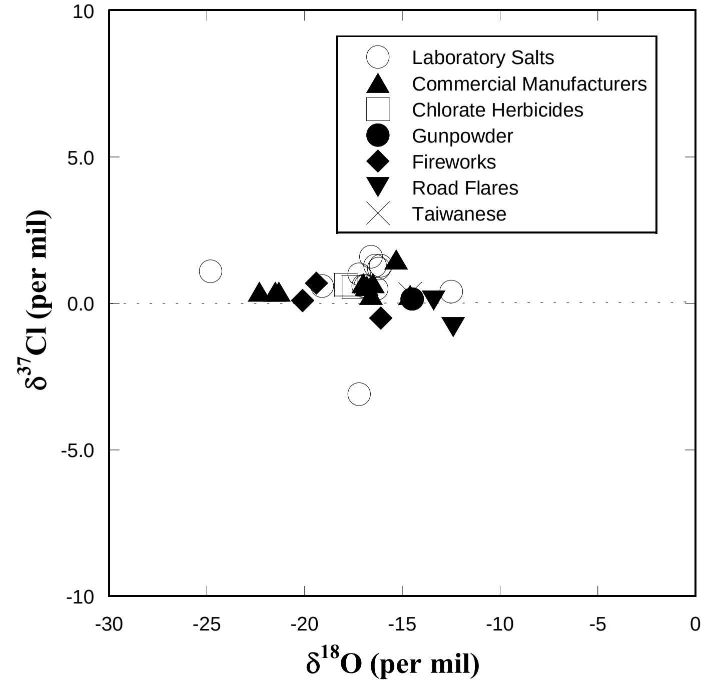


Figure 6.2. Values of δ^{37}Cl versus δ^{18}O for samples of synthetic ClO_4^- from two different manufacturers. Analytical uncertainty is ~±0.3 ‰. Dashed line is δ^{37}Cl reference value of 0 for SMOC.

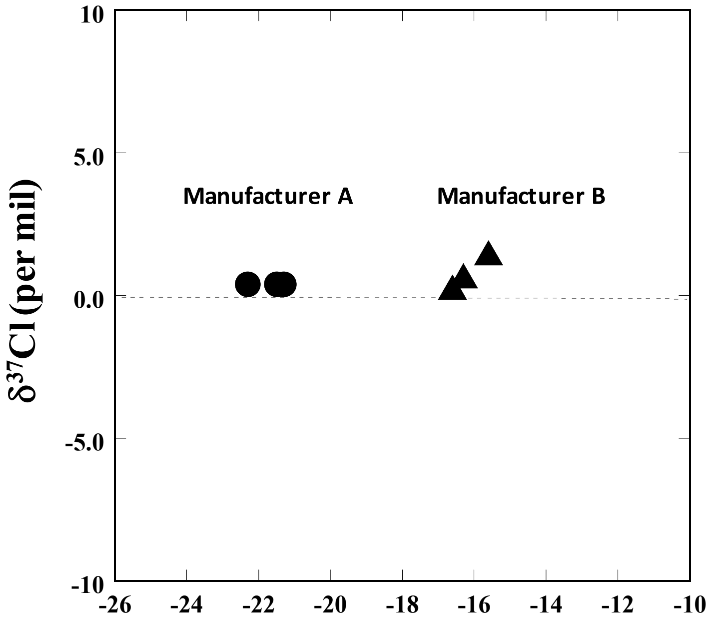


Figure 6.3. Production of perchlorate in household bleach exposed to sunlight in small quartz tubes.

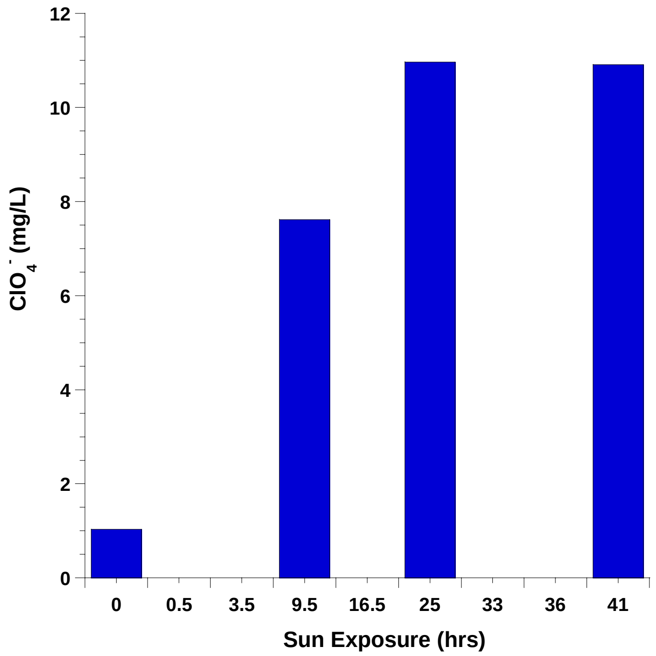
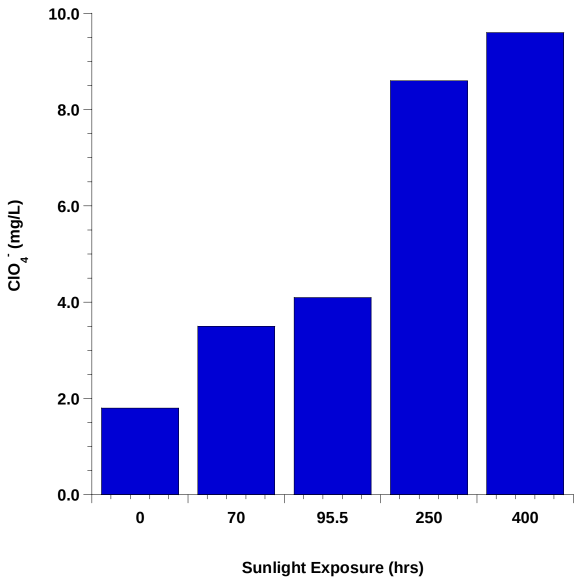


Figure 6.4. Production of perchlorate in household bleach exposed to sunlight in a large batch study using a flow-through quartz column.



6.1.2 Stable Isotopes of Chlorine and Oxygen in Natural Perchlorate

6.1.2.1 Chilean Nitrate Deposits and Imported Fertilizer

As described in Section 1.1.2, the most well-known source of natural ClO_4^- is in NO_3^- deposits from the Atacama Desert of Chile (Schilt, 1979; Ericksen, 1981, 1983; Dasgupta et al., 2005). These NO_3^- deposits, which are also called "Chilean caliche", were widely imported into the United States during the 20th century as a source of inorganic nitrogen fertilizer. It is estimated that ClO_4^- derived from Chilean fertilizers represents an equivalent source to that of synthetic products in terms of ClO_4^- exposure risk through incorporation of ClO_4^- into the food chain (Dasgupta et al., 2005).

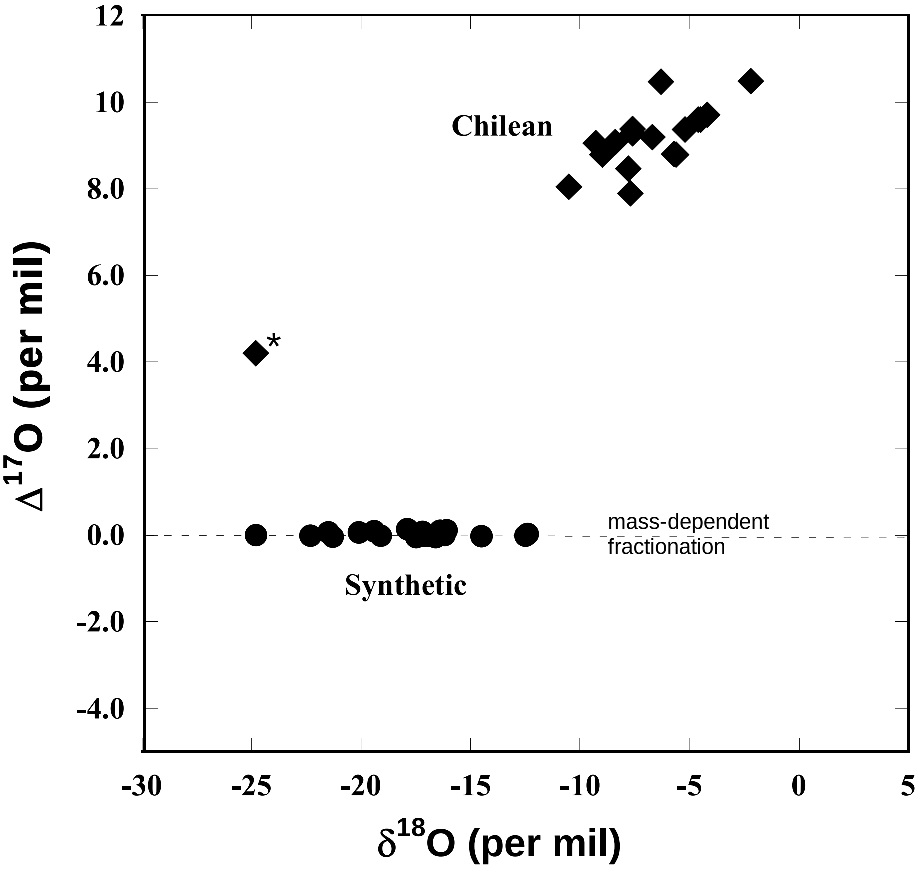
Values of $\delta^{18}O$ and $\Delta^{17}O$ in ClO_4^- from the Atacama Desert were first reported by Bao and Gu, (2004). The $\delta^{18}O$ values in the Chilean samples that they analyzed (three caliche samples and one sample of imported fertilizer) ranged from -24.8 ‰ to -4.5 ‰ and $\Delta^{17}O$ values ranged from +4.2 ‰ to +9.6 ‰, with an average value of +8.0 ‰. The original observation that Chilean ClO_4^- has substantial ^{17}O excess (i.e., ^{17}O higher than that expected from mass-dependent isotopic fractionation, which should yield $\Delta^{17}O$ near 0), was subsequently confirmed by analysis of a larger number of additional ClO_4^- samples from Atacama Desert caliche deposits, groundwater, and imported Chilean fertilizers from this region (Böhlke et al. 2005; Sturchio et al., 2006, 2012; Jackson et al., 2010) (Figure 6.5). These studies also documented that the $\delta^{37}Cl$ values of the Chilean materials are significantly lower than those of synthetic ClO_4^-, ranging from -14.5 ‰ to -11.8 ‰. The complete published data set is provided in Appendix A: Table A-1.

The high values of $\Delta^{17}O$ in the Chilean samples are interpreted to indicate an atmospheric origin of this natural ClO_4^- by photochemical reactions between volatile Cl species and ozone (O_3), the latter of which is also known to be characterized by large positive $\Delta^{17}O$ values (Johnson et al., 2000; Bao and Gu, 2004). The formation of ClO_4^- with O_3 as a reactant was also recently confirmed in laboratory studies (Kang et al., 2008; Rao et al., 2010), and subsequent isotopic analysis of the O_3-generated ClO_4^- revealed a large positive $\Delta^{17}O$ value (Jackson et al., unpublished data), further supporting the theory of atmospheric formation of natural ClO_4^- via O_3.

Dual isotope plots comparing δ^{37}Cl versus δ^{18}O and Δ^{17}O versus δ^{18}O in natural and synthetic ClO_4^- are provided in Figure 6.5. The plots are composed of data collected to date from this project as published in several scientific papers (Sturchio et al., 2006, 2011; Böhlke et al., 2009; Jackson et al., 2010). The data also include isotope values published by Bao and Gu (2004), separately from this project. The mean values for Chilean ClO_4^- for δ^{37}Cl, δ^{18}O and Δ^{17}O are -12.6 ± 1.5 ‰ (n = 13), -6.6 ± 2.1 ‰ (n = 17) and +9.2 ± 0.7 ‰ (n = 17), respectively. One anomalous value from Bao and Gu, (2004), labeled with an asterisk in Plot B, is excluded from the above averages, but additional samples have now been collected from different regions of the Atacama Desert to provide a more complete determination of the range in Δ^{17}O. The isotope data from these samples will be provided with the final report from SERDP Project ER-1435.

As shown in the dual isotope plots in Figure 6.5, there are consistent and significant isotopic differences between natural Chilean ClO_4^- and synthetic ClO_4^-. Most significantly, the high Δ^{17}O values for the Chilean materials (average of +9.2 ‰) clearly differentiate this ClO_4^- source from all synthetic sources, for which the average value Δ^{17}O value is near 0, consistent with typical mass-dependent isotopic fractionation of ^{16}O, ^{17}O, and ^{18}O (Figure 6.5, Plot A). The low δ^{37}Cl values (average of -12.6 ‰) also clearly distinguish Chilean ClO_4^- from all synthetic sources, which have an average δ^{37}Cl value of +0.8 ‰. Thus, both Δ^{17}O and δ^{37}Cl can be used to differentiate these two sources in forensic studies.

Figure 6.5. Values of $\Delta^{17}O$ versus $\delta^{18}O$ in Chilean and synthetic ClO_4^-. The single value with an asterisk is from Bao and Gu (2004).



6.1.2.2 Indigenous Sources in the Southwestern U.S.

As previously discussed in Section 1.1.3, research conducted during the past decade has revealed that natural ClO_4^- occurs in arid environments other than the Atacama Desert of Chile. Most significantly for forensic studies in the U.S., indigenous natural ClO_4^- has been widely detected in the southwestern U.S., as evidenced through various surveys of ClO_4^- in surface soils, vadose-zone profiles, wet and dry deposition, and groundwater in New Mexico, Texas, California and elsewhere in this region (Dasgupta et al., 2006; Plummer et al. 2006; Rajagopalan et al. 2006, 2009; Rao et al. 2007; Parker et al. 2008; Jackson et al., 2010; Lybrand et al., 2013). Recent detections of ClO_4^- in Antarctic soils and on Mars have caused additional interest in the mechanisms of formation and accumulation of natural ClO_4^- (Hecht et al. 2009; Ming et al. 2010; Catling et al. 2010; Kounaves et al. 2010).

The stable isotopic composition of indigenous natural ClO_4^- from several locations and environments (vadose zone, surface caliche deposits, groundwater) in the southwestern U.S. was determined during the course of this project. These sites were selected because previous studies indicate that they represent natural occurrences. Groundwater ClO_4^- samples were obtained from the Southern High Plains (SHP; including one sample from the adjacent rolling plains) of western Texas and eastern New Mexico (n=8) and from the Middle Rio Grande Basin (MRGB) of central New Mexico (n=2). The SHP wells were at 5 distinct sites, with two wells (MW2 and MW3) installed at the same location but screened at different intervals. These wells were sampled in duplicate (MW2A,B and MW3A,B) (Figure 6.6). A single sample (SHP-V) was obtained from a natural subsurface accumulation of salts within unsaturated sub-soils at the Range Ecology Research Site at Texas Tech University. This site is a 142 ha section of land that has been used to study numerous aspects of range ecology but has not been irrigated or subjected to other surface activity that would impact the presence of ClO_4^-. Lastly, ClO_4^- was obtained from near-surface caliche-type salt deposits on clay hills at four locations in the Death Valley region of the Mojave Desert, CA (Zabriskie, Bully Hill, Saratoga Hills, Confidence Hills in Figure 6.6). Clay-hills caliche salts in this area were studied previously because of their unusually high NO_3^-concentrations, which resemble those in the Atacama Desert (Böhlke et al., 1997).

ClO_4^- in groundwater was collected by pumping water from each well through columns containing ClO_4^--selective anion-exchange resin as described previously in Section 5.2.1.2. Groundwater from wells MW3, MW2, BW2, RR8, and RR16 was pumped through resin columns in the field at flow rates ranging from ~ 0.1 to 2 L min^{-1}. For the remaining wells, water was pumped into clean polyethylene drums (208-L capacity), which were then transported to TTU where the water was passed through ion-exchange columns, as described above. The total volume of water pumped through each column varied with ClO_4^- concentration, with the final objective being to extract at least 5 mg of ClO_4^- for purification and isotopic analysis. Groundwater was also collected for major anions, other isotopic analyses (NO_3^-, SO_4^{2-}, H_2O), major dissolved gases, and environmental tracers including ^3H, ^3He, SF_6, and chlorofluorocarbons (CFCs).

Perchlorate dispersed in the unsaturated zone (SHP-V) was collected by leaching soluble salts from the sub-soil and then passing the leachate through a resin column as described above for groundwater (see Section 5.2.2). Initially, depth-dependent samples were obtained by hand auger to evaluate the vertical distribution of salts in the unsaturated zone. Based on these data, sub-soil from approximately 2 to 4 m (depth range of maximum ClO_4^- concentration) was collected using a back hoe and placed on a tarp. Salts were extracted by mixing batches of sub-soil (40 to 60 L) and water (80 L) in a pre-cleaned cement mixer for ~10 minutes to form a slurry. Tap water from Lubbock, Texas was used for the extraction. Prior to use, the water was passed through a large column (~ 1,000 cm^3) packed with Purolite A-530E resin to reduce ClO_4^- to < 0.05 μg L^{-1}. After mixing, the slurry was allowed to settle for several hours, and then the water was decanted into polyethylene drums. The slurry in the drums was allowed to settle further overnight, after which the supernatant was pumped through a sediment pre-filter (50-μM pore-size; General Electric Co., Trevose, PA) and then through a resin column. Influent and effluent samples were taken routinely to determine the concentration of ClO_4^- applied to the column and the efficiency of perchlorate removal by the column. A total of ~5,600 kg of soil and ~3,000 L of water were processed for the extraction.

The specific location and depth of the caliche-type salt accumulations collected from Death Valley were based on the NO_3^- content of the deposits, which were determined by field testing. NO_3^- was used as an indicator of ClO_4^- based on previous data. Bulk samples (20 to 50 kg) from each location were shipped to TTU and portions of these samples were leached using ClO_4^--free (< 0.05 µg L^{-1}) distilled de-ionized water. The samples were sequentially extracted three times with a ~1:5 solid to water mass ratio each time. The ClO_4^- dissolved in the supernatant of these extracts was combined and collected on resin columns as described above. The concentrations of soluble salts in the bulk solids were estimated after drying and weighing the leached material after extraction. Aliquots of the leachate solutions were filtered and stored for chemical and isotopic analysis of solutes including ClO_4^-, NO_3^-, SO_4^{-2}, and Cl^-.

Procedures used for ClO_4^- extraction and purification from the resin columns and analysis of $\delta^{18}O$, $\Delta^{17}O$, and $\delta^{37}Cl$ were conducted as previously described in this document in Section 5. Perchlorate was eluted from the resin columns and purified at ORNL. Purified ClO_4^- in the form of $CsClO_4$ was shipped to the USGS laboratory in Reston, VA for analysis of $\delta^{18}O$ and $\Delta^{17}O$ on O_2 produced by decomposition. Chloride residue from the decomposed ClO_4^- was analyzed for $\delta^{37}Cl$ at the University of Illinois at Chicago, and doubly-purified AgCl salts were then analyzed for ^{36}Cl by AMS at the PRIME facility at Purdue University.

All of the indigenous samples collected from groundwater and vadose soils in the SHP and from groundwater in the MRGB were similar isotopically, despite the large areal extent over which they were collected, with $\delta^{37}Cl$ values ranging from +3.1 to +5.0 ‰, $\delta^{18}O$ values ranging from +0.6 to +3.8 ‰, and $\Delta^{17}O$ values ranging from +0.3 to +1.3 ‰. The data indicate that ClO_4^- from the SHP and MRGB regions of Texas and New Mexico is consistently different from both Chilean ClO_4^- and synthetic ClO_4^- when all relevant stable isotopic abundances are considered (^{16}O, ^{17}O, ^{18}O, ^{35}Cl and ^{37}Cl) (Figure 6.7). In Figure 6.7 and others throughout this document, samples from the SHP and the MRGB are combined under the heading "Southern High Plains". The small, but significantly positive $\Delta^{17}O$ values of these samples indicate that either (1) they were formed predominantly by a different mechanism than the Chilean ClO_4^-, which has much higher average $\Delta^{17}O$ (hypothesized to originate from O_3 as a reactant) or (2) the ClO_4^- was affected by post depositional O exchange (see Section 6.3 for additional information on post depositional reactions).

The ClO_4^- samples from the Death Valley caliche deposits, which have ClO_4^- concentrations ranging from 0.25 to 1.7 mg/kg (about 1-3 orders of magnitude lower than the Atacama deposits), are characterized by an isotopic signature that is distinctive from the Chilean and synthetic ClO_4^-, and from those from the SHP and MRGB. In comparison to the SHP samples, the Death Valley samples have lower $\delta^{37}Cl$ values (from -0.8 to -3.7 ‰) and much higher $\Delta^{17}O$ values (+8.6 to +18.4 ‰). As is apparent from Fig 6.7, Plot B, the $\Delta^{17}O$ values of the Death Valley samples are similar to or, in some instances, higher than those of the Chilean samples, indicating an important component of atmospheric origin and relative lack of post depositional exchange of O with terrestrial materials. The SHP and Death Valley samples can be considered together as U.S. indigenous sources and, even though there are substantial ranges in the individual isotope values, this indigenous grouping remains isotopically distinct from synthetic and Chilean ClO_4^- when all relevant isotopes are considered.

Given present data, it is not yet possible to fully explain the observed variations in the isotopic composition of natural ClO_4^- sources, other than to say that some of the Atacama and Death Valley ClO_4^- probably formed as a result of reactions with O_3 (due to the elevated $\Delta^{17}O$) The data permit the interpretation that natural ClO_4^- may have more than one formation mechanism, there may be global variations in the isotopic compositions of precursor compounds, and it may be subject to isotopic modification in the terrestrial environment. Resolving these issues would contribute to understanding atmospheric Cl chemistry, as well as the veracity of the isotopic approach for quantifying ClO_4^- sources in the environment. Nevertheless, despite uncertainty about processes responsible for some of the isotopic variations, this study indicates that natural ClO_4^- indigenous to the southwestern U.S. is distinguishable from synthetic ClO_4^- and from imported Atacama ClO_4^- on the basis of isotopic composition. These differences in isotopic composition may find important applications in resolving questions of ClO_4^- source apportionment for contaminated water supplies.

The complete dataset for these natural samples including all relevant field and geochemical measurements, as well as an extended discussion of the potential origin of these deposits was published previously by our research group (Jackson et al, 2010 and supporting information). The complete text of this manuscript is provided as Appendix C to this document.

Figure 6.6. Sample locations in the SHP, MRGB, and Death Valley, CA.
Figure from Jackson et al., 2010.

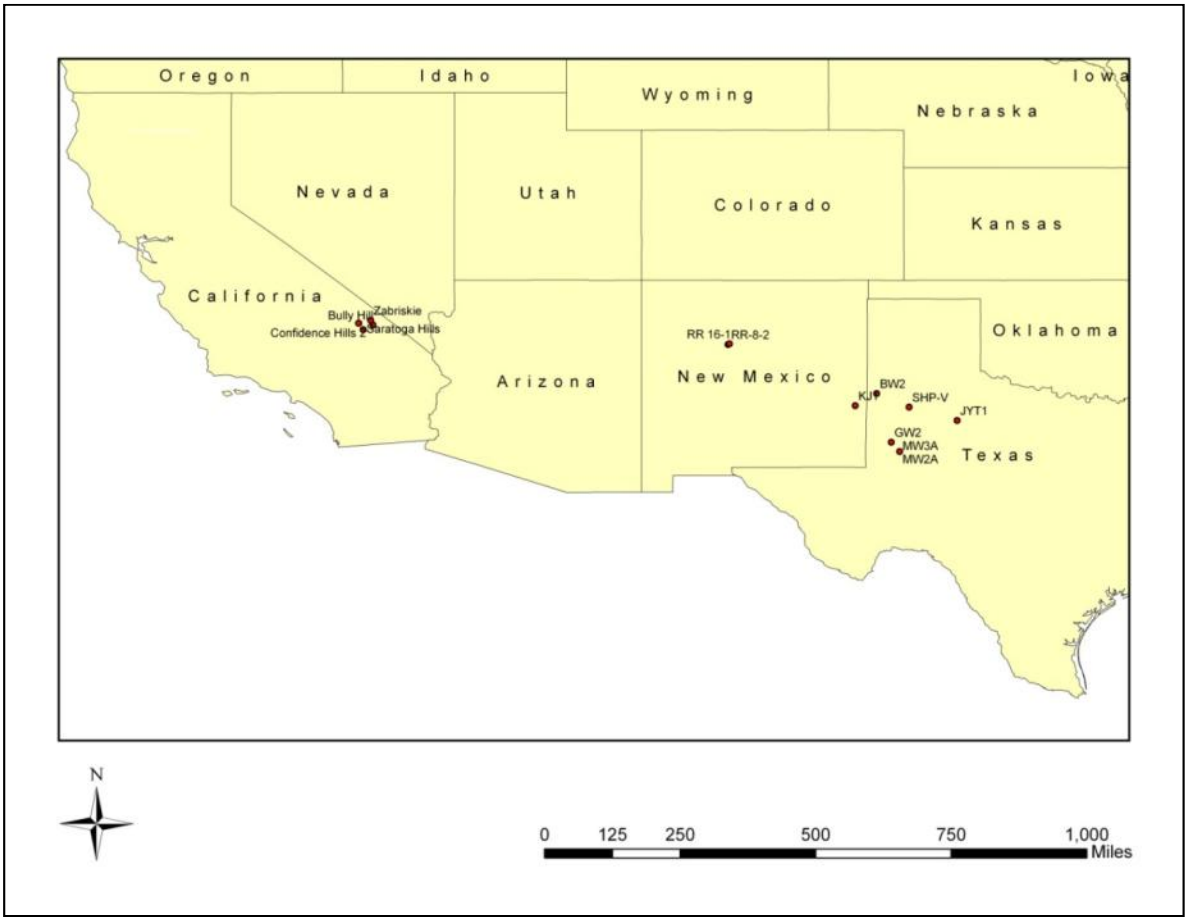
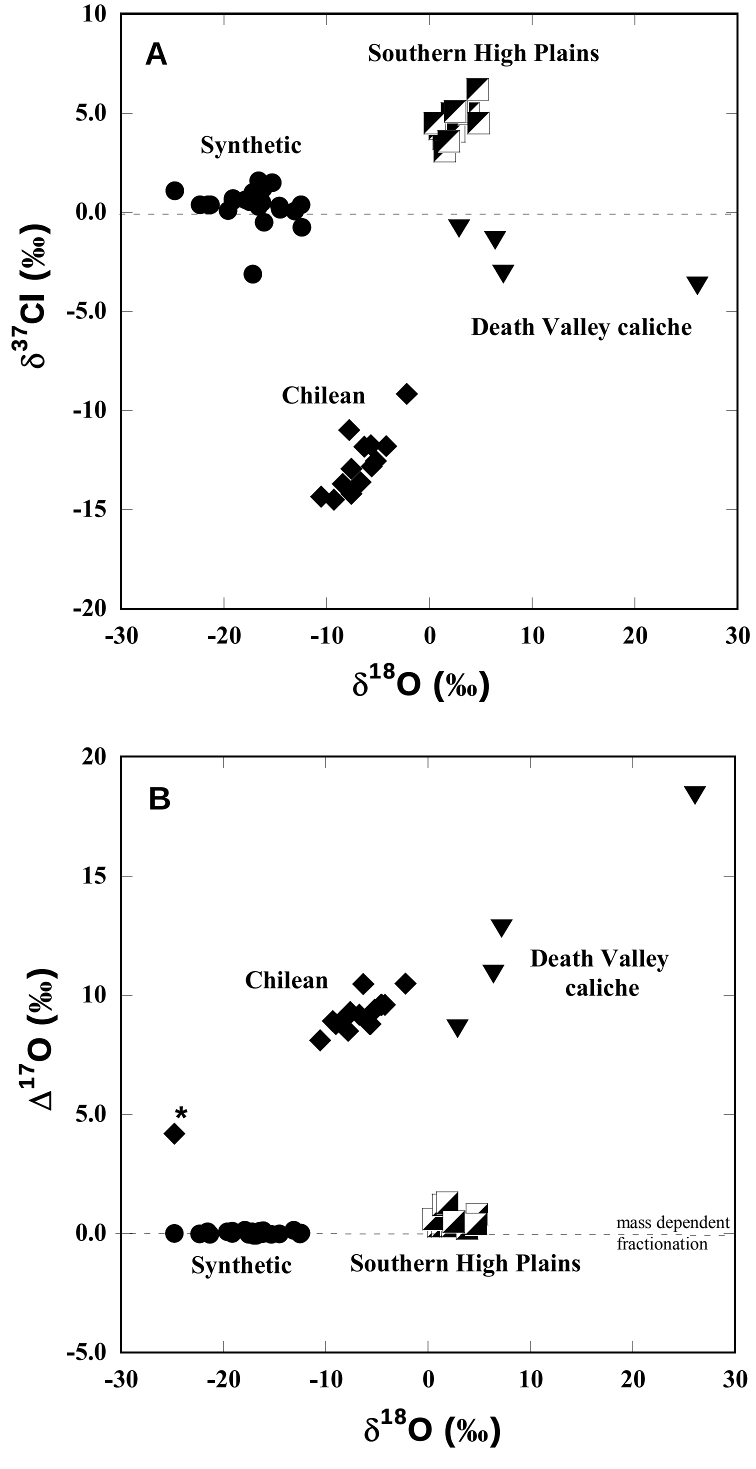


Figure 6.7. Comparison of δ^{37}Cl versus δ^{18}O (Plot A) and Δ^{17}O versus δ^{18}O (Plot B) in natural indigenous ClO_4^- in the U.S., natural Chilean ClO_4^-, and synthetic ClO_4^-. The single value on Plot B labeled with an asterisk from Bao and Gu (2004) is distinct from all other results from Chilean samples published to date.

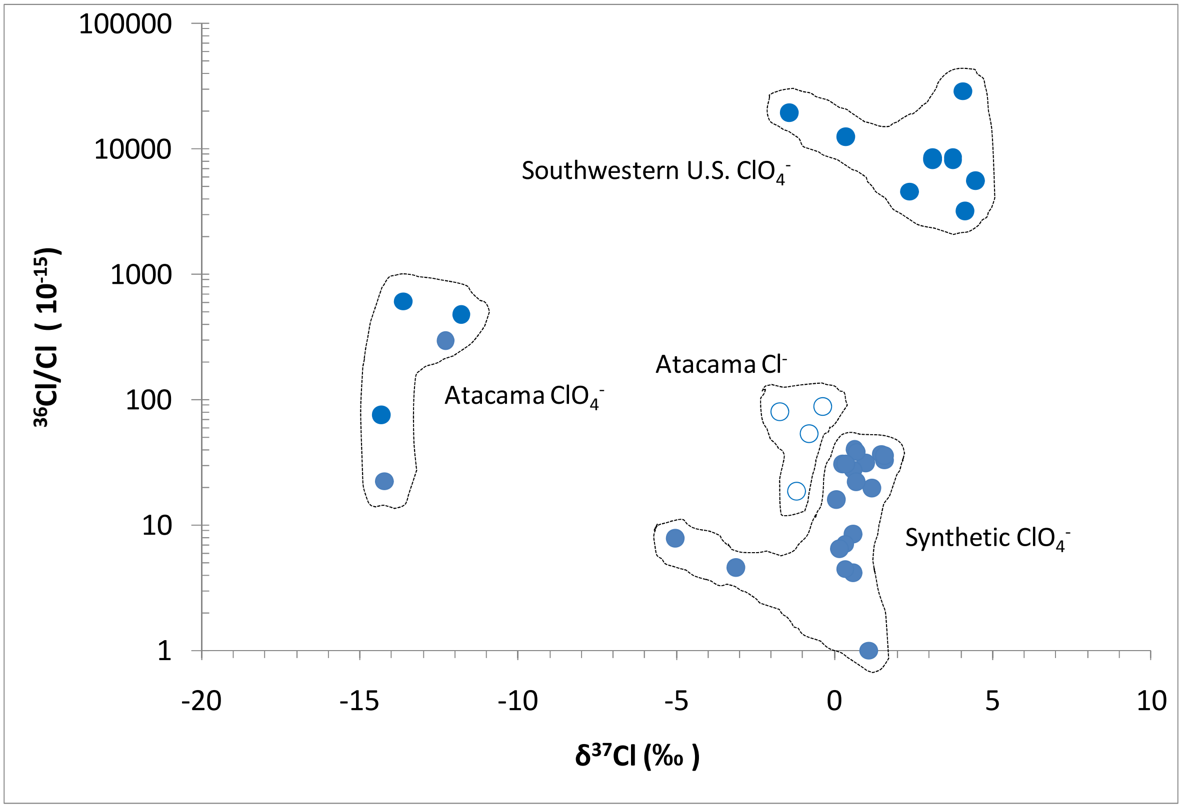


6.1.3 Abundance of ^{36}Cl in Synthetic and Natural Perchlorate

The abundance of the radioactive isotope ^{36}Cl (reported as atom fraction, or mole fraction, designated traditionally as ^{36}Cl/Cl) has proven to be another important tool for distinguishing ClO_4^- sources (see Section 5.2.7 for additional background). Chlorine-36 is present naturally in Cl^- in groundwater in the U.S., with ^{36}Cl/Cl values ranging from ~10 × 10^{-15} near coasts to as high as ~ 1700 × 10^{-15} in the central Rocky Mountains (Bentley et al., 1986; Phillips, 2000; Davis et al., 2003). Until recently, values of ^{36}Cl/Cl in ClO_4^- were unknown. However, our group found that values of ^{36}Cl/Cl in 35 different ClO_4^- samples from synthetic, Chilean, and Southwestern U.S. sources ranged over more than four orders of magnitude (Figure 6.8 and Sturchio et al., 2009). Synthetic ClO_4^- samples were characterized by relatively low values of ^{36}Cl/Cl from 0 × 10^{-15} to 40 × 10^{-15} (Sturchio et al., 2009). These values are consistent with Cl sources such as the geologically ancient halite-rich evaporate deposits (e.g., salt domes, bedded salts) from which large amounts of NaCl are mined commercially in the form of rock salt.

In contrast to synthetic samples, all indigenous natural ClO_4^- samples from the Southwest U.S. that were tested (including some of the SHP groundwater samples and Death Valley deposits described in the previous section and shown in Fig 6.7 with differing δ^{37}Cl and Δ^{17}O) had unusually high ^{36}Cl/Cl values, ranging from 3130 × 10^{-15} to 28,800 × 10^{-15}. The presence of bomb-generated ^{36}Cl from nuclear tests in the mid 1950's (Phillips, 2000; Davis et al., 2003) could not be ruled out for a few of the samples, but ^{36}Cl/Cl values as high as 8,400 × 10^{-15} were measured in ClO_4^- from groundwater in New Mexico with recharge ages estimated at > 5,000 yr (Plummer et al., 2006; Sturchio et al., 2009). High concentrations of ^{36}Cl in some ClO_4^- samples may point toward the stratosphere, rather than the troposphere, as an important area of atmospheric ClO_4^- formation (Sturchio et al., 2009). Natural ClO_4^- from Chilean deposits had ^{36}Cl/Cl values from 22 × 10^{-15} to 590 × 10^{-15}, much lower than any of the natural samples from the Southwest U.S. The Chilean samples originally may have had high ^{36}Cl/Cl values resulting from stratospheric production, but may have lost much of that activity via radioactive decay. This could be consistent with a relatively long history of Atacama ClO_4^- accumulation, as hyper-arid conditions in this region may have persisted for at least 3 to 8 Myr (Alpers and Brimhall, 1988; Hartley and Chong, 2002), which is 10 or more times the half-life of ^{36}Cl. Values of ^{36}Cl/Cl in Cl$^-$ from the Atacama Desert are similar to those of the associated ClO$_4^-$ as shown in Figure 6.8. The accumulation time of ClO$_4^-$ in the arid southwest U.S. appears to have been much shorter (of the order of 10^4 yr), and natural ClO$_4^-$ accumulated from the atmosphere during this time would be expected to possess most of its original ^{36}Cl activity (Jackson et al., 2010). Most importantly for forensic studies of ClO$_4^-$, in combination with stable isotope ratios of O and Cl, ^{36}Cl abundances can provide important supporting data to help differentiate synthetic, Chilean, and indigenous U.S. sources. The complete ^{36}Cl dataset and more detailed discussion was previously published by our group (Sturchio et al., 2009). This paper is provided in Appendix C.

Figure 6.8. Values of ^{36}Cl/Cl (mole fraction) versus δ^{37}Cl in representative samples of synthetic ClO$_4^-$ reagents and products, natural ClO$_4^-$ and Cl$^-$ extracted from soil and groundwater from the Atacama Desert, Chile, and natural ClO$_4^-$ extracted from groundwater and soil from the southwestern U.S. (modified from Sturchio et al. 2009).



6.2 Isotopic Fractionation of Chlorine and Oxygen during Perchlorate Biodegradation

6.2.1 Background

One important premise of a forensic investigation involving stable isotopes is that either (1) the stable isotope signatures in a molecule are preserved after deposition (by either natural mechanisms or contamination with synthetic sources) or (2) if they are not preserved, they are modified by known processes in a predictable fashion. One of the processes that is well known to alter the stable isotope composition of a molecule is biodegradation (e.g., Sharp, 2007; Hunkeler et al., 2008; Aelion et al., 2010; Hatzinger et al., 2013). In fact, systematic enrichments in the heavier isotopes of elements in reactive compounds (e.g., ^{13}C in MTBE, ^{15}N and ^{18}O in NO_3^-) have been used extensively to document biodegradation and to estimate kinetics of the process (e.g., USEPA, 2008; Meckenstock et al., 2004). One of the objectives of this project was to quantify fractionation factors for O and Cl in ClO_4^- during biodegradation. Other processes, including isotopic exchange with surrounding compounds, can also alter isotope values in a compound of interest, and must be evaluated. The isotopic effects of biodegradation on both Cl and O in ClO_4^- were investigated in both laboratory and field experiments by our group during the past few years (see Section 7.5 for field results), and studies have been performed to evaluate the potential isotopic effects of O exchange between ClO_4^- and H_2O (Section 6.3).

The fractionation of Cl and O stable isotopes through microbial reduction of ClO_4^- has been investigated in laboratory studies with pure cultures (Coleman et al., 2003; Sturchio et al., 2003, Sturchio et al., 2007) and in a field experiment involving a push-pull test (Hatzinger et al., 2009). The equations used to describe isotopic fractionation of reactants are provided in Section 6.2.2 (from Sturchio et al., 2007).

6.2.2 Terminology and Equations

The isotopic fractionation factor, α, is defined as

$$\text{[Eq. 6.1]} \qquad \alpha = R_A/R_B$$

where R is an isotope ratio (Equation 6.1), and A and B are two compounds (product and reactant, respectively). For O and Cl isotope ratios, R represents $N(^{18}O)/N(^{16}O)$ or $N(^{37}Cl)/N(^{35}Cl)$, respectively, where N is number of entities (atoms). Values of α can be obtained from experimental data by assuming the exponential function:

[Eq. 6.2] $R/R_0 = f^{\alpha-1}$

where R and R_0 are the O or Cl isotope ratios of the residual ClO_4^- and the initial (unreacted) ClO_4^-, respectively, and f is the fraction of ClO_4^- remaining. The δ values of ClO_4^- are calculated using the following relationship:

[Eq. 6.3] $(\delta + 1)/(\delta_0 + 1) = f^{\alpha-1}$

where δ is the isotopic composition of the ClO_4^- at any value f, and δ_0 is the isotopic composition at $f = 1$. The value of α can be calculated from the natural logarithm of Eq 6.2 as shown below:

[Eq. 6.4] $\alpha\text{-}1 = \ln(R/R_o)/\ln f$

The relation in Eq 6.4 describes the mass-dependent Rayleigh-type isotopic fractionation that accompanies a variety of natural processes (Clark and Fritz, 1997; Broecker and Oversby, 1971). Isotopic fractionation factors are commonly expressed in terms of ε, where

[Eq. 6.5] $\varepsilon = \alpha - 1$,

with ε typically reported in parts per thousand, or per mil (‰).

6.2.3 Fractionation Factors from Pure Culture Studies

Two independent studies by evaluated the isotopic fractionation of Cl in ClO_4^- by the bacterial species A*zospira suillum* with acetate as the electron donor and ClO_4^- as the sole electron acceptor (Coleman et al. 2003; Sturchio et al. 2003). Fractionation factors for Cl

($\varepsilon^{37}Cl$) ranged from -12.9 ‰ to -16.6 ‰ in these studies depending on culture conditions. Fractionation of Cl and O isotopes during microbial reduction of ClO_4^- was subsequently investigated during this project using two bacterial genera (*Azospira* and *Dechlorospirillum*), each incubated at two different temperatures (22°C and 10°C, respectively) (Sturchio et al., 2007). This study also evaluated the potential for O exchange during biodegradation of ClO_4^- using ^{18}O-enriched H_2O. The $\varepsilon^{37}Cl$ values in the various experimental treatments varied from -14.5 to -11.5 ‰, and $\varepsilon^{18}O$ values ranged from -36.6 to -29.0 ‰. The ε values were independent of bacterial strain and temperature, and there was no evidence for O exchange between ClO_4^- and H_2O. One critical finding from this work was that the ratio of $\varepsilon^{18}O/\varepsilon^{37}Cl$ was nearly constant in all experiments (independent of strain or temperature or rate of reaction) at 2.50 ± 0.04 over a range of f from 1.00 to 0.01 (Figure 6.9). The complete results from this evaluation are available in Sturchio et al., (2007), which is provided in Appendix C.

In a subsequent field study, water with ClO_4^- was injected into an aquifer that had previously been treated with soybean oil emulsion to stimulate ClO_4^- biodegradation, and then samples were collected over time from the injection well for analysis of stable isotopes and geochemical parameters. The detailed results of this experiment are provided in Section 7.5 and in Hatzinger et al., 2009). In summary, the *in situ* isotopic fractionation factors ($\varepsilon^{37}Cl$ and $\varepsilon^{18}O$) from this study were 0.3-0.4 times the values previously reported for pure cultures, and the differences were attributed to physical and chemical heterogeneity in the aquifer. Similar effects have been observed during a number of other field studies of *in situ* isotopic fractionation, and modeling has illustrated how physical processes in heterogeneous hydrologic systems can cause field isotopic fractionation data to differ from lab data (Mariotti et al., 1988; Brandes and Devol, 1997; Green et al., 2010; Hatzinger et al., 2013). However, despite the differences in the magnitudes of the individual isotope effects, the $\varepsilon^{18}O/\varepsilon^{37}Cl$ ratio was 2.6, which is in excellent agreement with the laboratory-determined value of 2.5 as shown in Figure 6.9 and described further below (Sturchio et al. 2007). This finding indicates that the fundamental process by which ClO_4^- is reduced was the same in laboratory and field settings, but the heterogeneity of the field setting is such that it can lead to underestimation of the extent of ClO_4^- reduction when using an isotopic approach based solely on laboratory fractionation factors (Section 7.5 and Hatzinger et al., 2009).

6.2.4 Implications of Isotope Fractionation of ClO_4^- for Forensic Investigations

The previous laboratory and field results concerning isotopic fractionation during biodegradation have implications for forensic studies. Isotopic analyses of O and Cl in ClO_4^- clearly show that different sources have distinct isotopic compositions, as described in Sections 6.1.1 and 6.1.2. However, variations in the isotopic composition of ClO_4^- in field samples could theoretically be caused by biodegradation or by mixing of isotopically distinct sources, and it is important to resolve these effects. Based on the laboratory and field studies conducted to date, biodegradation of ClO_4^- causes both $\delta^{18}O$ and $\delta^{37}Cl$ in the residual ClO_4^- (i.e., that remaining in the environment) to move along the slope shown in Figure 6.10. This trajectory (the slope of which is constant at $\varepsilon^{18}O/\varepsilon^{37}Cl = 2.5$) is roughly perpendicular to the area in which mixtures of synthetic and Chilean ClO_4^- would plot. Thus, biodegradation will not obscure the difference between these two major sources. In Figure 6.10, the f values plotted on the upper sloping line indicate the calculated values of $\delta^{18}O$ and $\delta^{37}Cl$ in synthetic ClO_4^- when 10 % ($f = 0.9$), 20 % ($f = 0.8$), etc. are biodegraded, according to the lab data. Based on the field results of Hatzinger et al. (2009), the f values would remain much closer to the source material (i.e., at 30 % biodegraded, the $\delta^{18}O$ and $\delta^{37}Cl$ values are predicted to be near $f = 0.9$ on the curve in Figure 6.10). Different field settings might yield somewhat different degrees of scale contraction along this fractionation line. Most critically, however, the slope of the progression of $\varepsilon^{18}O/\varepsilon^{37}Cl$ is the same in the flask and field, such that synthetic and Chilean ClO_4^- will not overlap isotopically as a result of biodegradation.

The $\delta^{18}O$ and $\delta^{37}Cl$ values for ClO_4^- derived from the SHP place this material near the trajectory for a small subset of synthetic ClO_4^- samples as shown in Figure 6.11. The synthetic samples with the highest $\delta^{18}O$ values (i.e., ~ -15 ‰) could overlap with SHP samples if they were extensively biodegraded. Similarly, it is possible that $\delta^{18}O$ and $\delta^{37}Cl$ values for a Chilean ClO_4^- sample could become similar to those from Death Valley if the Chilean ClO_4^- were substantially biodegraded. However, it is important to note that $\Delta^{17}O$ values are almost unaffected by mass-dependent processes, so that large differences in

$\Delta^{17}O$ between the sources would be preserved during degradation while $\delta^{18}O$ and $\delta^{37}Cl$ values were changing. Thus, from a practical perspective, potential "overlaps" in stable isotopic compositions caused by isotope effects of biodegradation are unlikely to cause mistakes in source delineation, particularly if ^{36}Cl analyses are conducted for samples and other supporting chemical and geochemical data are collected from sampling locations. For example, the potential for highly biodegraded (and isotopically fractionated) synthetic ClO_4^- to be confused for SHP natural ClO_4^- because of overlapping values of $\delta^{18}O$ and $\delta^{37}Cl$ can be further minimized by analyzing all samples in a forensic investigation for ^{36}Cl, as synthetic samples have low $^{36}Cl/Cl$ values (0×10^{-15} to 40×10^{-15}), whereas SHP and Death Valley samples have much higher $^{36}Cl/Cl$ values (3130×10^{-15} to $28,800 \times 10^{-15}$) (Sturchio et al., 2009), and $^{36}Cl/Cl$ values are not affected significantly by biodegradation. Similarly, Chilean and Death Valley samples analyzed to date have very different $^{36}Cl/Cl$ values.

In addition to ^{36}Cl, local geochemical parameters, including oxidation-reduction potential (ORP) and concentrations of dissolved O_2 (DO), organic carbon (DOC), NO_3^-, and N_2 (see Section 5.3) can provide important constraints on the potential for biodegradation. Bacteria require an organic or inorganic electron donor, as well as anoxic conditions to biodegrade ClO_4^- (Coates and Achenbach, 2004), and NO_3^- has been observed to impede biodegradation for many (but not all) ClO_4^- reducing strains (Farhan and Hatzinger, 2009; Chaudhuri et al., 2002). Thus, in aquifers with historically high levels of DO, ORP, and/or NO_3^-, biodegradation of ClO_4^- is unlikely. Similarly, low DOC (as one measure of potential organic electron donor abundance) also will limit biodegradation. Finally, when conditions are correct for ClO_4^- biodegradation, rates of this process are often very rapid and complete (making *in situ* and *ex situ* bioremediation viable treatment approaches; Hatzinger, 2005), unlike the slow kinetics often observed during biodegradation of chlorinated solvents, MTBE, and various other pollutants for which CSIA is applied. Thus, the potential for partially biodegraded and isotopically fractionated ClO_4^- to persist in an aquifer where biodegradation is occurring is less likely than for many other traditionally recalcitrant compounds.

Figure 6.9. Relation between ε^{18}O and ε^{37}Cl during bacterial reduction of ClO_4^- . The data presented represent results from laboratory studies in which ClO_4^- biodegradation by two strains was measured at two different temperatures (10 °C and 22 ^{o}). The isotopic fractionation factor ratio [$\varepsilon^{18}O/\varepsilon^{37}Cl = 2.5$] is independent of strain and temperature (figure from Sturchio et al. 2007).

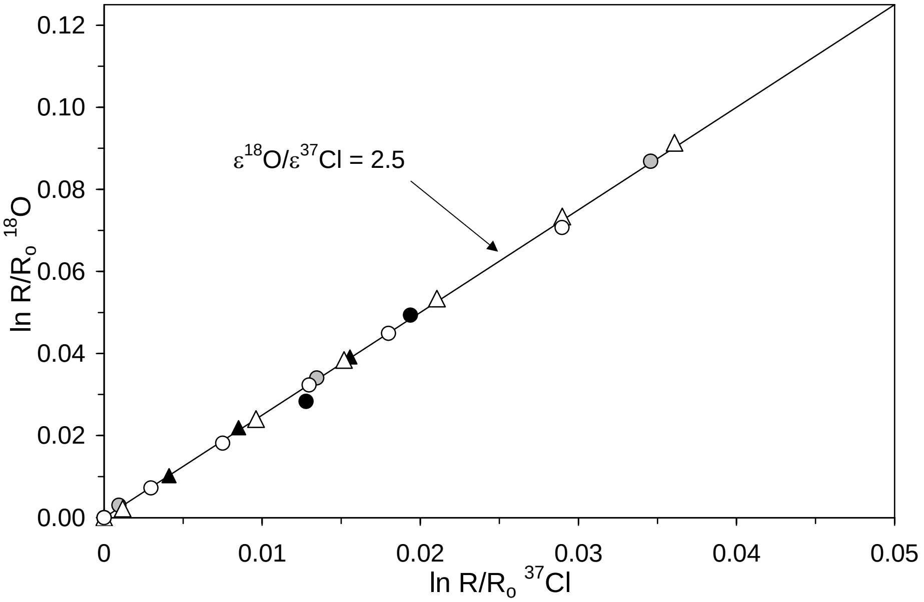


Figure 6.10. Relation between δ^{18}O and δ^{37}Cl values of synthetic and Chilean ClO_4^-, isotopic compositions of mixtures of these sources, and the isotopic compositions of residual ClO_4^- during biodegradation. The extent of biodegradation is given by *f*, the residual fraction, assuming $\varepsilon^{18}O = -36.25$ ‰ and $\varepsilon^{37}Cl = -14.5$ ‰; $\varepsilon^{18}O/\varepsilon^{37}Cl = 2.5$.

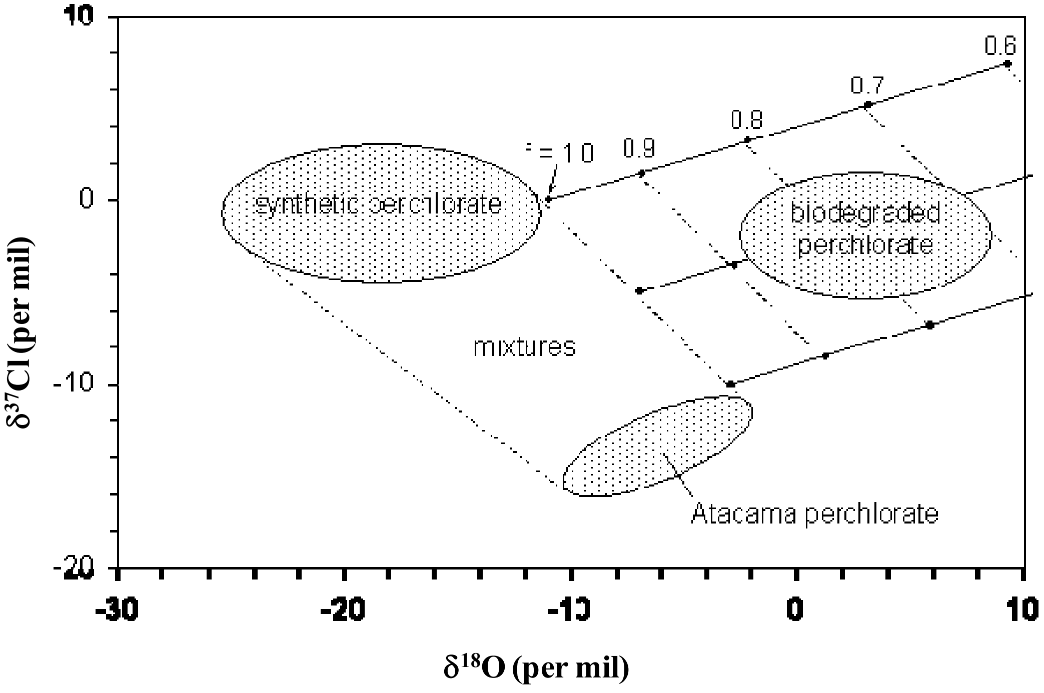
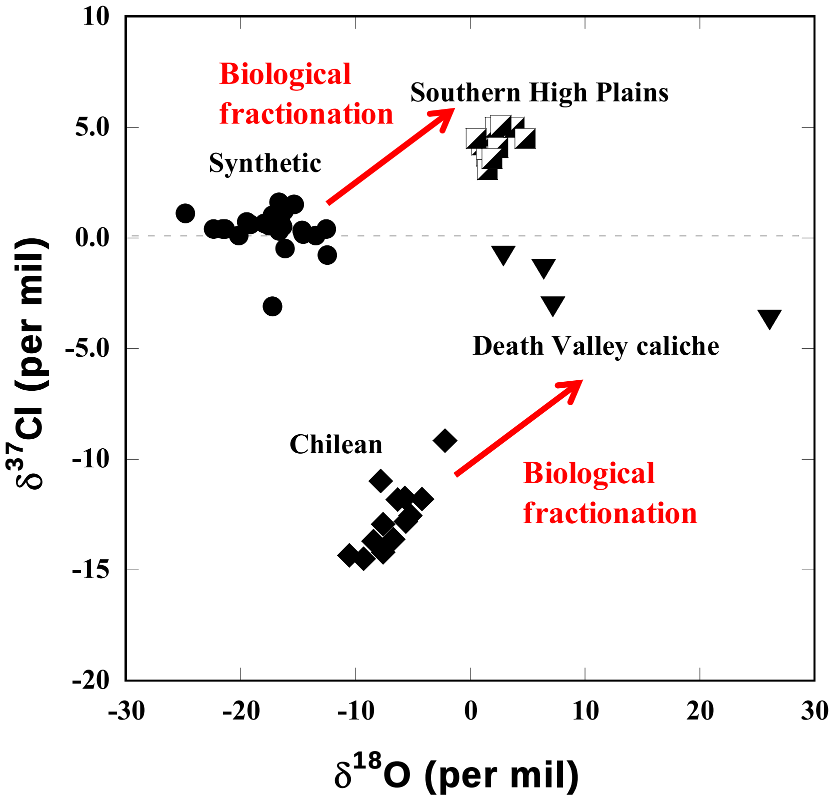


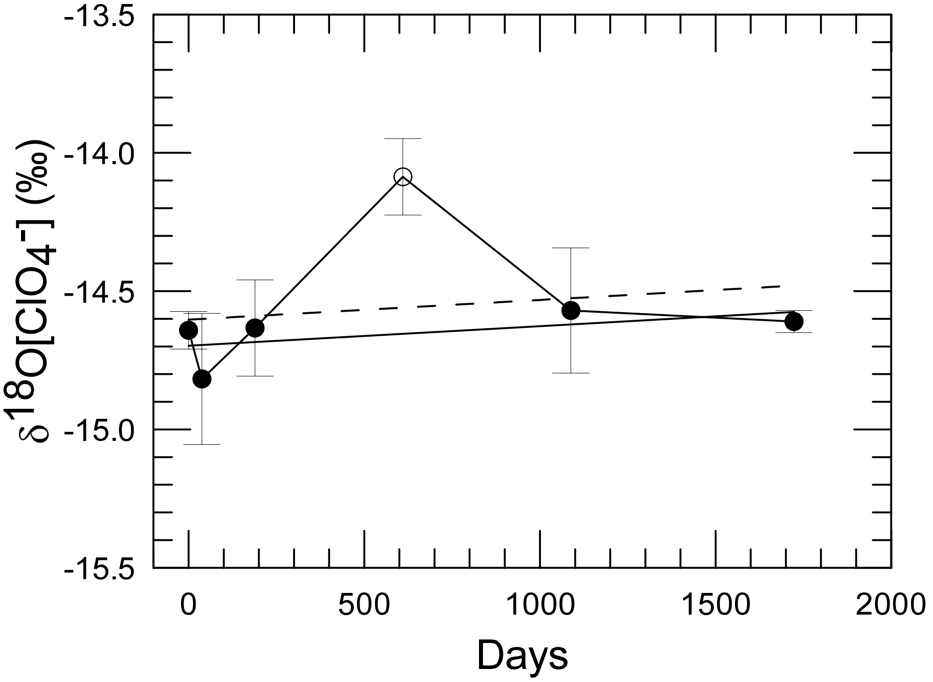
Figure 6.11. Microbial isotopic fractionation trajectory compared to δ^{18}O and δ^{37}Cl values of various ClO_4^- sources. Arrows indicate direction of change for $\varepsilon^{18}O/\varepsilon^{37}Cl = 2.5$. Other isotopic data ($\Delta^{17}$O values and ^{36}Cl/Cl ratios) also are used to evaluate whether observed differences in δ^{18}O and δ^{37}Cl values can result from biodegradation.



6.3 Isotopic Exchange of Oxygen between Perchlorate and Water

Besides biological isotopic fractionation, exchange of O in ClO_4^- with surrounding H_2O in an aquifer or elsewhere could lead to post depositional changes in the $\delta^{17}O$ and $\delta^{18}O$ values of ClO_4^-. Because Cl is the central atom in ClO_4^- and is bonded to four O molecules, exchange of Cl may be less likely. The USGS evaluated the potential for the exchange of O by ClO_4^- in a long-term study. During this evaluation, ClO_4^- (from $HClO_4$) with a known O isotopic composition was mixed with ^{18}O-enriched H_2O ($\delta^{18}O = +156$ ‰), and the mixture was sealed and incubated at room temperature (22 ± 1 °C). Periodically, subsamples of the solution were removed and the O isotopic composition of the ClO_4^- was measured by IRMS as described previously. After nearly 5 yr of incubation, evidence for exchange of O between the ^{18}O-enriched H_2O and the ClO_4^- was negligible (Figure 6.11) (Böhlke et al., unpublished data). Based on the current data from this study, the half-life of O isotope exchange between ClO_4^- and H_2O is > 4,500 yr. These results extend those of a previous investigation indicating minimal exchange of O between ClO_4^- and H_2O, with a half-life of > 100 yr (Hoering et al. 1958). Field data so far indicate that the integrity of the ClO_4^- source O isotopic ratios is maintained over at least several decades under normal groundwater conditions. This was indicated, for example, by the isotopic composition of known synthetic ClO_4^- near the end of a groundwater flow path with modeled transit time of around 30-50 yr from the source near Henderson, NV (Böhlke et al., 2005). It was indicated also by the detection of ClO_4^- with isotopic composition similar to that of Chilean nitrate fertilizer in groundwater on Long Island, NY 20-40 yr after the groundwater was recharged (Böhlke et al., 2009), as summarized in Section 7.1.

Figure 6.11. Values of δ^{18}O in ClO_4^- during long-term incubation in ^{18}O-enriched H_2O.



7.0 RESULTS PART II: SITE INVESTIGATIONS

The database of results presented in Section 6 describes three principal ClO_4^- sources that are likely to be found in soils and groundwaters in the U.S. (i.e., synthetic ClO_4^-, Chilean nitrate fertilizer-derived ClO_4^-, indigenous natural ClO_4^-) and shows that these sources are isotopically distinct when all relative stable isotope ratios of O and Cl (expressed as δ^{37}Cl, δ^{18}O, and Δ^{17}O) are taken into consideration (Bao and Gu, 2004; Böhlke et al., 2005, 2009; Sturchio et al. 2006, 2011; Jackson et al., 2010). The mole fraction of radioactive ^{36}Cl (expressed as ^{36}Cl/Cl) in the different sources is also a useful distinguishing characteristic among the three sources (Sturchio et al. 2009). In addition, current results indicate that O exchange between ClO_4^- and H_2O is insignificant in water over at least decades if not centuries, so the isotopic characteristics of source ClO_4^- can be maintained in groundwater, at least on anthropogenic time scales (Böhlke et al., 2005, 2009). Finally, although ClO_4^- is subject to biodegradation under appropriate conditions (i.e., anoxic, low NO_3^-, available electron donor, presence of ClO_4^--reducing bacteria), this process appears to result in predictable stable isotope effects that will not substantially alter Δ^{17}O or ^{36}Cl/Cl values and generally will not cause any one source to be isotopically indistinguishable from another. Thus, even if a given occurrence of ClO_4^- is partially biodegraded, the initial source(s) generally can be determined. Also, evaluation tools exist to determine the likelihood that biodegradation has affected ClO_4^- by examining other chemical indicators in a sample.

Based on these findings, we conducted source-attribution studies using ClO_4^- stable isotope ratio analysis at various locations, including Long Island, NY, the Stringfellow Superfund Site in Glen Avon, CA, the Lower Umatilla Basin, OR, and the University of Massachusetts, Dartmouth, MA. We also performed a study to assess *in situ* biological fractionation of ClO_4^- in groundwater at a site where an emulsified oil had previously been injected to promote ClO_4^- biodegradation. The results from these investigations are summarized in Sections 7.1-7.5. The investigation of natural ClO_4^- sources in the Southwest U.S. (West Texas and New Mexico) also could be described as a field investigation. These data were described separately in Section 6 as the results from these areas suggest that these are distinct "source" types of ClO_4^-. In addition to these investigations, several other studies have been conducted by outside groups using the isotopic techniques developed herein, including studies performed in Pasadena, CA (Slaten et al., 2010), Redlands, CA (Sturchio et al., 2012) and Chino, CA (Sturchio et al., 2008, 2011). The data from these studies can be obtained from the references cited above.

7.1 Suffolk County, Long Island, New York.

7.1.1 Characteristics of Sites and Wells

The objective of this forensic evaluation was to assess probable sources of ClO_4^- in groundwater at multiple locations within Suffolk County on Long Island, New York. The full details are presented in Appendix C (Böhlke et al., 2009). Perchlorate has been detected in groundwater in numerous locations on Long Island, with various sources possible based on current and past activities (Abbene, 2006; Munster, 2008). These sources include fireworks production and use, agricultural fertilizer application (historical and current), road flares, military facilities including missile launch sites, disinfection with bleach, and others. The well locations are shown in Figure 7.1. Samples were collected from two production wells in the Northport area of western Suffolk County by placing an IX column on a slipstream from each well, as shown in Figure 7.2. These wells, which are screened 93 ± 10 m and 117 ± 9 m below ground surface (bgs) are within the Magothy aquifer. This region was primarily agricultural in the 1950s, but much of the land is now residential. Samples were also obtained from two shallow groundwater monitoring wells at a former BOMARC (Boeing and Michigan Aerospace Research Center) missile site near Westhampton, New York. This site was deactivated in 1969 and was converted to a training facility for police by Suffolk County. Activities at the site at the time of this study included weapons training and fireworks disposal by open burning in a pit. Both wells were upgradient from the former missile silos and downgradient from a firing range and fireworks disposal pit. Finally, a monitoring well transect was sampled in the North Fork area in the northeast part of Suffolk County (Depot Lane). This transect consisted of three nested monitoring wells running in a northwest-southeast array across the middle of the North Fork Peninsula. Land use in this area is primarily agricultural. These wells are screened within the surficial upper glacial aquifer (Schubert et al., 2004). The deepest well screens are just above a lower confining unit, which begins at approximately -35 to -31 m elevation (Bohn-Buxton et al., 1996).

Figure 7.1. Location map of groundwater wells sampled for ClO_4^- source identification on Long Island, New York (modified from Böhlke et al., 2009).

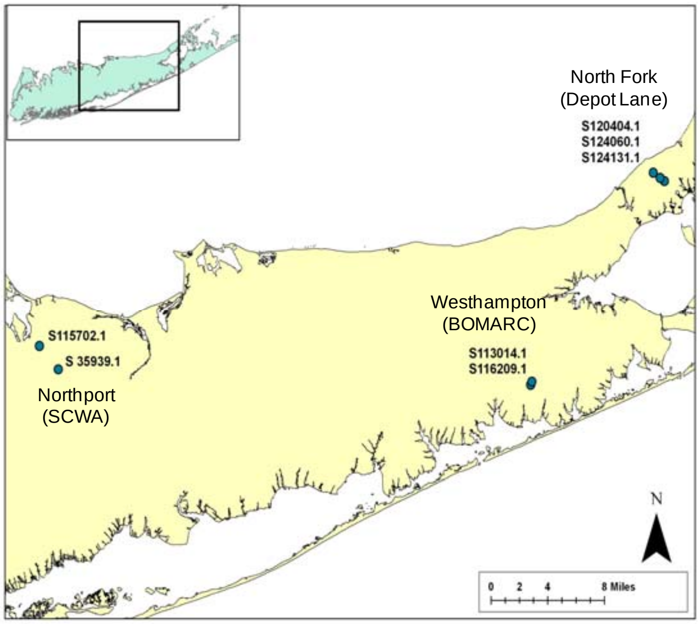


Figure 7.2. Sample collection setup for ClO_4^- from a public supply well on Long Island, New York.

7.1.2 Sample Collection and Analyses

Groundwater field parameters were measured at each well (DO, pH, conductivity, and temperature) and samples were collected essentially as described in Section 5.2.1 of this document. In addition to ClO_4^- collection for Cl and O isotopic analyses, groundwater samples were collected for isotopic analyses of N, S, and O in NO_3^- and SO_4^{2-}, for concentration analyses of ClO_4^-, anions, trace elements, and major dissolved gases (Ar, N_2, O_2, and CH_4), and for groundwater-age dating (^3H, ^3He, SF_6, and chlorofluorocarbons (CFCs) as described in Section 5.3 and Table 5.1). Samples were obtained between December, 2006 and April, 2008.

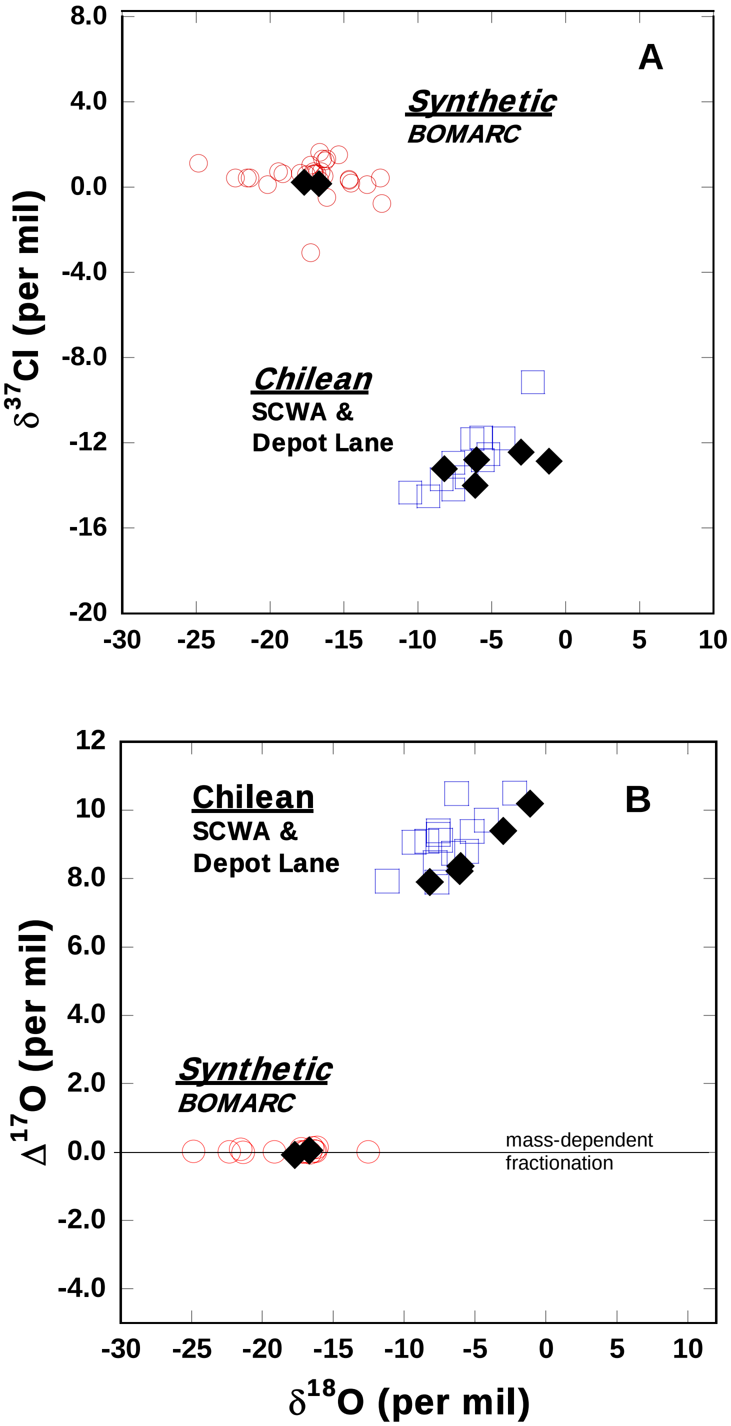
7.1.3 Results of Chlorine and Oxygen Isotopic Analyses of Perchlorate

Perchlorate was detected at the highest concentrations at the former BOMARC site (~ 360 – 4,300 μg/L), where fireworks disposal and military activities were considered the most likely sources. The Suffolk County production wells had ClO_4^- concentrations of 8.4 to 11.2 μg/L and the deep nested wells at Depot Lane had concentrations from ~ 4.6 to 10 μg/L. The shallow nested wells at Depot Lane had concentrations of only 0.2 to 1.0 μg/L, which was too low to permit collection of samples for isotopic analysis using available equipment. The $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ values of the ClO_4^- collected from the BOMARC wells (n = 2) were consistent with values typical of synthetic ClO_4^-, while samples from the Northport production wells (n = 2) and the deep Depot Lane wells (n = 3) were consistent with natural ClO_4^- from Chile (Figure 7.3). There was no indication of ClO_4^- biodegradation or denitrification in the site groundwater (see Böhlke et al., 2009 in Appendix C for the complete dataset)

The two BOMARC wells, which contained unusually high concentrations of ClO_4^-, were near a fireworks disposal pit. The groundwater in the wells also had anomalously high concentrations of K, Sr, and Sb, as determined by ICP-MS analysis. These elements commonly are used for color and brightness in fireworks (Conklin, 1985). Although various local sources of synthetic ClO_4^- may be present at this site, leaching of unexploded fireworks as the cause of groundwater contamination is supported by presence of a fireworks disposal pit in the area, the extremely high ClO_4^- levels in each of the wells, the anomalously high concentrations of trace elements common to many fireworks, and the young ages of the groundwaters (1-2 yr, based on environmental tracer data).

In contrast to the BOMARC wells, the Cl and O isotopic compositions of ClO_4^- from the Depot Lane wells and Northport production wells were consistent with ClO_4^- found in Chilean nitrate deposits and fertilizers. Groundwater in these wells also had relatively high concentrations of NO_3^- and other constituents that are typical of recharge beneath fertilized agricultural land in this region, such as Ca, Mg, and SO_4^{2-} (see Böhlke et al., 2009 for data and further explanation). No other ClO_4^- sources, including the U.S. indigenous sources, are currently known to have the distinctive combination of low δ^{37}Cl, low δ^{18}O, and high Δ^{17}O values that characterize the Chilean ClO_4^-. Thus, the data indicate that the ClO_4^- in these wells was derived from the historical use of Chilean nitrate fertilizers on Long Island. Age dating of groundwater supports this hypothesis (see Section 7.1.4 and Figure 7.4). It is apparent from the data that the distinctive Cl and O isotopic compositions of the Chilean ClO_4^- were not altered substantially by O exchange or other plant, soil, or mineral reactions during transport and aging in the Long Island aquifers.

Figure 7.3. Comparison of δ^{37}Cl versus δ^{18}O (Plot A) and Δ^{17}O versus δ^{18}O (Plot B) in ClO_4^- from wells on Long Island with those of synthetic and Chilean source materials. The data from the Long Island wells are plotted as black diamonds, the data from synthetic sources as open red circles, and those from Chilean samples as open blue squares.



7.1.4 Groundwater Dating and Other Supporting Data

Groundwater dating provided valuable information during this study. Apparent recharge dates and ages of groundwater (time in saturated zone after recharge) were estimated from concentrations of various atmospheric tracers including ^3H-^3He, SF_6, and CFCs, as summarized in Böhlke et al. (2009). Based on the tracer data, a composite mean apparent age was estimated for groundwater in each well, and the results ranged from ~ 1 to 41 yr with uncertainties of the order of 2-5 yr. The groundwater in the BOMARC wells was recharged within the previous 2 yr prior to groundwater sample collection. The presence of recently recharged water is consistent with fireworks from the disposal pit area as a source of ClO_4^- contamination. At the North Fork (Depot Lane) transect wells, apparent groundwater ages ranged from ~ 1 to 39 yr and increased with depth as did the mean concentration of ClO_4^-, while the relatively high levels of NO_3^- remained almost constant with groundwater depth and age (Figure 7.4).

The consistently lower ClO_4^- concentrations in younger groundwater, with the relatively constant NO_3^-, were interpreted by Böhlke et al. (2009) to reflect changing agricultural practices, with quantities of ClO_4^- bearing Chilean fertilizer declining and being replaced by other sources without ClO_4^- over the past several decades (possibly including low-ClO_4^- Chilean fertilizer in recent years). This groundwater trend (decreasing ClO_4^- and constant or slightly increasing NO_3^-) resembles qualitatively the overall patterns of Chilean and non-Chilean fertilizer use in the United States since the mid-1900s (Figure 7.5). This interpretation is also consistent with Chilean ClO_4^- as a source in the Northport area production wells, as the composite apparent groundwater ages at these wells were 35 and 41 yr, respectively, similar to those of the deeper wells in the Depot Lane transect that had Chilean ClO_4^-. These groundwaters apparently recharged when land use was more agricultural than at present.

7.1.5 Summary of Long Island Perchlorate Source Study

The stable isotope results ($\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$) for ClO_4^- and key supporting chemical and environmental tracer data collected from several wells on Long Island provide strong evidence for the presence of ClO_4^- derived from Chilean nitrate fertilizer as well as that from a synthetic source, presumably fireworks disposal. The groundwater at all locations was aerobic and undenitrified, and ClO_4^- apparently was not affected isotopically by biodegradation or exchange processes in the subsurface. In an agricultural region, ClO_4^- concentrations and the ratio of ClO_4^-/NO_3^- increased with increasing groundwater age (from ~ 1 to 40 yr based on atmospheric tracers), most likely as a result of declining application rates of Chilean nitrate fertilizer. Stable Cl and O isotopic analyses of ClO_4^- indicates that past use of imported Chilean nitrate fertilizer on Long Island has led to legacy contamination of some aquifer units, even though this fertilizer may have been applied in relatively small quantities as long as 40 or more years ago. Additional details concerning the stable isotope data from Long Island and the results of the supporting analyses is provided in Böhlke et al., 2009 (Appendix C).

Figure 7.4. Vertical distribution of NO_3-N and ClO_4^- concentrations in nested wells along a transect in the North Fork area of Long Island. The estimated time since recharge of the groundwater at different depths in the DL 4 well nest is also given. Figure modified from Böhlke et al (2009).

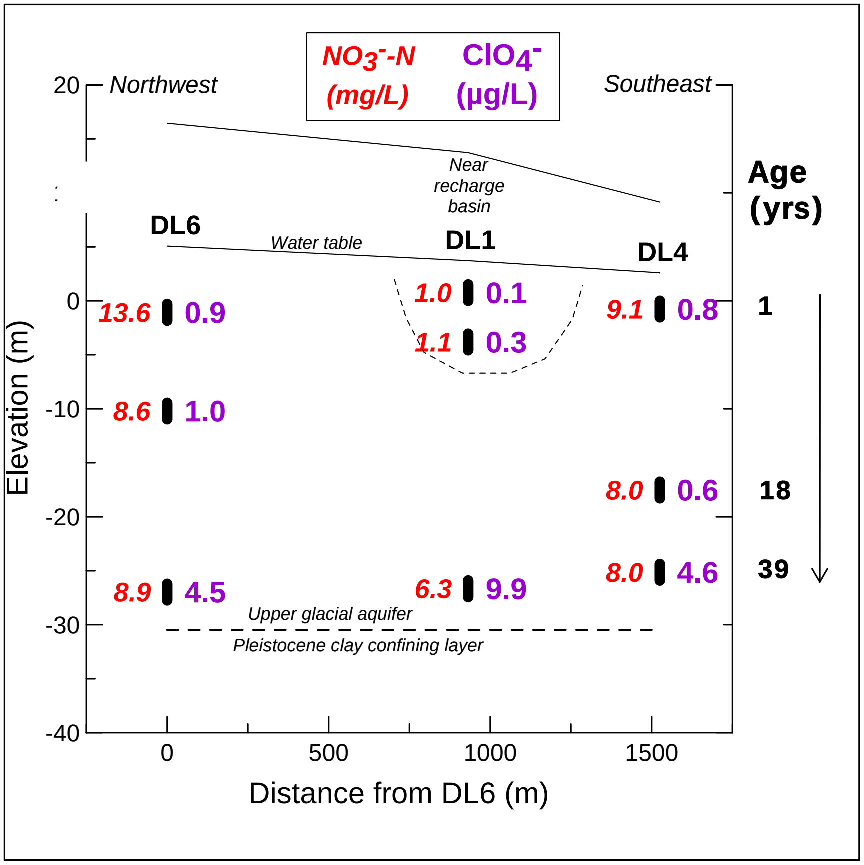
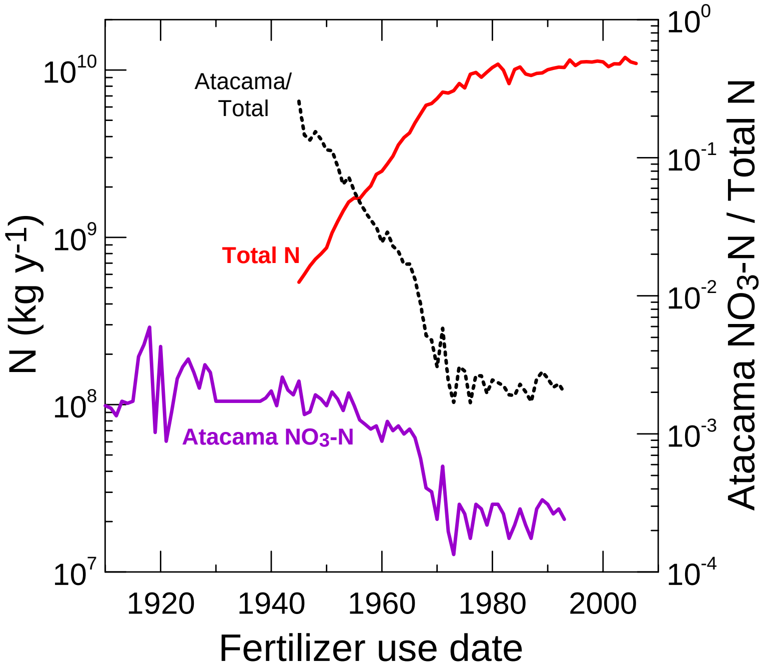


Figure 7.5. National trends of Chilean fertilizer use (Atacama NO_3^-) and total N fertilizer use in the U.S. (modified from Böhlke et al., 2009).



7.2 Stringfellow Superfund Site, Glen Avon, CA

Our research group worked in conjunction with the California Department of Toxic Substance Control (DTSC) to evaluate the isotopic characteristics of ClO_4^- in groundwater in the vicinity of the Stringfellow Superfund Site (Stringfellow) in Glen Avon, CA. Stringfellow is a hazardous waste disposal facility that operated from 1956 to 1972, receiving over 100 million liters of hazardous waste, including wastes from users/manufacturers of rocket fuel (DTSC, 2006). The site, which included unlined ponds, was drained and capped in the 1980s and numerous extraction wells were installed to capture contaminated groundwater. This water is treated in one of several different treatment facilities. In 2001, ClO_4^- was detected in wells that are known to be impacted by Stringfellow. However, an extensive investigation revealed a low concentration of ClO_4^- in groundwater throughout the Glen Avon area, some of which may be associated with sources other than Stringfellow (DTSC, 2006; Figure 7.6). In collaboration with DTSC and Kleifelder Consultants (contractor to DTSC), our research group conducted stable isotope analysis of four groundwater samples collected from the Glen Avon area to determine if all of the ClO_4^- in these samples is synthetic in origin, or whether natural ClO_4^- from fertilizer or indigenous sources also may occur in this region.

7.2.1 Groundwater Samples, Perchlorate Collection, and Isotope Analysis

ClO_4^- was collected from two groundwater wells and two water treatment facilities in the vicinity of Stringfellow by associates from Kleinfelder Consultants using columns prepared by our group (Figure 7.7). The groundwater wells were from 4549 Pedley Road (4549) and 4695 Tyrolite Road (4695). The water treatment plant samples were from the Lower Canyon Treatment Facility (LCTF) in Zone 3 and the Community Treatment Plant (CTP). The latter two samples constitute water collected from a series of wells rather than a single well as for 4549 and 4695. Well 4549 is marked incorrectly as 11549 in Figure 7.7. The initial wells were selected based upon hydrogeologic data, plume mapping, and other considerations. Complete ClO_4^- isotopic data ($\delta^{37}Cl$, $\delta^{18}O$, $\Delta^{17}O$, and $^{36}Cl/Cl$ values) were obtained for all four samples. The ClO_4^- collection, purification, and stable isotope methods were generally as described previously in this document. In summary, for ClO_4^- collection from the two wells, groundwater from each well was pumped at a flow rate of ~ 2 L/min through a small PVC column containing perchlorate–selective resin (Purolite A530-E). The water was initially passed through a 0.45-um-pore size cartridge filter to remove any small sediment prior to entering the ion-exchange column. Enough water was passed through each column to collect ~ 10 mg of ClO_4^- (assuming all ClO_4^- was trapped). For the LCTP sample, a small IX column was attached to a sampling port preceding the plant, so that mixed water from all wells feeding the plant was sampled. Finally, for the CTP, Purolite A530E resin from an existing commercial ion exchange system was collected and extracted to obtain ClO_4^- for isotopic analysis. This is the same resin used in the small sampling columns. As with the LCTP, water entering the CTP is derived from multiple wells.

After sampling was complete, each column (or for CTP, bulk resin sample) was sealed and shipped to ORNL for ClO_4^- extraction and purification. The ClO_4^- was eluted and purified as detailed previously in this document and in Hatzinger et al., 2011. For sample LCTF, the initial ClO_4^- eluted from the column was purified separately from the ClO_4^- eluting later from the column. Isotopic analysis of these samples was conducted separately, and the results were averaged. In the final step for all samples, ClO_4^- was converted to an insoluble cesium salt, and purity was determined by Raman spectroscopy. Once purified, the ClO_4^- samples were shipped to the USGS in Reston, VA for analysis of oxygen isotopes. The combusted residue from the oxygen isotope analysis was then analyzed at the UIC for $\delta^{37}Cl$, and at the Purdue University PRIME facility for ^{36}Cl.

Figure 7.6. Perchlorate concentration contours downgradient of the Stringfellow Superfund Site, Glen Avon, CA. Figure provided by Roger Paulson, DTSC.

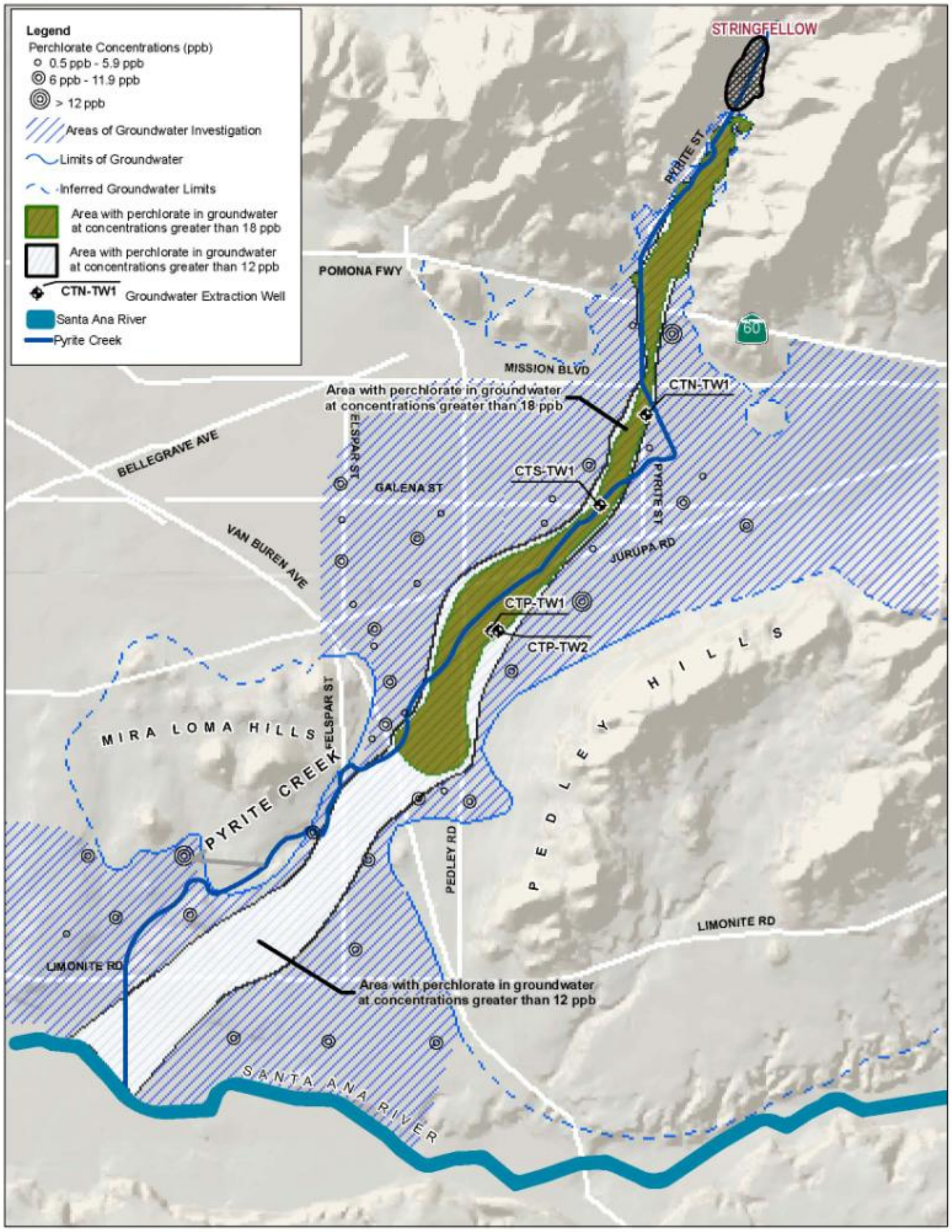
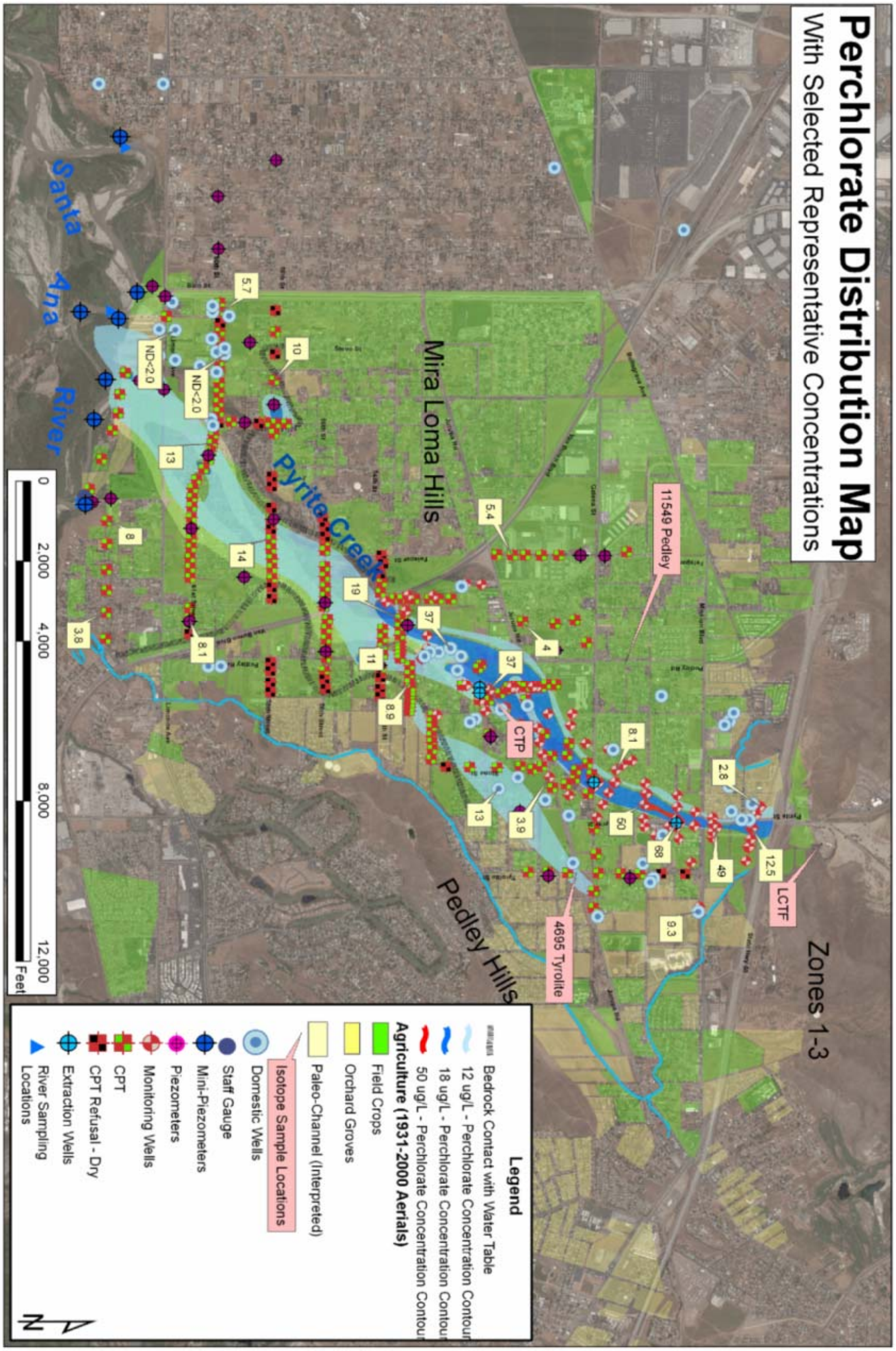


Figure 7.7 Location of wells sampled near the Stringfellow Superfund Site, Glen Avon, CA. Figure provided by Roger Paulson, DTSC.



7.2.2 Stringfellow ClO_4^- Stable Isotope Results

The isotopic values for ClO_4^- obtained from groundwater wells in the Stringfellow Area are provided in Table 7.1. A comparison of the groundwater stable isotope values with the published values from synthetic and natural sources is provided in Figure 7.8. Because only a small number of samples were collected, it is not possible to obtain a regional view of ClO_4^- origin from this dataset. It is our understanding that DTSC is considering conducting a more comprehensive study at the site. However, the isotope data suggest that two of the samples consist primarily of synthetic ClO_4^- (CTP and LCTF) mixed with a small percentage of natural ClO_4^-. When mixtures of two or more types of ClO_4^- are present in a sample, the isotope data will reflect the percentage of each type in the mixture (see Figure 6.10). The isotope data suggest that the other two samples, Pedley 4549 and Tyrolite 4695, have a much greater percentage of natural ClO_4^- than either CTP or LCTF, and that this natural ClO_4^- is predominantly Chilean in origin. Their isotopic values place them mid-way between those for the synthetic and Chilean ClO_4^-. However, an offset in the ^{18}O values for Pedley 4549 and Tyrolite 4695 (Figure 7.8B) also indicates that a component of indigenous natural ClO_4^- may be present in the mixture. This is confirmed by ^{36}Cl data (see next section).

In addition to $\delta^{18}O$, $\Delta^{17}O$ and $\delta^{37}Cl$, analysis of the long-lived radioactive isotope ^{36}Cl was conducted for all samples. As previously described in Section 6.1.3, previous studies by our group have revealed that the radioactive isotope ^{36}Cl (generally reported as an atom or mole fraction as $^{36}Cl/Cl$) is significantly elevated in all natural indigenous samples of ClO_4^- thus far collected from the SHP and Death Valley regions, ranging from 3130×10^{-15} to $28,800 \times 10^{-15}$ (Appendix C; Sturchio et al., 2009). The elevated $^{36}Cl/Cl$ ratios are hypothesized to be the result of relatively recent stratospheric formation of the ClO_4^- in these regions. By comparison, relatively low $^{36}Cl/Cl$ values were observed for both synthetic ClO_4^- ($^{36}Cl/Cl$ from 0×10^{-15} to 40×10^{-15}) and Chilean ClO_4^- ($^{36}Cl/Cl$ values from 22×10^{-15} to 590×10^{-15}), the former because it is synthesized electrochemically from Cl^- with a low $^{36}Cl/Cl$ amount, and the latter presumably because this material is millions of years old, and much of the initial cosmogenic ^{36}Cl has decayed over this time (Sturchio et al., 2009).

The data from the Stringfellow site show a slight elevation of ^{36}Cl/Cl in the CTP and LCTF samples, with ^{36}Cl/Cl values of 943 x 10^{-15} and 986 x 10^{-15}, respectively (Table 7.2). Taken with the stable isotope values, these data indicate that there is likely to be a small percentage of natural indigenous (SHP-type) ClO_4^- present in addition to synthetic ClO_4^-. If one assumes an average ^{36}Cl/Cl value in the natural indigenous SHP ClO_4^- of ~ 11,000 × 10^{-15} (average of SHP and Death Valley samples analyzed to date), and that the remainder of the ClO_4^- in the well is synthetic with a ^{36}Cl/Cl ratio of 0 × 10^{-15}, then ~ 9 % SHP-type ClO_4^- could result in these values. This percentage would correlate to ~ 8 μg/L of the 97 μg/L entering the CTP and ~ 2 μg/L of the 22 μg/L entering the LCTF (these samples are from multiple wells). However, the actual amount of ^{36}Cl/Cl in the natural ClO_4^- in the Glen Avon area is not known, so the percentages given are just rough estimates. Higher ^{36}Cl/Cl values were observed for Pedley 4549 (^{36}Cl/Cl = 4015 x 10^{-15}) and Tyrolite 4695 (^{36}Cl/Cl = 3825 x 10^{-15}) wells. The ClO_4^- concentrations in these wells also were much lower (8.9 μg/L and 11 μg/L, respectively). Making the same assumptions as for the previous samples, ~ 3-4 μg/L of the ClO_4^- in these wells could be of the SHP-type. The ^{36}Cl/Cl data are consistent with the presence of a low concentration of SHP-type natural ClO_4^- in groundwater in the Stringfellow area. This ClO_4^- was most likely flushed to groundwater through irrigation, as is hypothesized for much of the natural ClO_4^- present in the SHP region of TX and NM (Rajagopolan, 2006, 2009; Jackson et al., 2004, 2005, 2006).

When all four isotope values are considered together, the data indicate that there is a significant percentage of Chilean-type ClO_4^- present in the Pedley 4549 and Tyrolite 4695 wells, as well as both indigenous ClO_4^- and synthetic ClO_4^-. The low δ^{37}Cl and δ^{18}O values combined with the elevated Δ^{17}O are characteristic of the Chilean ClO_4^- only. When graphed on dual isotope plots (Figure 7.8), the samples clearly trend appreciably toward the Chilean source material. The CTP sample, and to a lesser extent, the LCTF sample, while being predominantly synthetic, may also contain a small percentage of Chilean ClO_4^-, based on the stable isotope data.

The presence of Chilean ClO_4^- derived from past agricultural applications in groundwater in the Chino Basin Hydrogeologic Area (which includes Stringfellow) was previously reported by Sturchio et al., 2008 and summarized with forensic data from other sites in

Sturchio et al., 2011. The ClO_4^- in 9 of the 10 wells sampled during the Chino Basin study was predominantly of Chilean origin based on stable isotope results (Figure 7.9 and 7.10; modified from Sturchio et al., 2008). With a few exceptions, the $\Delta^{17}O$ values exceeded +7 ‰ and the $\delta^{37}Cl$ values were ~ -12 ‰ or lower, consistent with Chilean-fertilizer derived ClO_4^-. This finding is consistent with the fact that the western Chino Basin was once predominantly agricultural land, with significant citrus production. Antedotal evidence suggests that Chilean fertilizer was widely used on citrus in California (Sturchio et al., 2008, 2011).

Interestingly, the one sample with the most significant deviation in isotopic signature among the Chino dataset was collected from the most easterly region of the study area (denoted sample 199 in Figures 7.10 and 7.11). This well also had a lower concentration than many of the other wells sampled (Figure 7.10). Based on all of the isotopes measured, sample 199 from the Chino Basin study appears to consist of a mixture of Chilean ClO_4^- (presumably derived from fertilizer) and natural SHP–type material. The offset in the $\delta^{18}O$ values for the 4549 Pedley and 4695 Tyrolite samples from the Stringfellow wells, compared to what would be expected for a mixture of just synthetic and Chilean ClO_4, and the elevated $^{36}Cl/Cl$ values, also indicates the presence of a small component of SHP-type ClO_4^- in these wells. This would be consistent with the data for sample 199. However, as previously noted, a much larger regional dataset, including collection of supporting parameters, is required to better understand the origin of ClO_4^- in the Glen Avon region.

7.2.3 Conclusions from Stringfellow Stable Isotope Data

Based on the stable isotope data collected, groundwater entering the Lower Canyon Treatment Facility (LCTF) in Zone 3 and the Community Treatment Plant (CTP) contains primarily synthetic ClO_4^- with the remainder being natural ClO_4, of mixed SHP and Chilean origin. The two groundwater wells sampled at 4549 Pedley Road and 4695 Tyrolite Road have a much higher percentage of natural Chilean ClO_4^- than samples from the treatment plant locations based on their $\Delta^{17}O$ values. The $\delta^{37}Cl$ and $\delta^{18}O$ values are consistent with this source allocation. The $^{36}Cl/Cl$ and $\delta^{18}O$ data also suggest that the 4549 Pedley Road and 4695 Tyrolite Road samples contain a component of natural indigenous

ClO_4^- of the SHP-type. A much larger regional dataset is required to better understand the origin and source distribution of perchlorate in the Stringfellow region.

Table 7.1. Isotope Values for Wells Sampled near the Stringfellow Superfund Site.

Sample ID	ClO_4^- (µg/L)[1]	$\delta^{18}O$ (‰)	$\delta^{37}Cl$ (‰)	$\Delta^{17}O$ (‰)	$^{36}Cl/Cl$ (* 10^{-15})	Notes
LCTF (Zone 3)[2]	97	-17.9	-0.3	0.6	943	Multiple wells
CTP (E stream)	22	-15.9	-1.5	1.2	986	Multiple wells; resin system
4549 Pedley Rd	8.9	-8.4	-5.0	4.0	4013	One well
4695 Tyrolite Rd	11	-9.5	-8.0	4.5	3825	One well

[1] Concentration values provided by Roger Paulson (DTSC) from Stringfellow database. The concentrations were not taken at the time of sample collection for perchlorate analysis. The reported values were from May 10, 2006 for 4695 and March 23, 2007 for 4549. For CTP, an average concentration from April 05 – May 30, 2007 is reported, and for LCTF, the average extraction well concentrations on April 19, 2007 are reported.

[2] These values represent averages from duplicate analyses. The effluent from the resin columns was collected in two separate batches during perchlorate extraction. Both were purified and analyzed separately, then the averaged.

Figure 7.8. Comparison of δ^{37}Cl versus δ^{18}O (Plot A) and Δ^{17}O versus δ^{18}O (Plot B) of Stringfellow samples (orange symbols) compared to natural indigenous ClO_4^- in the U.S. (Southern High Plains and Death Valley caliche), natural Chilean ClO_4^-, and synthetic ClO_4^-.

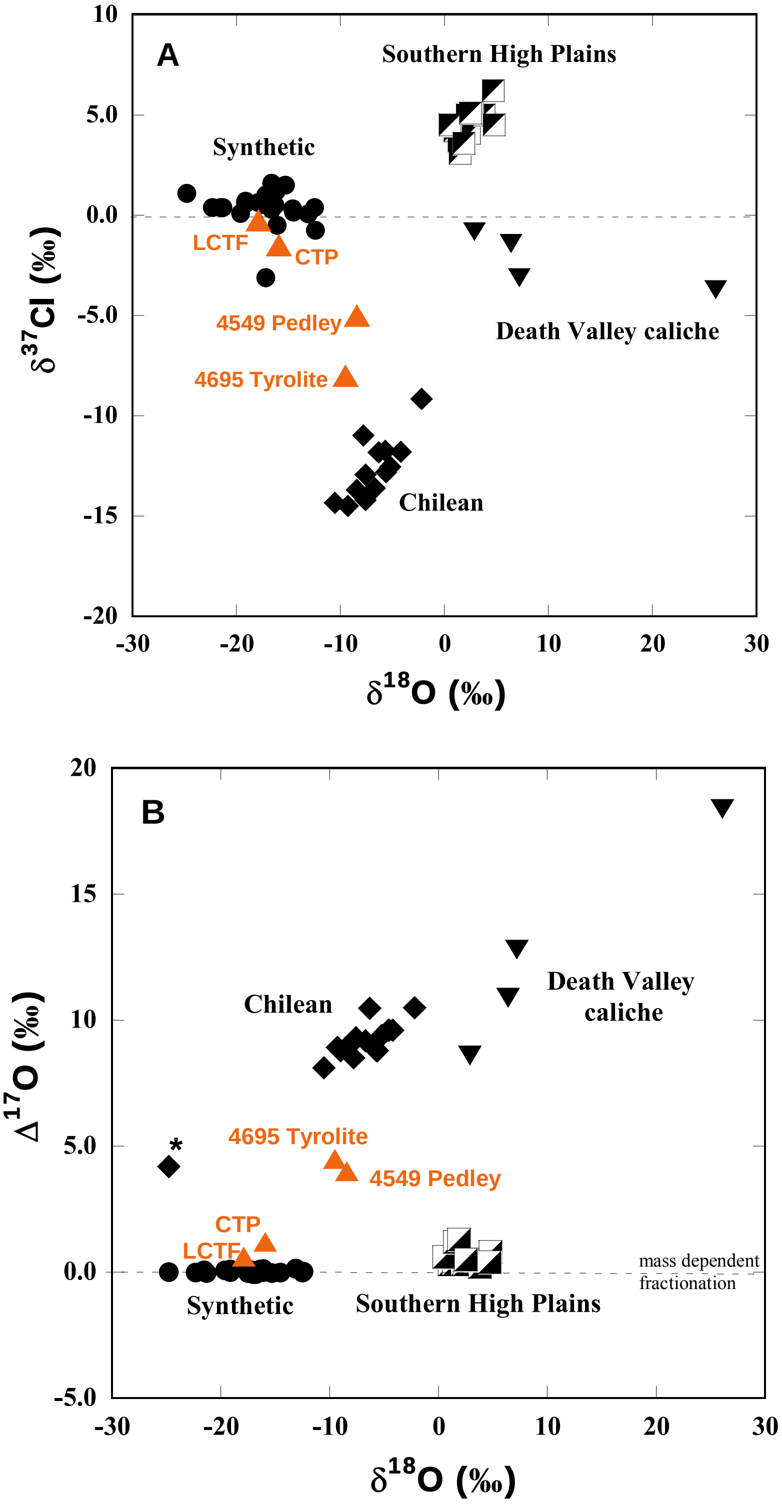


Figure 7.9 Location of wells sampled in the Chino Basin. The location of the Stringfellow site is also shown. Figure modified form Sturchio et al., 2008.

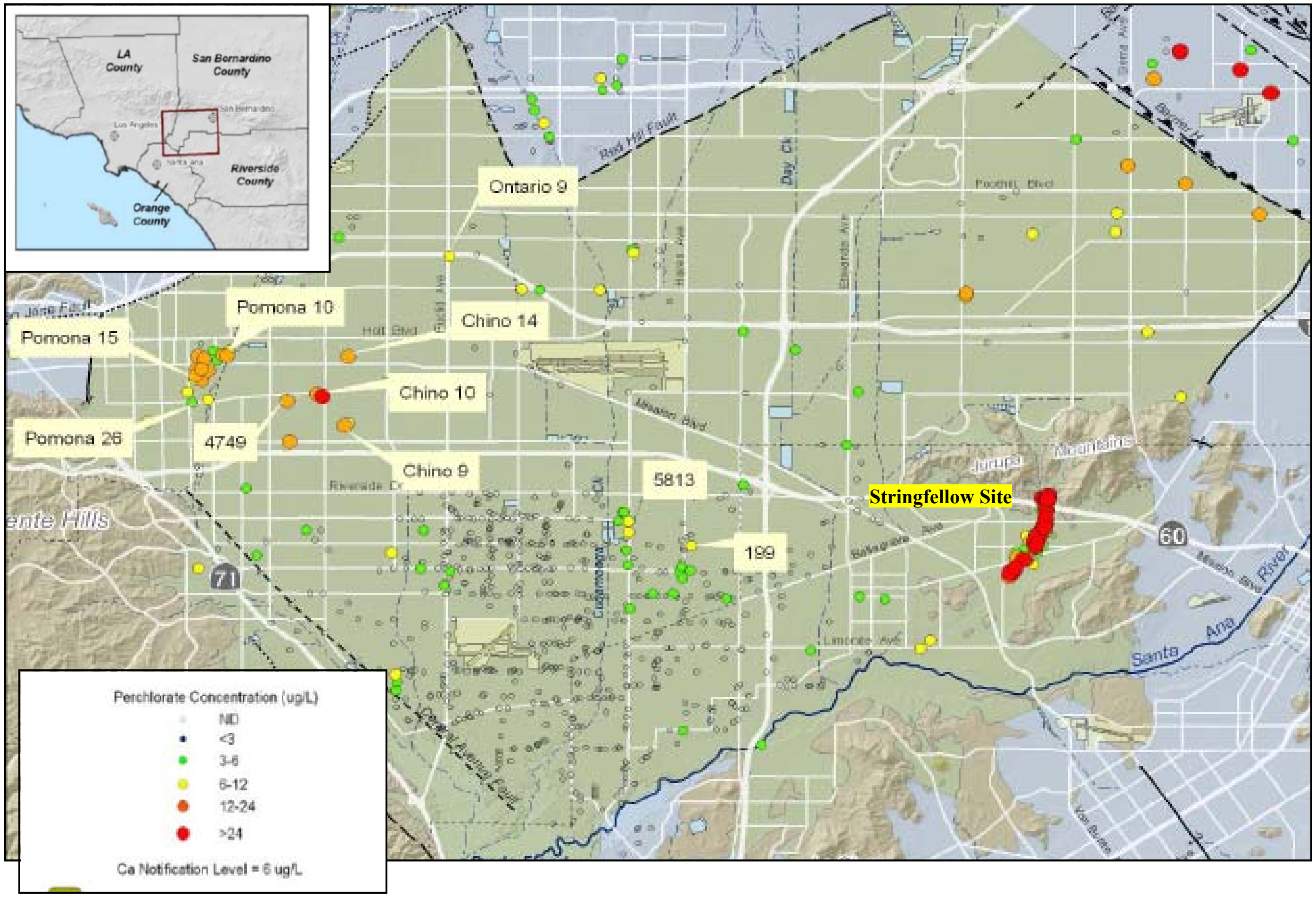


Figure 7.10. Land use map of the Chino Basin circa 1949. Figure modified from Sturchio et al., 2008.

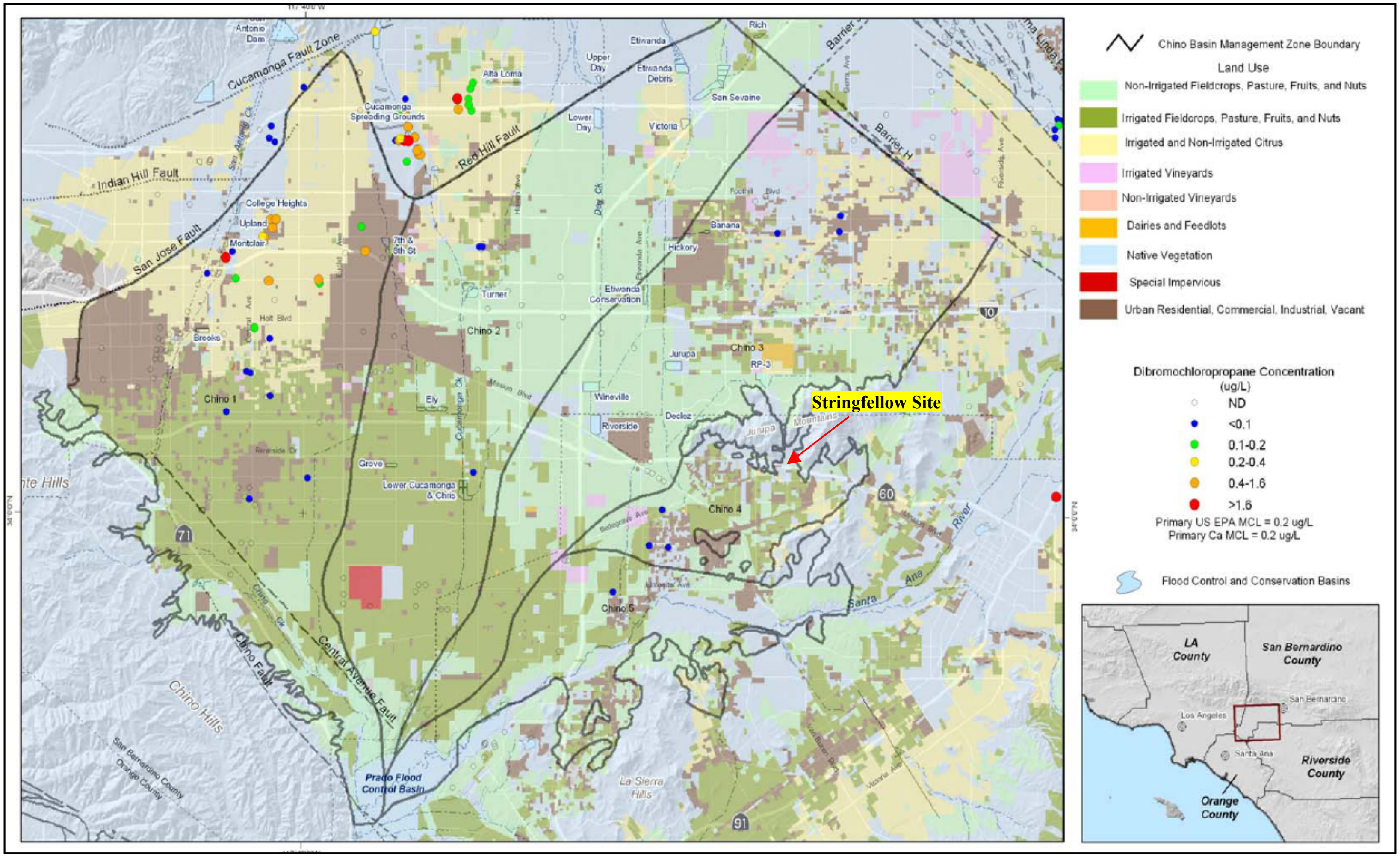
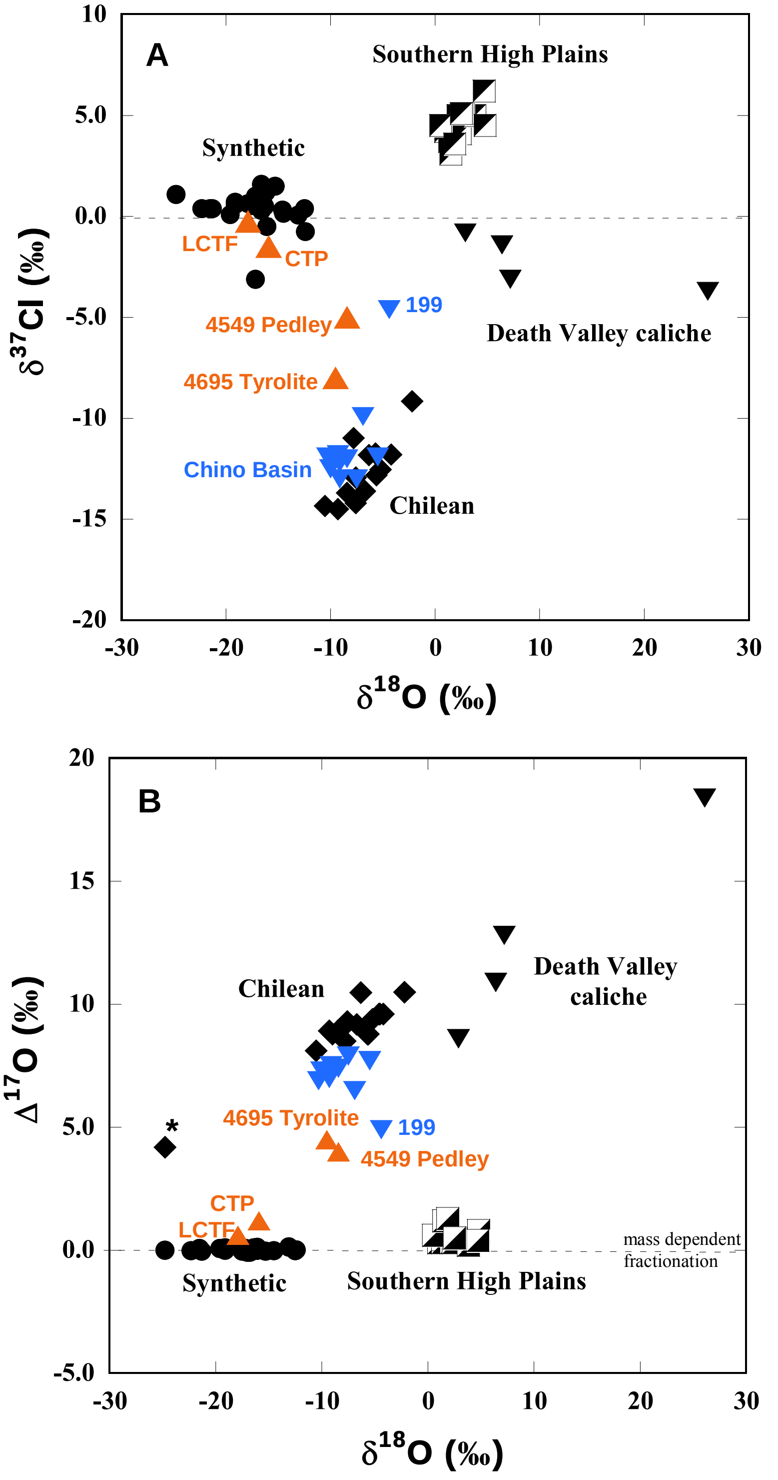


Figure 7.11. Comparison of δ^{37}Cl versus δ^{18}O (Plot A) and Δ^{17}O versus δ^{18}O (Plot B) of Stringfellow samples (orange symbols), Chino CA samples (blue symbols) compared to natural indigenous ClO_4^- in the U.S. (Southern High Plains and Death Valley caliche), natural Chilean ClO_4^-, and synthetic ClO_4^-.



7.3. University of Massachusetts, Dartmouth, Fireworks Display

7.3.1 Background

The Massachusetts Department of Environmental Protection (MADEP) conducted a study beginning in 2004 to assess the potential impact of a community fireworks display on soil and groundwater ClO_4^- concentrations. The study was conducted at the University of Massachusetts Dartmouth (UMD) campus at a location that hosted yearly fireworks displays beginning in 1995 (with the exception of 2003). As part of their research, MADEP installed eight groundwater wells in the vicinity of the fireworks display, and monitored those wells for ClO_4^- and other parameters on 10 separate occasions from 2004-2006. The complete results of this study are available online (http://www.mass.gov/dep/cleanup/sites/umdrep.pdf). Our research group collected samples and performed stable isotope analysis of ClO_4^- in two of the UMD monitoring wells to evaluate the isotopic characteristics of fireworks-derived ClO_4^- in groundwater. This study was performed in collaboration with SERDP Project ER-1429 "Evaluation of Alternate Causes of Widespread, Low Concentration Perchlorate Impacts to Groundwater" (Evan Cox, PI; Geosyntec, 2008).

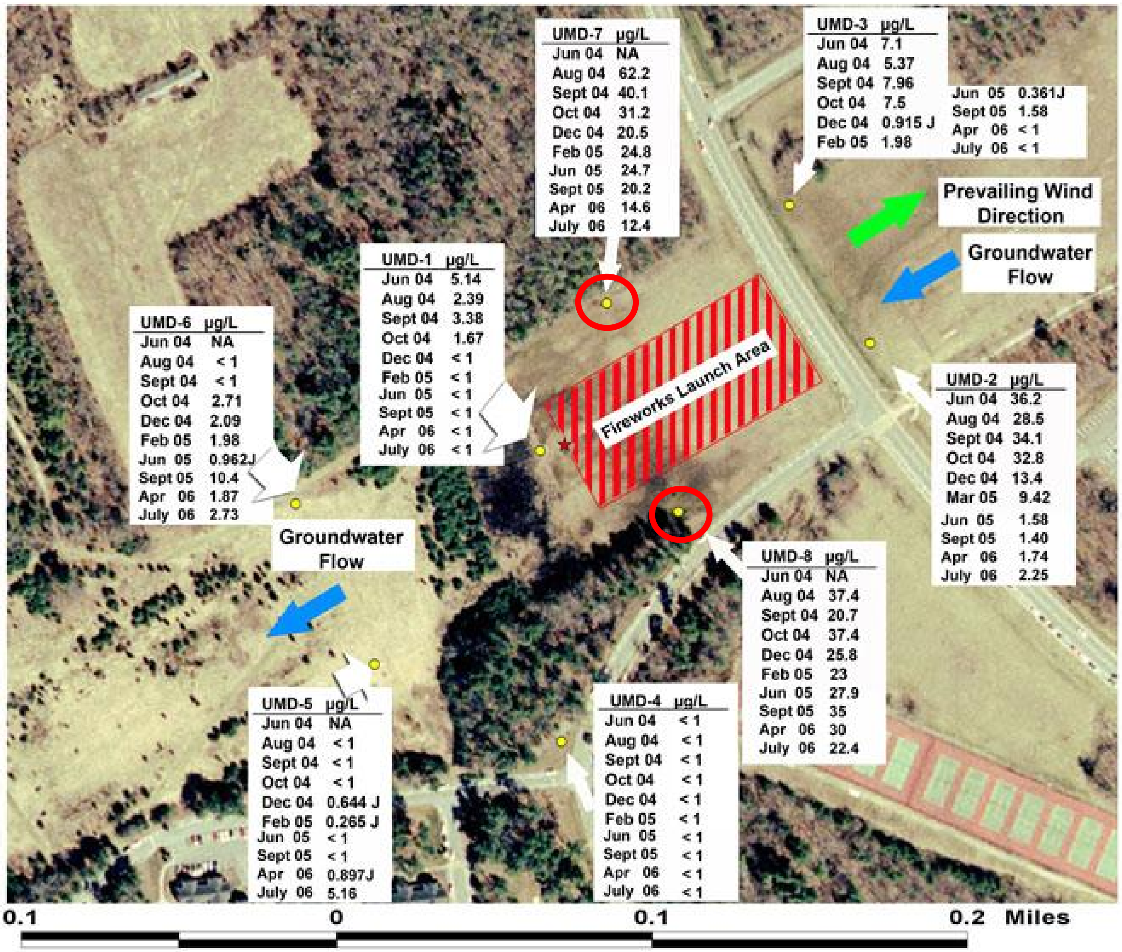
7.3.2 Sample Collection

Low-flow sampling was performed at each of the eight wells at the UMD site prior to stable isotope sampling. The locations of the wells in relation to the fireworks display area, and the historical concentrations of ClO_4^- in these wells, are shown in Figure 7.12. Once field parameters at each well were stable, groundwater samples were collected for analysis of ClO_4^-, anions, and cations/metals (filtered). The low-flow sampling was performed in conjunction with Robin Swift of Geosyntec Consultants as part of SERDP Project ER-1429. Soil sampling also was conducted for this SERDP project (Geosyntec, 2008).

Once the low-flow sampling was complete, and samples for cations and anions were collected, groundwater was passed through small glass columns (13 cm length x 2.2 cm diam.; Ace Glass) containing ClO_4^--selective ion exchange resin (Purolite A-530E). A 5-um pore size cartridge filter (Pall-Gelman) was used prior to the resin column to remove sediment form the groundwater, as both wells were slightly turbid. For Well UMD-7, which had a ClO_4^- concentration of ~ 9.9 µg/L at sampling (Shaw analysis of column influent), 340 L of water was passed through the sampling column at a flow rate of ~ 600 mL/min. For Well UMD-8 (ClO_4^- concentration of ~ 18.9 µg/L), duplicate columns were collected. A total of ~ 300 L of groundwater was passed through Column UMD-8a and ~ 227 L was passed through Column UMD-8b. The flow rate to the columns was ~ 450 mL/min. The resin columns were preserved in the field by adding 0.05 N HCl to reduce pH to < 2.0. The extraction, purification, and stable isotope analysis of ClO_4^- from the columns was conducted as described previously in Section 5.

Two small cardboard pouches filled with powder (termed "charges" throughout) were collected at the surface of the site at separate locations. These charges presumably were present within the aerial fireworks, but did not detonate during the display. A partially buried road flare also was found at the surface of the site, and samples of the powder within the flare were collected. The powder within the fireworks charges and the road flare was dissolved in laboratory DI water (10 mg/mL), and the ClO_4^- and anion concentrations were measured (Shaw Environmental, Inc). Cations also were measured on the powdered materials by Alpha Woods Hole Lab, Westminster, MA. The samples from both of the fireworks charges and the road flare were purified and analyzed for ClO_4^- stable isotopes described previously in Section 5.

Figure 7.12. Groundwater wells at the UMD fireworks site. The historical ClO_4^- concentrations in each well are provided. The wells sampled for ClO_4^- stable isotope analysis are indicated with a red circle. The map is modified from MADEP, (2007)



UMD-7	μg/L
Jun 04	NA
Aug 04	62.2
Sept 04	40.1
Oct 04	31.2
Dec 04	20.5
Feb 05	24.8
Jun 05	24.7
Sept 05	20.2
Apr 06	14.6
July 06	12.4

UMD-3	μg/L
Jun 04	7.1
Aug 04	5.37
Sept 04	7.96
Oct 04	7.5
Dec 04	0.915 J
Feb 05	1.98
Jun 05	0.361J
Sept 05	1.58
Apr 06	< 1
July 06	< 1

UMD-1	μg/L
Jun 04	5.14
Aug 04	2.39
Sept 04	3.38
Oct 04	1.67
Dec 04	< 1
Feb 05	< 1
Jun 05	< 1
Sept 05	< 1
Apr 06	< 1
July 06	< 1

UMD-6	μg/L
Jun 04	NA
Aug 04	< 1
Sept 04	< 1
Oct 04	2.71
Dec 04	2.09
Feb 05	1.98
Jun 05	0.962J
Sept 05	10.4
Apr 06	1.87
July 06	2.73

UMD-2	μg/L
Jun 04	36.2
Aug 04	28.5
Sept 04	34.1
Oct 04	32.8
Dec 04	13.4
Mar 05	9.42
Jun 05	1.58
Sept 05	1.40
Apr 06	1.74
July 06	2.25

UMD-8	μg/L
Jun 04	NA
Aug 04	37.4
Sept 04	20.7
Oct 04	37.4
Dec 04	25.8
Feb 05	23
Jun 05	27.9
Sept 05	35
Apr 06	30
July 06	22.4

UMD-5	μg/L
Jun 04	NA
Aug 04	< 1
Sept 04	< 1
Oct 04	< 1
Dec 04	0.644 J
Feb 05	0.265 J
Jun 05	< 1
Sept 05	< 1
Apr 06	0.897J
July 06	5.16

UMD-4	μg/L
Jun 04	< 1
Aug 04	< 1
Sept 04	< 1
Oct 04	< 1
Dec 04	< 1
Feb 05	< 1
Jun 05	< 1
Sept 05	< 1
Apr 06	< 1
July 06	< 1

7.3.3 Results and Discussion

The two uncombusted fireworks charges obtained at the UMD location each contained appreciable quantities of ClO_4^- (389,000 and 355,000 mg/kg, respectively), as well as Al, Mg, and K, each of which were > 70,000 mg/kg (Table 7.2). The quantity of ClO_4^- in the road flare, which was partially buried at the site, was not determined before stable isotope ratio analysis, but ClO_4^- concentrations on the order of 50,000 mg/kg have been reported for safety flares (Aziz et al., 2006). The road flare also had much higher concentrations of Ca and Sr compared to the fireworks, and lower concentrations of Al and Mg. Further details on the composition of fireworks and flares and potential correlations between cations and ClO_4^- in soils the UMD site can be found in the final report for SERDP Project

ER-1429 (Geosyntec, 2008; http://www.serdp.org/Program-Areas/Environmental-Restoration/ Contaminated-Groundwater/Emerging-Issues/ER-1429).

Four of the wells at the site were characterized by anoxic groundwater, and each had a negative ORP value, ranging from -29 to -102 mV at the time of sample collection (Table 7.4). These wells also were characterized by high concentrations of dissolved Fe (> 20 mg/L), consistent with reducing conditions. ClO_4^- was detected in Well UMD-3 at a trace concentration (0.3 μg/L) but was < 0.5 μg/L in the other three anoxic wells. Any ClO_4^- entering groundwater near these wells would likely be subject to rapid biodegradation under the geochemical conditions present. In contrast, the other 4 wells at the UMD site had ORP values exceeding +200 mV and DO exceeding 6.8 mg/L. ClO_4^- was present in each of these wells, with the highest concentrations being in UMD-7 and UMD-8, the wells selected for stable isotope sampling.

The $\delta^{18}O$, $\delta^{37}Cl$ and $\Delta^{17}O$ values for ClO_4^- collected from the UMD-7 and UMD-8 wells, as well as from the fireworks charges and road flare found onsite are presented in Figure 7.13 and in Table 7.3. Stable isotope values for a commercial flare (Orion) and a commercial firework, each of which were purchased in TN, are also shown on Figure 7.13. Analysis of ^{36}Cl was not performed for these samples, as they were collected prior to initiating this work. The stable isotope data from wells UMD-7 and UMD-8 are completely consistent with all of the synthetic sources measured to date, having $\delta^{37}Cl$ and $\Delta^{17}O$ values near 0, and $\delta^{18}O$ values of ~ -17 ‰. The $\delta^{18}O$ of the ClO_4^- collected from the two wells was marginally heavier than that from the two fireworks charges (~ 2 ‰), but very near that of another commercial fireworks sample analyzed for the project (Figure 7.13). The sample was marginally lighter (~ 4 ‰) than that from the road flare. Because of the inherent variability in $\delta^{18}O$ among synthetic samples, and the very limited dataset, it is not possible to differentiate whether the ClO_4^- in the groundwater was flare or fireworks derived, but the data are consistent with either of these sources or a mixture of both.

Table 7.2. Cations and Anions in the Fireworks Charges and Road Flare Sample Collected from the UMD Fireworks Site.

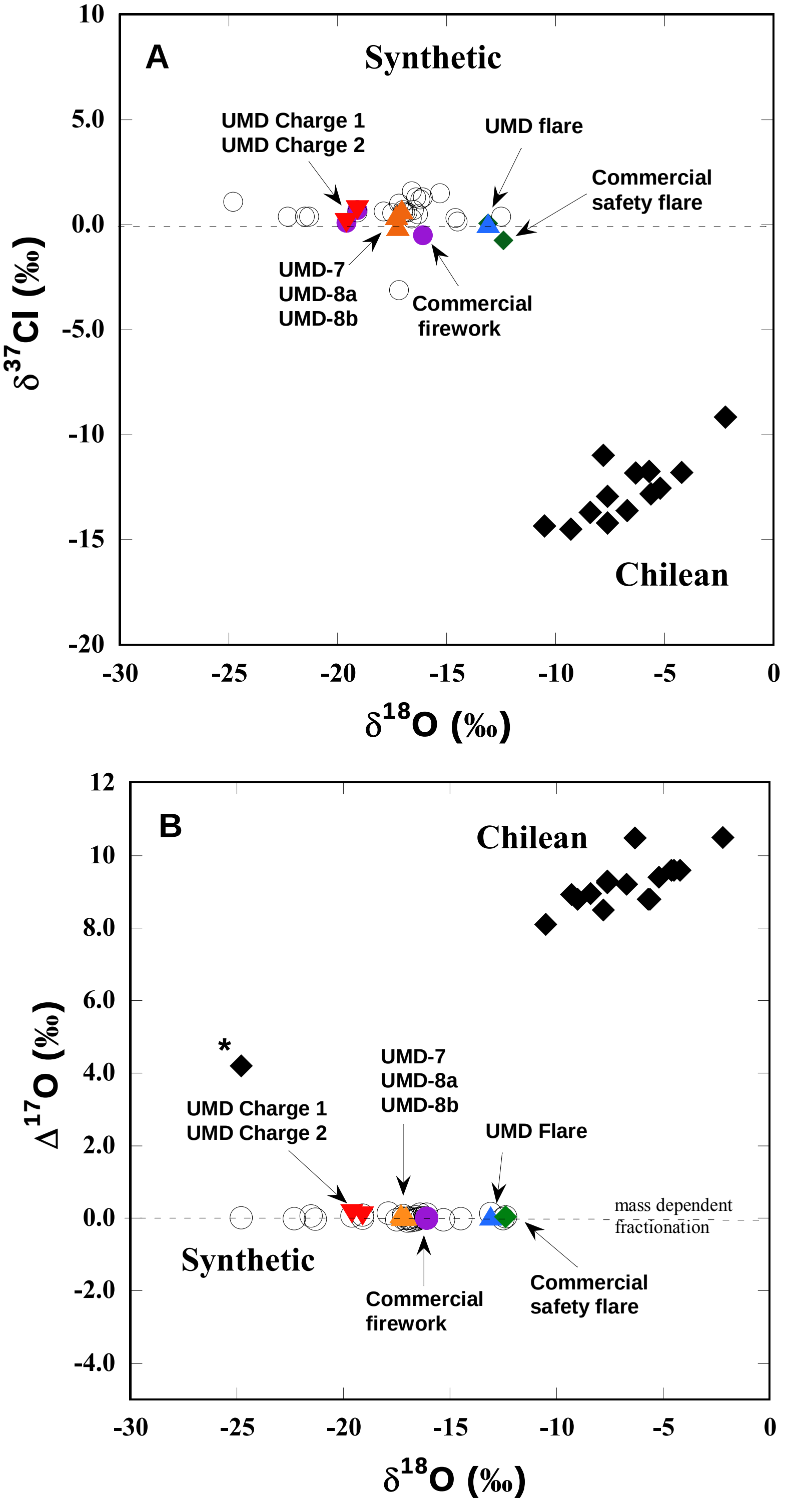
Analyte	Fireworks Charge 1 mg/kg	Fireworks Charge 2 mg/kg	Road Flare mg/kg
Aluminum	77000	120000	50
Antimony	1.2	1.2	1.2
Arsenic	1.2	1.2	1.2
Barium	440	190	4200
Beryllium	0.50	0.50	0.50
Cadmium	0.76	1.0	0.50
Calcium	1700	720	55000
Chromium	61	94	12
Cobalt	0.50	0.50	0.50
Copper	110	170	2.0
Iron	540	680	250
Lead	6.0	7.6	1.2
Magnesium	80000	120000	25
Manganese	350	490	5.0
Nickel	3.9	5.5	1.2
Potassium	160000	160000	18000
Selenium	5.0	5.0	5.0
Silver	0.50	0.50	0.50
Sodium	120	150	140
Strontium	18	22	210000
Thallium	0.25	0.25	0.25
Vanadium	12	12	12
Zinc	180	260	25
Perchlorate	389000	355000	NA
Nitrate	16	273	NA
Chlorate	18800	12100	NA

NA – data not available.

Table 7.3. Stable Isotope Values ($\delta^{18}O$, $\delta^{37}Cl$ and $\Delta^{17}O$) for ClO_4^- Samples Collected at the UMD Fireworks Site.

Sample	$\delta^{37}Cl$	$\delta^{18}O$	$\Delta^{17}O$
UMD-7	+0.73	-17.06	+0.06
UMD-8a	-0.07	-17.23	+0.05
UMD-8b	+0.47	-17.30	+0.12
UMD Charge-1	+0.71	-19.44	+0.09
UMD Charge-2	+0.12	-20.07	+0.07
UMD Flare	+0.07	-13.41	+0.13

Figure 7.13. Comparison of δ^{37}Cl versus δ^{18}O (Plot A) and Δ^{17}O versus δ^{18}O (Plot B) of UMD groundwater samples (orange symbols), UMD fireworks charges (red symbols), UMD safety flare (blue symbol), a commercial fireworks sample (purple symbol) and a commercial safety flare sample (green symbol) with natural Chilean ClO_4^-, and synthetic ClO_4^-.



Among the eight wells at the site, UMD-7 and UMD-8 had the highest concentrations of ClO_4^- as previously discussed. These two wells also had elevated concentrations of some of the trace metals/cations typically associated with fireworks (See Table 7.2), including Sr (> 300 μg/L), Ba (> 85 μg/L), Rb (> 17 μg /L), as well as the more common cations, Ca, Na, Mg, and K (Table 7.4). Well UMD-3, while not having detectable ClO_4^-, presumably due to the low ORP in the well (i.e., the ClO_4^- biodegraded), also had elevated levels of many of these trace metals/cations. Correlations between ClO_4^- and the various elements cited above are complicated by the fact that four of the wells at the site were anoxic. However, the data do suggest that, at least under oxic conditions, several of the metals and cations commonly found in fireworks can be expected to co-contaminate groundwater that has been impacted by ClO_4^- from this source. These results confirm some of the data from the former BOMARC site on Long Island that also was sampled during this project, in which anomalously high concentrations of Sr, Sb and K were observed in groundwater which was contaminated with high concentrations of ClO_4^- via a fireworks disposal area (Bohlke et al., 2009).

Table 7.4. ClO_4^-, NO_3^-, DO, ORP and Cations in Wells at the UMD Fireworks Site.

Well ID	ClO_4^- µg/L	NO_3^--N µg/L	ORP mV	DO mg/L	Ca mg/L	Na mg/L	Mg mg/L	K mg/L	Si mg/L	Sr mg/L	Al mg/L	Fe mg/L	Mn mg/L	B mg/L	Ag mg/L
UMD-1A	< 0.5	< 0.1	-102	0.5	10.4	12.9	4.46	2.3	7.53	0.107	0.003	22.1	1.69	<0.02	<0.05
UMD-2A	5.0	0.2	-64	1.1	6.6	5.67	2.46	1.8	5.34	0.073	<0.001	25.1	1.07	<0.02	<0.05
UMD-3A	< 0.5	< 0.1	-77	0.7	28.9	59.5	9.71	3.5	4.52	0.366	<0.001	22.9	0.60	<0.02	<0.05
UMD-4A	< 0.5	< 0.1	-29	0.5	4.42	13.2	3.64	0.8	4.89	0.034	0.163	22.8	0.20	<0.02	<0.05
UMD-5A	4.8	< 0.1	+267	7.8	2.94	4.43	0.70	0.5	2.19	0.011	0.073	<0.02	0.07	<0.02	<0.05
UMD-6A	2.5	< 0.1	+290	8.7	0.37	4.70	0.55	0.5	3.03	0.006	0.407	<0.02	0.03	<0.02	<0.05
UMD-7A	9.9	0.3	+223	6.8	56.7	95.9	21.4	5.7	7.86	0.474	0.081	<0.02	0.04	<0.02	0.06
UMD-8A	18.9	0.3	+204	7.1	31.0	99.9	12.5	5.8	8.52	0.308	0.015	0.04	0.06	<0.02	<0.05

Anions were measured by IC at Shaw.
Cations were measured by ICP-MS at USGS.
DO and ORP were taken from a field meter by Robin Swift, Geosyntec.

Table 7.4. ClO_4^-, NO_3^-, DO, ORP and Cations in Wells at the UMD Fireworks Site (continued)

Well ID	As µg/L	Ba µg/L	Cd µg/L	Co µg/L	Cu µg/L	Li µg/L	Mo µg/L	Ni µg/L	Pb µg/L	Rb µg/L	Sb µg/L	Se µg/L	U µg/L	V µg/L	Zn µg/L
UMD-1A	0.2	47.9	<0.05	2.4	<0.1	<0.001	0.4	1.7	<0.05	7.5	<0.1	<1	<0.05	0.3	<1
UMD-2A	<0.1	56.5	<0.05	0.90	<0.1	0.003	0.6	2.1	<0.05	3.8	<0.1	<1	<0.05	0.3	<1
UMD-3A	0.2	113	<0.05	1.1	<0.1	0.001	0.4	1.5	<0.05	11.7	<0.1	<1	<0.05	0.2	<1
UMD-4A	0.2	18.6	<0.05	2.2	0.3	<0.001	0.2	2.8	<0.05	2.6	<0.1	<1	0.18	0.6	2
UMD-5A	<0.1	5.3	<0.05	0.10	0.4	<0.001	<0.1	0.3	<0.05	0.8	<0.1	<1	0.08	0.2	<1
UMD-6A	<0.1	7.4	0.05	0.90	0.3	<0.001	<0.1	1.3	<0.05	0.9	<0.1	<1	0.08	0.1	1
UMD-7A	<0.1	118	0.09	0.28	0.3	0.003	<0.1	1.7	<0.05	17.6	<0.1	<1	<0.05	0.1	2
UMD-8A	<0.1	86.6	0.07	0.30	0.6	0.002	<0.1	1.8	<0.05	20.1	<0.1	<1	<0.05	0.2	53

Anions were measured by IC at Shaw.
Cations were measured by ICP-MS at USGS.
DO and ORP were taken from a field meter by Robin Swift, Geosyntec.

7.4 Lower Umatilla Basin, OR

7.4.1 Introduction

The detection of elevated NO_3^- concentrations in groundwater over a large area of the Lower Umatilla Basin of Northeastern Oregon led to the establishment of a 352,000 acre Groundwater Management Area (GWMA) by the Oregon Department of Environmental Quality (DEQ) in 1990 (Oregon DEQ, 2006) (Figure 7.14). An investigation was conducted by DEQ in 1992 in which 207 wells in the GWMA were sampled and analyzed for NO_3^- and a variety of other geochemical parameters. Many of these wells were re-sampled in 2003 to determine whether NO_3^- concentrations had changed in the region during the previous decade. In addition to NO_3^- and various geochemical parameters, analysis of ClO_4^- was also conducted during the 2003 sampling event. Perchlorate was detected (1 to 25 μg/L) in 72 of the 133 wells (54 %) for which groundwater data were collected, with a mean concentration of 2.57 μg/L (Oregon DEQ, 2006). Moreover, ClO_4^- was observed over a wide area and in both shallow alluvial wells (64/119) and deeper basalt wells (6/11) (Figure 7.15).

The source(s) of ClO_4^- in the Lower Umatilla Basin are unknown. The study region is semi-arid (~ 22 cm rainfall per yr; Wozniak, 1995), highly agricultural, and extensively irrigated from the Columbia River. As such, the mobilization of natural “indigenous” ClO_4^- from vadose soils to groundwater is one possible explanation for the widespread occurrence. This scenario is similar to that observed in the SHP of West Texas, where widespread irrigation is hypothesized to have mobilized significant quantities of ClO_4^- from the unsaturated zone to groundwater (Jackson et al., 2004, 2005; Dasgupta et al., 2006; Rajagopalan et al., 2006; Rao et al., 2007). However, the GWMA also includes current and former military installations (Boardman Bombing Range, Cold Springs Bombing Range, Umatilla Chemical Depot) and a former Boeing rocket engine testing facility. Thus, the list of possible ClO_4^- sources includes natural deposits, Chilean nitrate fertilizer for agriculture, past military and aerospace activities, and bleach used to treat large-scale drip irrigation systems (Oregon DEQ, 2006). Road flares and fireworks should also not be ruled out as possible contributing factors.

Umatilla region hydrology is complex because of complicated geology, mixed land use, irrigation with both groundwater and surface water, local wastewater disposal, and many other factors. Groundwater flow is generally from S to N toward the Columbia River, but local patterns can deviate from this regional pattern (Frans et al., 2009; Kahle et al., 2011). Groundwater characteristics may or may not be related to local land use characteristics because (1) sampled groundwaters may be old and reflect past land use, and (2) samples collected below the water table are likely to have infiltrated and recharged some distance away from the sampling site.

7.4.2 Sampling Locations

The objective of our research was to select a subset of wells in the GWMA to analyze for ClO_4^- stable isotopes, $^{36}Cl/Cl$ ratios, and other supporting parameters in order to provide some insight into the contributing sources of ClO_4^- in the region. Our research team worked with Mr. Harry Craig from the US EPA, Mr. Phil Richerson from Oregon DEQ, and other individuals knowledgeable about the GWMA to compile a list of wells for sampling. Most of the wells sampled were screened in alluvial sediments that overlie the Columbia River Basalt Group (Wozniak, 1995). The alluvial sediments include sands, silts, and gravels deposited largely during the Pleistocene Epoch. The alluvial aquifer is a major source of private water for rural residents and of municipal water for several of the cities in the region, including Hermiston and Boardman. The alluvial aquifer is considered to be susceptible to contamination from surface activities because water readily passes through the unsaturated zone to the alluvium (Wozniak, 1995). Primary sources of recharge water include irrigation water, and leakage from canals, streams, and reservoirs; rainwater is only a minor source of groundwater recharge. A few of the wells were screened into the basalt or at the interface of the basalt and alluvium (termed "weathered basalt"). The groundwater flow in the Boardman-Umatilla area where most of our sampling was conducted is generally to the north, with discharge to the Columbia River (Wozniak, 1995). The depths and screen intervals of the sampled wells are provided in Table 7.5.

Eight wells were selected for stable isotope sampling. The well locations are provided in Figure 7.16 and photos of some of the sampling locations are provided in Figure 7.17. The selected wells include two near the active Area 11 landfill at the Umatilla Chemical Depot

(UMCD11-1 and UMCD11-7), formerly called the Umatilla Ordnance Depot, a military facility that dates back to World War II and includes a large number of bunkers for the storage of military munitions. These wells are present in rangeland, near munition bunkers, in a region that is not currently subject to irrigation. Three wells (POM-15, POM-13, and S1) were located north (POM-13 and S1) and northeast (POM-15) of the Boardman Bombing Range, an active US Navy facility. All three wells were near irrigated land. MW-20 was located on the Three Mile Canyon Farm, in a region that was actively planted to crops and watered via circle-pivot irrigation. There was also evidence of significant fertilization with manure in this location. BGW-001 also was located on the Three Mile Canyon Farm, but in an area adjacent to the former Boeing jet engine test facility, a site that is now used as a cattle yard and area for the composting of cattle manure. Groundwater in this area is contaminated with trichloroethene (TCE) from former activities at the Boeing site. The final well that was sampled, M&P Dairy, was present in rangeland, but in close proximity to an irrigation canal and large stands of irrigated hybrid poplar trees.

7.4.3. Groundwater Sampling and ClO_4^- Stable Isotope Analysis.

Groundwater samples were collected in June, 2007 using a portable submersible pump, with the exception of well S1, where a dedicated well pump was used. Groundwater from each well was passed through a flow cell, and specific geochemical parameters (oxidation-reduction potential, dissolved oxygen, specific conductance, temperature and pH) were measured with time using low-flow sampling as described previously in Section 5.2.1.2. When all parameters stabilized, samples were collected for various supporting parameters, including anions, cations, and H_2O and NO_3^- stable isotopes, as previously described in Table 5.1. Samples for ClO_4^- isotopic analysis were collected by pumping water through columns containing Purolite A530E anion exchange resin (~ 0.7 to 2.5 L/min) until an amount of water containing a total of 5-10 mg of ClO_4^- had passed through each column. The total volume of groundwater passed through each column ranged from ~ 300 L for the M&P Dairy well to ~ 1400 L for UMCD11-1. All columns were saturated with 0.05 N HCl and stored at 4^oC for preservation when ClO_4^- sample collection was complete.

The collected ClO_4^- was then extracted from the columns, purified, and analyzed as described previously in this chapter and in other references published by our group (Böhlke et al., 2005, 2009; Sturchio et al., 2006, 2007, 2011; Jackson et al., 2010; Hatzinger et al., 2011). Briefly, ClO_4^- was eluted from the resin columns, precipitated as $CsClO_4$, purified, and tested for purity at ORNL. Aliquots of $CsClO_4$ were reacted with C to produce CO for $\delta^{18}O$ analysis, and decomposed to produce O_2 for $\delta^{18}O$ and $\delta^{17}O$ analysis, at USGS in Reston, VA. CsCl from decomposition was converted to AgCl, and then reacted with CH_3I to produce CH_3Cl for $\delta^{37}Cl$ analysis at University of Illinois, Chicago (UIC). Some of the AgCl was doubly-purified and shipped to the PRIME laboratory at Purdue University for analysis of $^{36}Cl/Cl$ by AMS (Sturchio et al., 2009).

7.4.4 Supporting Parameters

Samples were collected for isotopic analysis of H_2O and NO_3^-, as well as major and minor element chemistry, major dissolved gases (Ar, N_2, O_2, and CH_4), and atmospheric environmental tracers (^3H, SF_6, and chlorofluorocarbons (CFCs) (See Table 5.1). These parameters are useful for estimating the timing of ClO_4^- infiltration and its relation to other natural and anthropogenic chemicals. Major anions (Cl^-, NO_3^-, SO_4^{2-}, and Br^-) were analyzed by ion chromatography following EPA Method 300.0. Major dissolved gases, stable isotope ratios in H_2O and NO_3^- (δ^2H, $\delta^{18}O$, and $\delta^{15}N$), CFCs and SF_6 were analyzed at the USGS in Reston, VA. Tritium was analyzed by electrolytic enrichment and scintillation counting at the USGS in Menlo Park, CA.

Figure 7.14. Map of the Lower Umatilla Basin Groundwater Management Area, OR, where sampling was conducted. Map from Oregon DEQ, 2006.

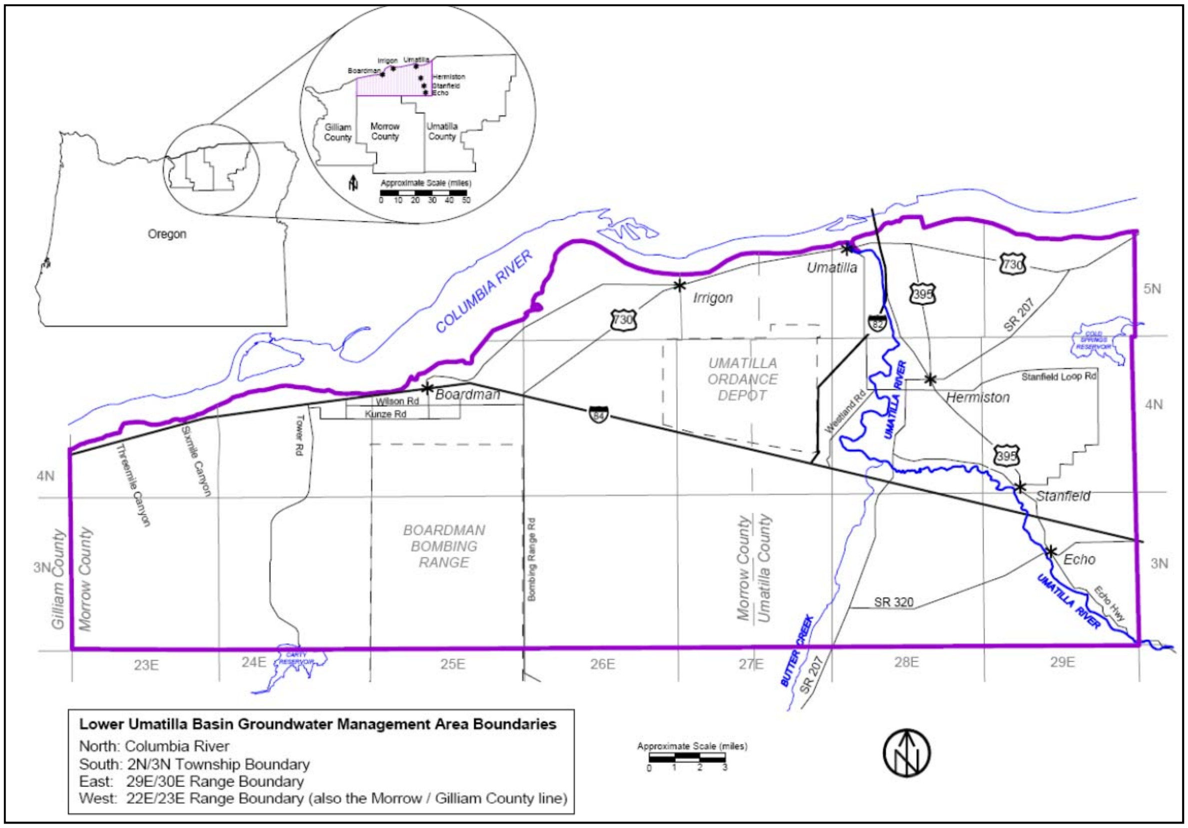


Figure 7.15. Perchlorate concentrations in groundwater wells in the Lower Umatilla Basin Groundwater Management Area, OR. Map from Oregon DEQ (2006).

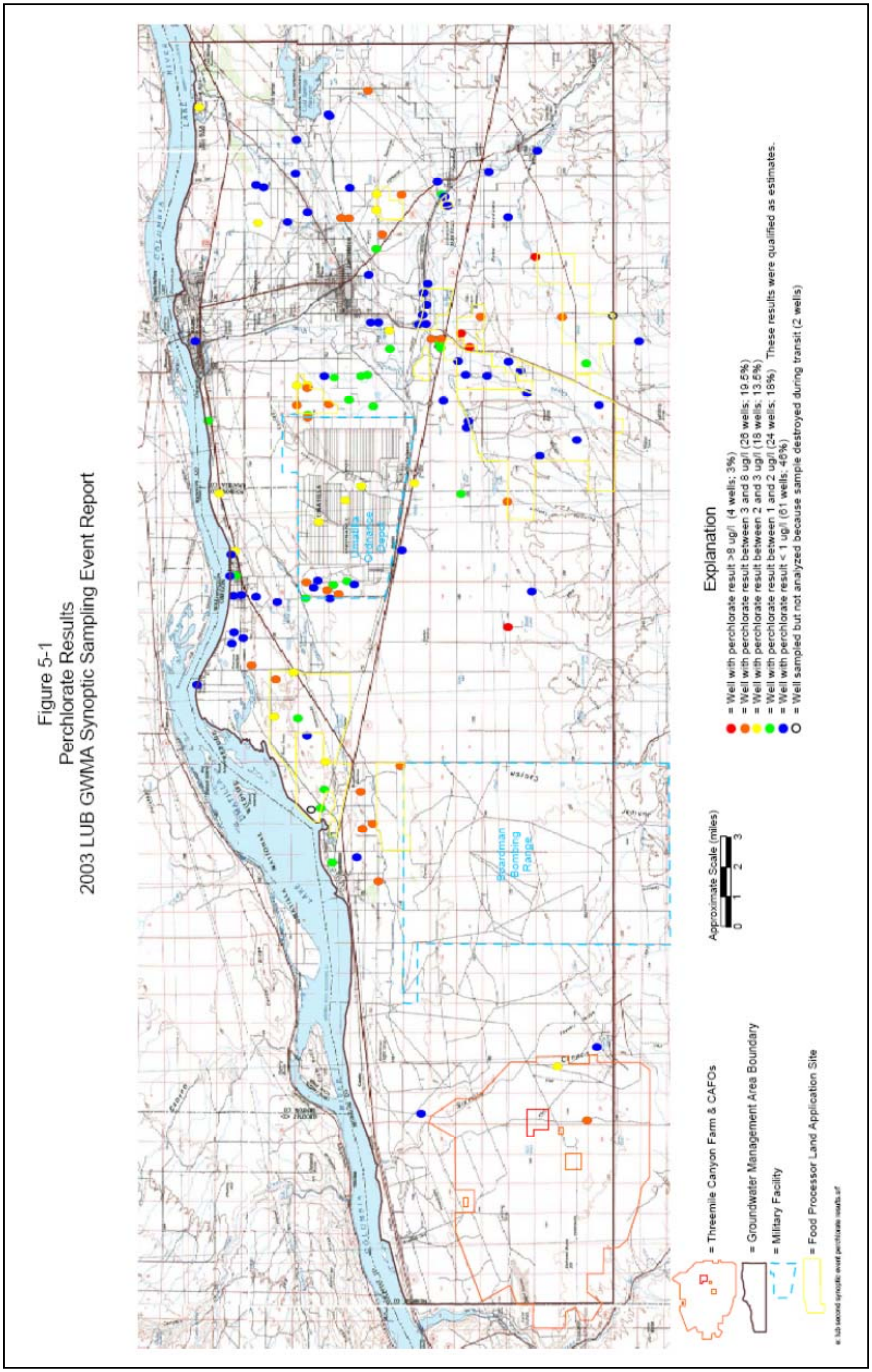


Figure 7.16. Location map of wells sampled for ClO_4^- isotope analysis in the Lower Umatilla Basin, OR.

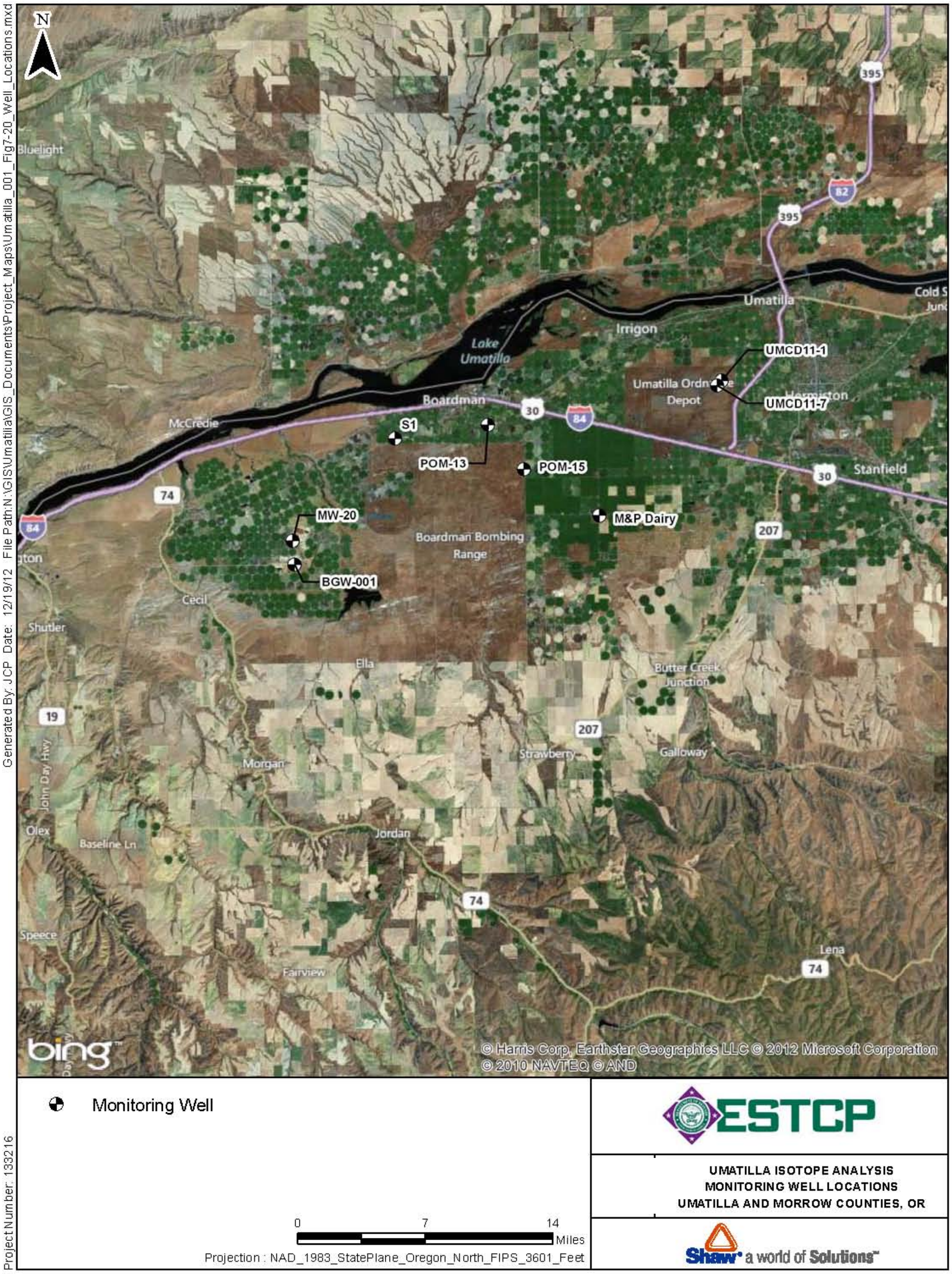


Figure 7.17. Photos of some of the Umatilla area sampling locations.

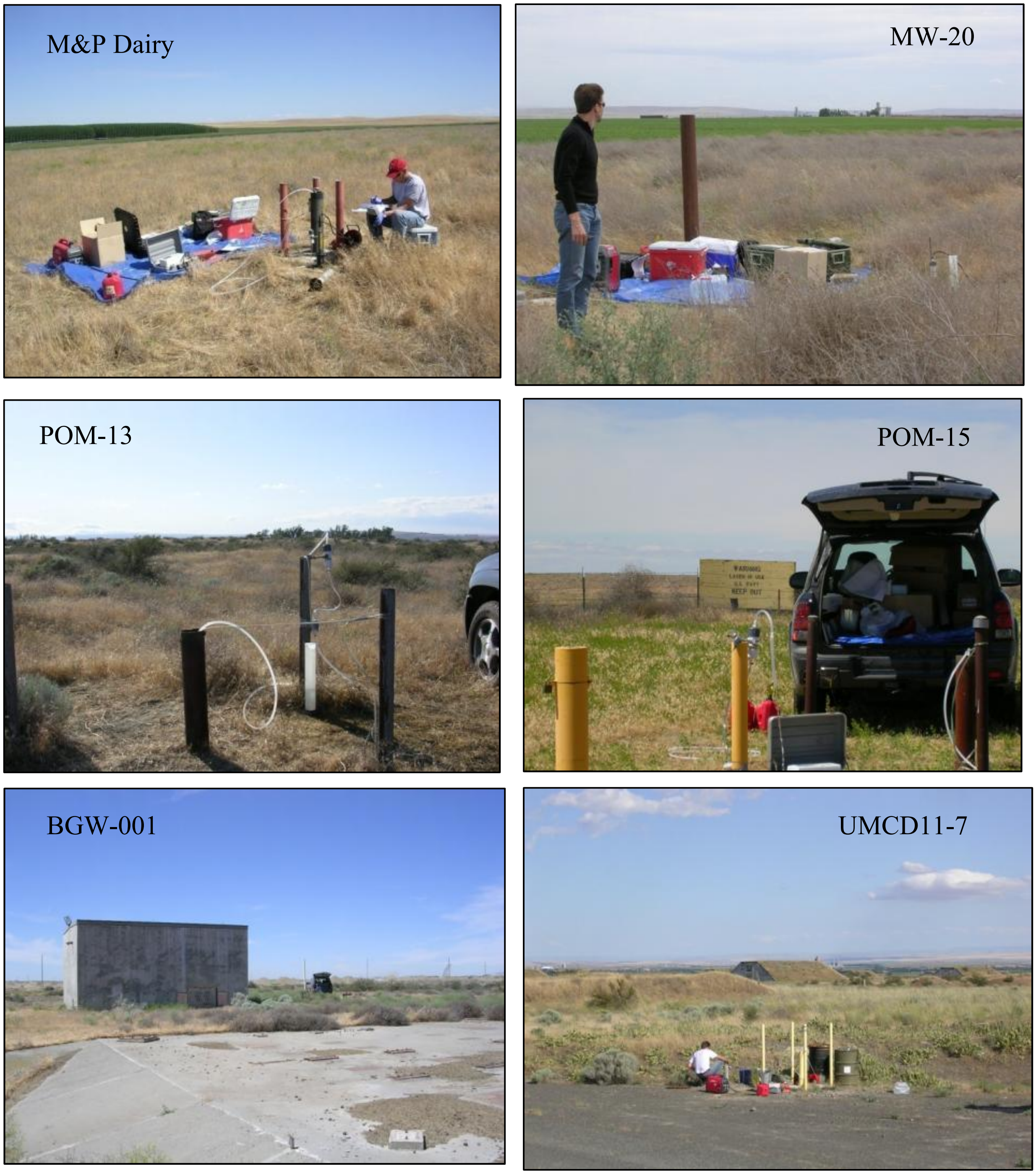


Table 7.5. Characteristics of Groundwater Wells sampled in the Lower Umatilla Basin Groundwater Management Area (GWMA).

Well ID	Latitude	Longitude	Land surface (ft)[1]	Groundwater elevation (ft bgs)	Screen depth (ft bgs)	Formation
POM-13	45.82027778	-119.6641667	389	30.2	48-58	Alluvium/ weathered Basalt
POM-15	45.7844659	-119.623979	477	53.6	75-85	Alluvium/ weathered Basalt
M&P Dairy	45.747227	-119.538720	633	75.3	84-94	Alluvium
UMCD11-1	45.853	-119.3981	657	140.3	156-166	Alluvium
UMCD11-7	45.8493	-119.4032	656	149	155-165	Alluvium
BGW-001	45.71078	-119.88516	613	19.5	18-28	Alluvium/ weathered basalt
MW-20	45.72972222	-119.8869444	607	6.9	19-29	Alluvium
S1	45.81019668	-119.76966408	380	NA	19-80	Basalt

7.4.5 Results and Discussion

7.4.5.1 Geochemical Conditions

The groundwater sampled during this project was oxic with dissolved oxygen concentrations ranging from 7.5 to 9.9 mg/L and oxidation-reduction potentials (ORP) ranging from +22.2 to + 101.9 mV (Table 7.6). Groundwater pH was neutral (6.7 to 7.7). Concentrations of ClO_4^- at the time of sampling in June, 2007 varied from 3.8 μg/L in well MW-020 on Three Mile Canyon Farms to 34.7 μg/L in the M&P Dairy well. Seven of the eight wells sampled had NO_3^--N concentrations exceeding the Federal MCL of 10 mg/L, with 3 of those wells exceeding 30 mg/L. Sulfate concentrations varied from 31.8 to 118 mg/L and Cl^- varied from 24.3 to 186 mg/L.

7.4.5.2 Stable Isotopic Composition of Cl and O in ClO_4^-

Stable isotope data for ClO_4^- ($\delta^{18}O$, $\Delta^{17}O$, $\delta^{37}Cl$) were obtained for all eight wells (Figure 7.18 and Table 7.6). The ClO_4^- stable isotope data from three of the wells (M&P Dairy, BGW-001, MW-20) were similar to those from wells sampled in the Southern High Plains (SHP), as shown in Figure 7.18. An interesting difference is that the $\Delta^{17}O$ values of these three Umatilla samples (+1.7 to +2.9 ‰) were slightly higher than the SHP values (+0.2 to +1.3 ‰, including the Middle Rio Grande Basin; MRGB). It should be noted that the two MRGB samples (RR-8 and RR-16 in Appendix A; Table A-1) were the highest among all of the SHP samples, at +1.2 ‰ and +1.3 ‰, respectively. Additional discussion on the characteristics and stable isotope values of ClO_4^- from the SHP can be found in Jackson et al., (2010), which is included in Appendix C. The detection of natural indigenous ClO_4^- in arid northern Oregon expands the area over which this source of ClO_4^- has now been observed, and modifies slightly its range of isotopic characteristics.

Among the other wells sampled, UMCD11-1 and UMCD11-7 also appear to be composed largely of natural SHP-type ClO_4^-, possibly mixed with smaller amounts of synthetic ClO_4^-. The Port of Morrow Wells, POM-13 and POM-15, appear to be composed primarily of synthetic ClO_4^-, with relatively minor fractions of SHP-type ClO_4^-, based upon the $\delta^{18}O$, $\Delta^{17}O$ and $\delta^{37}Cl$ values. In contrast to the others, the sample from private well S1 appears to have a substantial component of Chilean-type ClO_4^-, combined with both synthetic and SHP-type ClO_4^-.

7.4.5.3 $^{36}Cl/Cl$ Results

In addition to $\delta^{18}O$, $\Delta^{17}O$ and $\delta^{37}Cl$, analysis of the long-lived radioactive isotope ^{36}Cl (half-life = 301,000 yrs) was conducted for all samples from Umatilla. As previously described in Sections 5.2.7 and 7.2.2, past studies by our group have revealed that the isotopic abundance of ^{36}Cl (generally reported as an atom or mole fraction as $^{36}Cl/Cl$) is significantly elevated in all natural indigenous samples of ClO_4^- thus far collected from the SHP and Death Valley regions, ranging from $3{,}130 \times 10^{-15}$ to $28{,}800 \times 10^{-15}$ (Appendix C; Sturchio et al., 2009). The elevated $^{36}Cl/Cl$ ratios are hypothesized to be the result of stratospheric formation of the ClO_4^-. By comparison, relatively low $^{36}Cl/Cl$ values were observed for both synthetic ClO_4^- ($^{36}Cl/Cl$ from 0×10^{-15} to 40×10^{-15}) and Chilean ClO_4^- ($^{36}Cl/Cl$ values from 22×10^{-15} to 590×10^{-15}), the former because it is synthesized electrochemically from Cl^- with a low ^{36}Cl abundance, and the latter presumably because this material is generally millions of years old, and therefore its initial ^{36}Cl has been lost through radioactive decay (Sturchio et al., 2009).

The data from the Umatilla site reveal elevated $^{36}Cl/Cl$ ratios in all of the samples collected (Table 7.6; Figure 7.19). Hypothetical mixing lines are presented in Figure 7.19, presuming $^{36}Cl/Cl$ and $\delta^{37}Cl$ endpoints of 31×10^{-15} and 1 ‰, respectively, for synthetic ClO_4^-, 236×10^{-15} and -12.7 ‰, respectively, for Chilean ClO_4^-, and $15{,}347 \times 10^{-15}$ and +3.7 ‰, respectively, for natural indigenous ClO_4^-. These end member values are representative of previously reported values for each of these sample types, but may or may not be appropriate for local end members. These curves are preliminary representations, and may be modified with further analysis of the data. High values of $^{36}Cl/Cl$ ratios were detected in the three samples that most closely resemble pure SHP-type ClO_4^- based upon all relevant stable isotope data. Slightly lower ratios were present in ClO_4^- obtained from wells UMCD11-7 and UMCD11-1, although the values still fell within the range of those previously observed for SHP and Death Valley ClO_4^-. Thus, based upon these data, the UMCD11-7 and UMCD11-1 samples could be purely SHP-type ClO_4^- (somewhat extending the stable isotopic range of this source) or, based on the hypothetical mixing calculations shown in Figure 7.19, they could be mixtures containing components of synthetic ClO_4^- and natural SHP-type ClO_4^-.

The $^{36}Cl/Cl$ ratio of ClO_4^- collected from private well S1 supports the interpretation that this sample contains indigenous natural ClO_4^- along with a Chilean component. Further analysis incorporating all four isotopic parameters simultaneously may refine these endmember assumptions and mixing percentages. For example, a higher $^{36}Cl/Cl$ ratio of the indigenous endmember could accommodate a possible synthetic component in S1 and increase the apparent fraction of synthetic component in the POM samples. Nevertheless, the general patterns indicate that all three major source types are present in varying amounts in this study area. The two wells for which the $^{36}Cl/Cl$ data are somewhat more difficult to interpret are POM-13 and POM-15. The stable isotope data suggest that these wells consist predominantly of synthetic ClO_4^- with some SHP-type mixed in, while the $^{36}Cl/Cl$ results suggest a higher % of SHP-type ClO_4^-. POM-15 is also offset appreciably from the theoretical mixing line between synthetic and indigenous natural ClO_4^-, because the $\delta^{37}Cl$ value is somewhat lower than expected.

The presence of small amounts of bomb-generated ^{36}Cl from nuclear tests in the mid 1950's (Phillips, 2000; Davis et al., 2003) might have contributed to some of the highest $^{36}Cl/Cl$ values in ClO_4^- from groundwater samples containing bomb-related tritium (e.g., POM-13 and POM-15). However, $^{36}Cl/Cl$ values as high as $8{,}400 \times 10^{-15}$ were measured in ClO_4^- from groundwater in New Mexico with recharge ages estimated at > 5,000 yr, so values like these apparently can occur in natural ClO_4^- that predates bomb testing (Plummer et al., 2006; Sturchio et al., 2009). A ^{36}Cl dataset and more detailed discussion was previously published by our group (Sturchio et al., 2009), and is provided in Appendix C.

7.4.5.4 Dissolved Gases, Recharge Conditions, Redox Status, and Age Data

Major dissolved gas analyses confirm all samples were highly oxygenated and there was no clear evidence of excess N_2 from denitrification. As NO_3^- reduction typically follows O_2 reduction and precedes or accompanies ClO_4^- reduction, these gas data indicate that the isotopic composition of ClO_4^- in the groundwater was not likely to have been altered by biodegradation. Three samples (POM-13, POM-15, and UMCD-11) gave estimated temperatures during recharge (air-water equilibrium) around 10-12 °C with small amounts of excess air (0.6-2.1 ccSTP/L), based on the unfractionated excess air model. One sample (MW-20) gave similar T (11 °C) but much higher concentration of excess air, whereas one sample (UMCD11-7) gave higher T with normal excess air. Some samples may have been degassed slightly, possibly during pumping (BGW-001, M&P Dairy).

Concentrations of tritium (^3H) ranged from 0 to 7 tritium units (TU). Four samples (MW-20, M&P Dairy, UMCD11-1, UMCD11-7) had ^3H concentrations less than the detection limit of around 0.5 TU (2 sigma), indicating meteoric water that precipitated before the era of nuclear-bomb testing (before 1950s). Three samples (POM-13, POM-15, S1) had ^3H around 3-7 TU, potentially consistent with values expected in post-bomb meteoric waters that precipitated since about the early 1980s in this region, allowing for uncertainty in the rate of increase of ^3H concentrations with distance from the Pacific Coast (Michel, 1989). One sample (BGW-1) had ^3H around 1 TU, possibly indicating a mixture of pre-bomb and post-bomb water.

Seven of the samples (minus S1) were analyzed for chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6) to determine possible ranges of recharge dates. Samples most likely to yield consistent age data by the methods applied are POM-13 and POM-15, which had post-bomb ^3H along with concentrations of CFCs and SF_6 indicating apparent recharge dates around the middle to late 1980s (POM-13) and middle 1970s to early 1980s (POM-15). Preliminary dispersion models fit to all the tracer data from POM-13 and POM-15 yielded mean ages of around 19 and 33 years, respectively, with dispersion parameters of around 0.2 using the TracerLPM program (Jurgens et al., 2012). Several samples with undetectable (pre-bomb) ^3H had measurable concentrations of CFCs and SF_6 indicating post-bomb exchange with air. Possible interpretations include: (1) Old groundwater (no ^3H) was used for irrigation and CFCs and SF_6 were incorporated during recharge and can be used to estimate post-bomb recharge dates. (2) Pre-bomb precipitation infiltrated slowly through the unsaturated zone before arriving at the water table, where CFCs and SF_6 were acquired during recharge. (3) Samples were recharged before bomb testing and variably contaminated by local non-atmospheric sources of CFCs and SF_6, such that recharge dates cannot be determined; this option might be supported by high levels of contamination by CFC-11 (trichlorofluoromethane) and CFC-12 (dichlorodifluoromethane) at UMCD11-1 and UMCD11-7, and possibly by excess SF6 at M&P Dairy. (4) Samples are mixtures dominated by old (pre-bomb) recharge with much smaller fractions of much younger recharge containing relatively high concentrations of CFCs and SF_6; this option probably cannot account for observations unless combined with some contamination. Assuming the first interpretation is correct, estimated apparent recharge dates for some of the low-^3H samples could be from the 1960s to 1970s (M&P Dairy), middle 1970s to middle 1980s (MW-20), and late 1970s to late 1980s (UMCD11-1, UMCD11-7, BGW-1). From these data, given local variability in sources of irrigation water, it is possible (though not proven) that all of the samples contained groundwater that recharged recently enough to contain ClO_4^- from any or all of the sources indicated by isotope data.

7.4.5.5 Isotopic Composition of Water and Nitrate

Hydrogen and oxygen isotope ratios (δ^2H and $\delta^{18}O$ values) of H_2O were measured in the samples to determine possible origins of the water in each well (Figure 7.20). According to Kahle et al., (2011), irrigation in the Umatilla basin uses a heterogeneously distributed mixture of groundwater and surface water, with mean annual fractions of around 72 % surface water and 28 % groundwater (1985-2007). Annual recharge from precipitation was estimated to be of the order of 0.2 to 1.0 inches, whereas recharge from irrigation return flow can be more than 20 inches locally. Old regional groundwaters in the Columbia Plateau aquifer system with low ^{14}C concentrations (0-20 pmc) commonly have relatively low $\delta^{18}O$ values (around -19 to -16 ‰) that may include Pleistocene (glacial-age) recharge, whereas “modern” groundwaters with relatively high ^{14}C values (80-120 pmc) may have generally higher $\delta^{18}O$ values around -17 to -13 ‰ (Kahle et al., 2011). Relatively low $\delta^{18}O$ values similar to the “Pleistocene” groundwater values also are characteristic of modern surface water in Columbia River and Snake River, with headwaters in areas of higher elevation and(or) latitude, whereas higher $\delta^{18}O$ values closer to the “modern” groundwater values have been reported from the Deschutes River, Yakima River, and John Day River, with headwaters closer to the Umatilla basin (Coplen and Kendall, 2000). Data from the Columbia, Snake, Deschutes, and Yakima Rivers plot along a hypothetical meteoric water line with d-excess (i.e., ^{2}H excess) value of around +7 ‰, consistent with regional precipitation values (Figure 7.20).

Wells sampled in the current study had relatively high δ^{18}O values ranging from about -14 to -12 ‰ and low d-excess values from about -7 to 0 ‰, significantly lower than likely local meteoric water lines (Figure 7.20). Among the wells, those with higher δ^{2}H and δ^{18}O values tend to have lower d-excess values. These data indicate the well waters may have been affected more or less by evaporation somewhere prior to recharge (e.g., in ponds, irrigation systems, etc.). The most evolved wells (i.e., furthest from the local meteoric mixing line or most evaporated) are MW-20, UMCD11-1, and UMCD11-7. The least evolved wells are BGW-1, M&P Dairy, and POM-15. These groundwaters apparently were not derived directly from the Columbia River without alteration, but they could represent partially evaporated Columbia River-type water or possibly evaporated Pleistocene groundwater. The sampled groundwater data are most like the John Day River data, which has summertime samples with relatively high δ^{18}O and low d-excess values and a slope in δ^{2}H vs. δ^{18}O similar to that of the groundwaters.

Nitrogen and oxygen isotope ratios (δ^{15}N and δ^{18}O) in NO_3^- were measured to determine if any of the wells had characteristics indicating distinctive sources or transformations of NO_3^-. The ranges of δ^{15}N and δ^{18}O values were not large and they are generally consistent with NO_3^- derived from nitrification of organic N (Table 7.6). There was no clear evidence of isotopic fractionation caused by NO_3^- reduction (e.g., denitrification). This is consistent with the highly oxygenated character of the samples, and it supports the interpretation that the isotopic composition of ClO_4^- was not altered substantially by biodegradation in the subsurface. Highest δ^{15}N and lowest δ^{18}O values were from UMCD11-7 and UMCD-11, in relatively highly evaporated water with no bomb tritium and moderately high NO_3^- concentrations. According to Frans et al., (2009), these samples may have been affected by wastewater irrigation northeast of the wells. Samples with the highest NO_3^- concentrations

(POM-13, POM-15, S1) had relatively low $\delta^{15}N$ values, like those commonly attributed to N fertilizer application.

Figure 7.18. Comparison of δ^{37}Cl versus δ^{18}O (Plot A) and Δ^{17}O versus δ^{18}O (Plot B) in ClO_4^- from groundwater samples (red symbols) with natural indigenous ClO_4^- of the US (Southern high Plains and Death Valley caliche), natural Chilean ClO_4^-, and synthetic ClO_4^-.

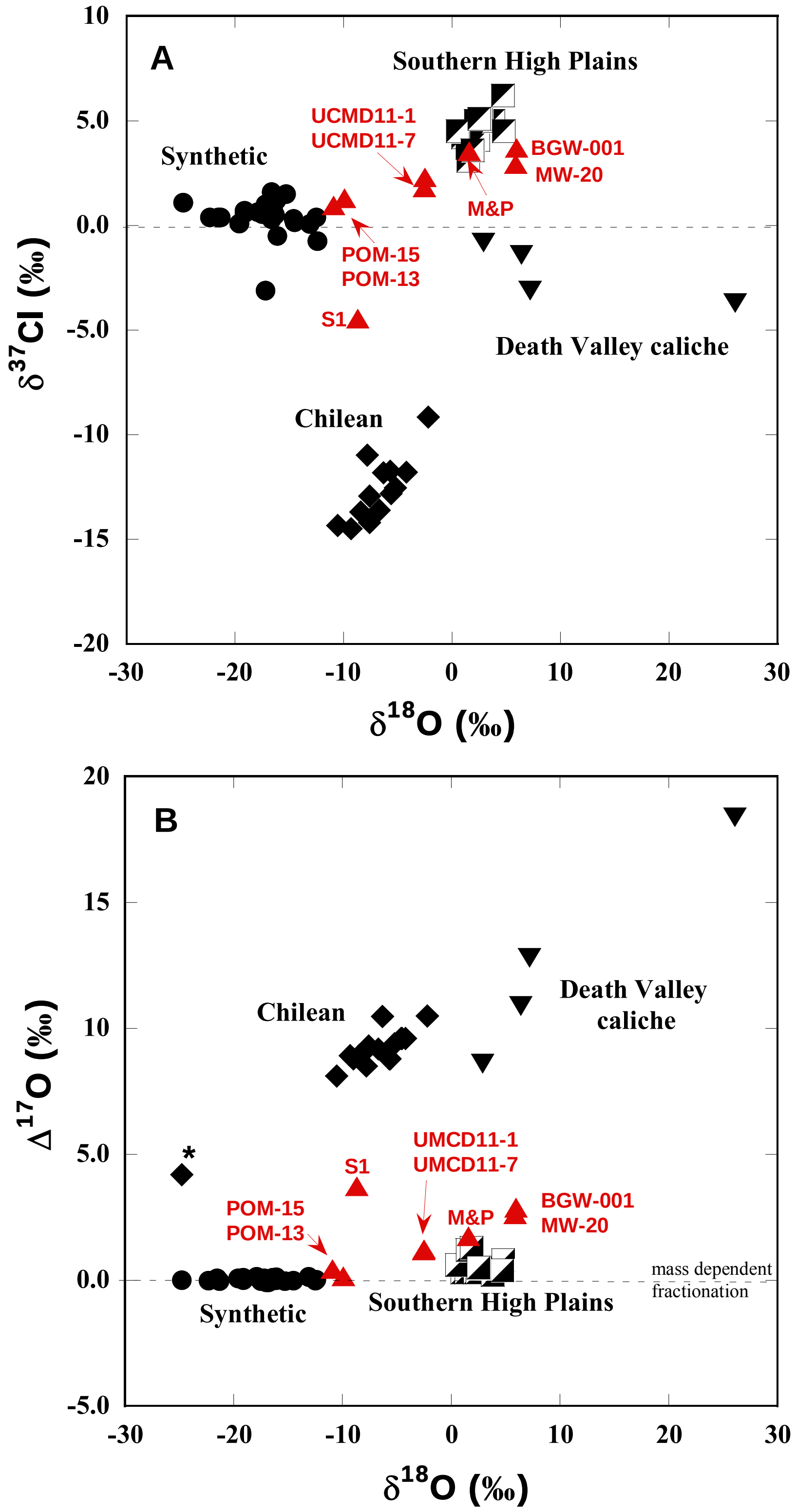


Figure 7.19. Comparison of ^{36}Cl/Cl versus δ^{37}Cl in ClO_4^- from Umatilla (red symbols) with natural indigenous ClO_4^- in the U.S. (Southern High Plains and Death Valley caliche), natural Chilean ClO_4^- and Cl^-,and synthetic ClO_4^-. Red curves indicate hypothetical mixtures between an endmember with relatively high ^{36}Cl/Cl (represented by BGW-001) and endmembers with either Chilean or synthetic isotopic characteristics. The first 10 hash marks on the mixing lines originating from the Chilean and synthetic endmembers represent 1% intervals and the following hash marks on each line are in 10% intervals.

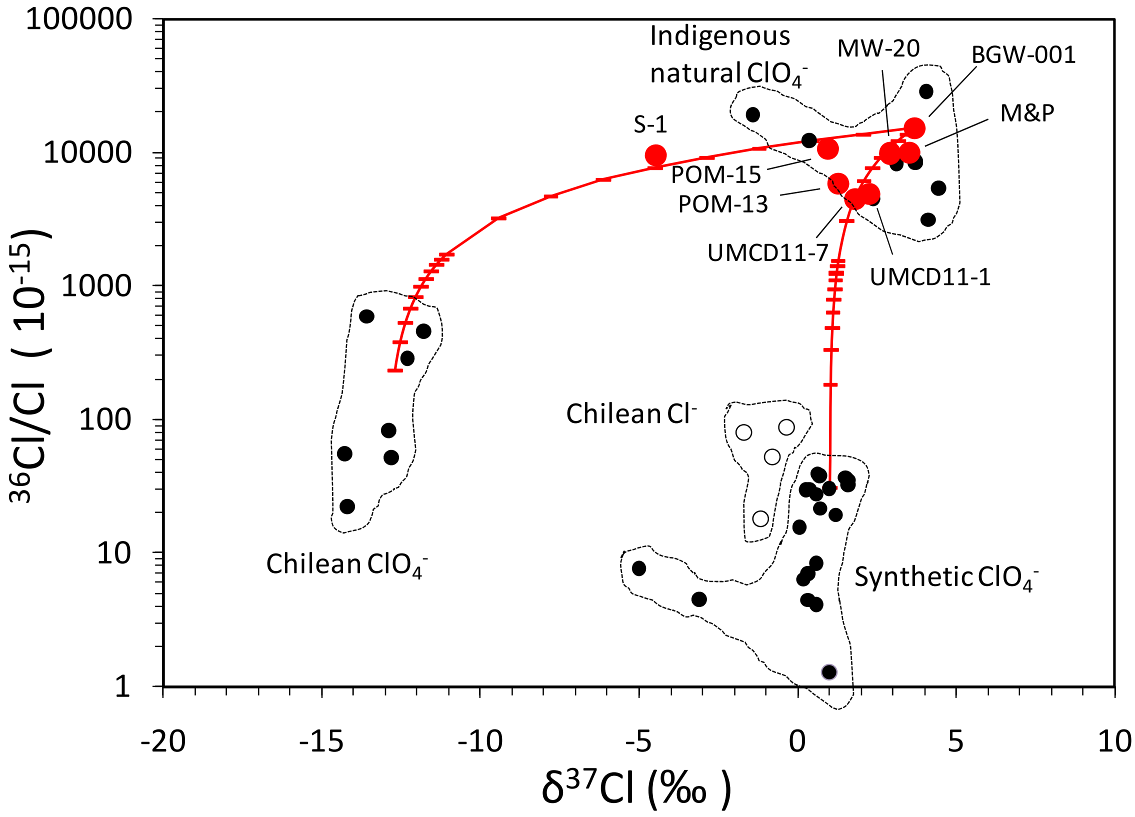
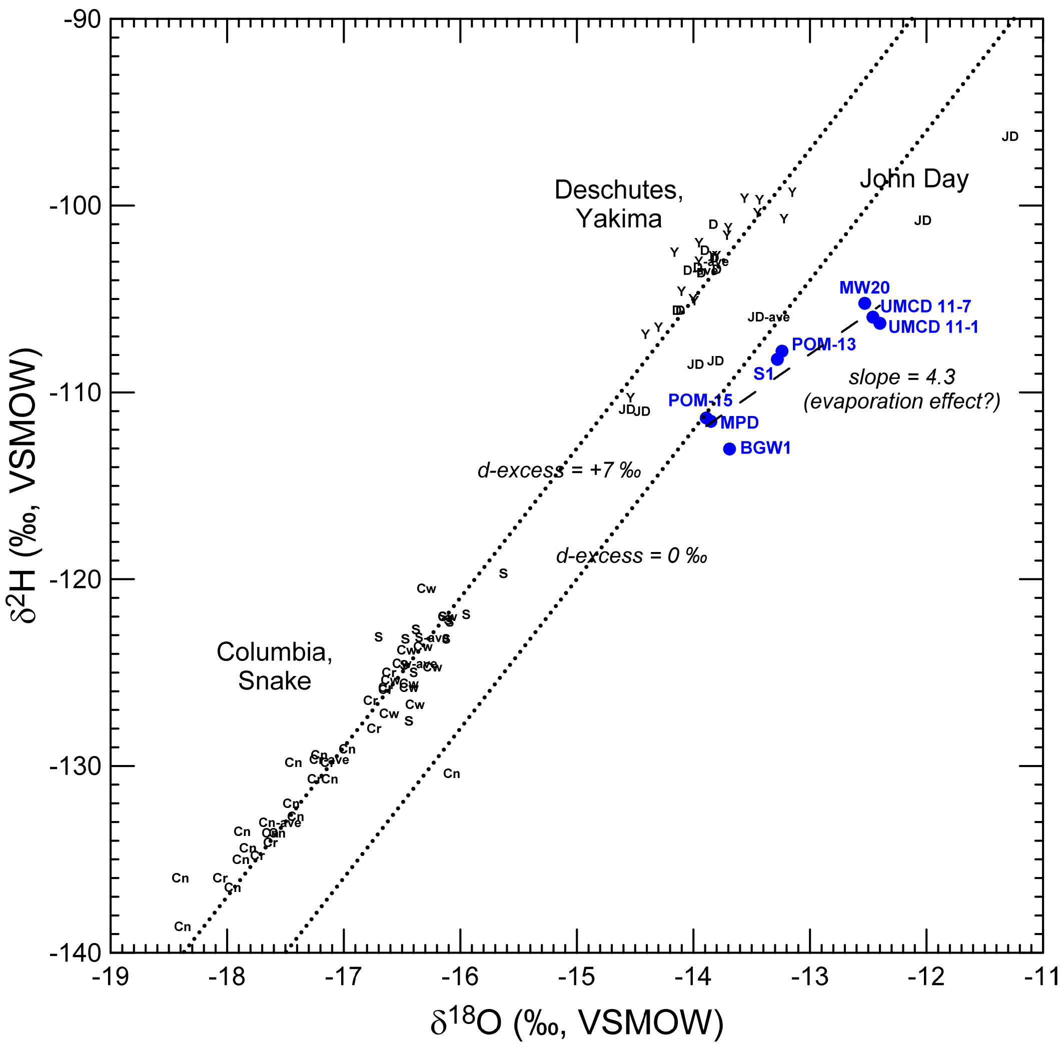


Table 7.6. Isotopic and Geochemical Data from Umatilla Area Groundwater Samples.

		ClO_4^- isotopes					NO_3^- isotopes							
Well ID	**ClO_4^- (μg/L)[1]**	**$\delta^{18}O$ (‰)**	**$\delta^{37}Cl$ (‰)**	**$\Delta^{17}O$ (‰)**	**$^{36}Cl/Cl$ ($*10^{-15}$)**	**NO_3-N (mg/L)**	**$\delta^{18}O$ (‰)**	**$\delta^{15}N$ (‰)**	**DO (mg/L)**	**Temp (^oC)**	**pH**	**SO_4^- (mg/L)**	**Cl^- (mg/L)**	**ORP (mv)**
POM-13	7.2	-9.9	+1.3	+0.16	5880	38.9	-3.7	+1.0	8.7	16.8	7.2	118.0	74.7	+99
POM-15	3.8	-10.9	+1.0	+0.43	10700	49.4	-2.1	+1.3	9.4	18.3	7.6	90.9	67.6	+72
M&P Dairy	34.7	+1.6	+3.5	+1.74	10000	21.7	-6.0	+2.3	8.5	18.4	6.8	64.9	249	+111
UMCD11-1	7.6	-2.5	+2.3	+1.23	4950	17.0	-6.7	+5.2	9.1	20.4	7.6	58.9	24.3	+53
UMCD11-7	10.5	-2.5	+1.8	+1.18	4530	14.0	-6.3	+5.9	8.5	21.8	7.7	57.2	33.2	+62
BGW-001	11.0	+6.0	+3.7	+2.89	15900	17.4	-1.7	+4.0	9.9	17.5	7.5	70.2	186	+72
MW-20	11.5	+5.9	+2.9	+2.62	9920	3.8	-2.4	+3.5	9.8	15.5	7.3	31.8	159	+22
S1	5.9	-8.7	-4.4	+3.73	10800	32.7	-3.4	+1.6	7.5	16.3	7.4	64.1	53.5	+36

Figure 7.20 Isotopic composition of H (δ^2H) and O (δ^{18}O) in H_2O in groundwater samples (blue, this study) and river waters in the region (Coplen and Kendall, 2000). River data are plotted with labels centered on the values for the Deschutes River (D, at Moody, near Biggs, OR), Yakima River (Y, at Kiona, WA), John Day River (JD, at McDonald Ferry, OR), Columbia River (Cn, at Northport, WA; Cw, at Warrendale, WA), and Snake River (S, at Burbank, WA). Hypothetical curves representing constant conventional d-excess values for meteoric water ([d-excess ‰] = [δ^2H ‰] – 8 x [δ^{18}O ‰]) are shown for reference. River data could be consistent with a regional meteoric water line with d-excess around +7 ‰. Effects of evaporation may be indicated by low d-excess values (≤ 0 ‰) and low slope (4.3) for groundwater samples and some of the John Day River data.



7.4.6 Conclusions

Isotope data from the GWMA in the Lower Umatilla Basin indicate the presence of three different types of ClO_4^- in varying proportions: natural indigenous ClO_4^- similar to the "SHP type", Chilean ClO_4^- likely derived from imported fertilizer, and synthetic ClO_4^-. Natural "SHP-type" ClO_4^- appears to be a component in sampled groundwater throughout the region. In several of the wells, including BGW-001, M&P Dairy, MW-020, UMCD11-1 and UMCD11-7 this type of natural ClO_4^- appears to be dominant, based the combination of stable isotope data and $^{36}Cl/Cl$ data. The $\Delta^{17}O$ values for ClO_4^- from two of the wells, BGW-001 and MW-20, are higher than previously reported for SHP-type ClO_4^-, although much lower than those of ClO_4^- from the clay hills of Death Valley (Jackson et al., 2010). The reason for the difference in $\Delta^{17}O$ between SHP and Death Valley samples is unknown, and may reflect either different mechanisms of formation and/or slow isotopic exchange between the Death Valley type ClO_4^- and H_2O, which ultimately could result in slowly declining $\Delta^{17}O$ of ClO_4^- in a moist environment. These hypotheses, including the difficulties with each, are discussed in more detail in Jackson et al., (2010), which is provided in Appendix C.

Two of the other wells that were sampled, POM-13 and POM-15, appear to be mixtures of synthetic and SHP-type ClO_4^-, with the majority of the ClO_4^- being synthetic in origin based upon the isotope results. Those wells have post-bomb ^3H concentrations and apparent groundwater ages less than 50 years, consistent with the presence of synthetic ClO_4^-. One of the sampled wells (S1) appears to contain a substantial component of Chilean ClO_4^-, as indicated particularly by high $\Delta^{17}O$ and low $\delta^{37}Cl$. The combination of widespread irrigation with both river water and groundwater (which may introduce ClO_4^- and complicates interpretation of groundwater dating), and complex local hydrogeology, makes forensic interpretation of ClO_4^- sources in the Lower Umatilla Basin challenging. However, the data clearly show that the "SHP-type" ClO_4^- predominating in groundwater in West Texas and New Mexico is also an important groundwater source in this area, thus extending the range of this material to the northwestern US. Synthetic and Chilean-type ClO_4^- were also present in a few wells based on stable isotope data.

7.5 *In Situ* Fractionation of Cl and O Isotopes in ClO_4^-

7.5.1 Background

ClO_4^- and NO_3^- are both subject to biological degradation in groundwater under anoxic conditions when a suitable organic or inorganic electron donor is present. Because of this, *in situ* bioremediation via substrate addition is an important treatment approach for these contaminants (ITRC, 2008; Hatzinger, 2005). Natural attenuation of ClO_4^- and NO_3^- is also likely in anoxic groundwater, but little research has been conducted to evaluate the occurrence of this process for ClO_4^-. Monitored Natural Attenuation (MNA) is an accepted remediation strategy for chlorinated solvents, petroleum hydrocarbons, and other contaminants when *in situ* biodegradation can be verified through multiple lines of evidence, including microbiological, geochemical, and metabolite analyses. Stable isotope analysis is a valuable technique to support MNA because it allows contaminant biodegradation to be verified and distinguished from transport or mixing-related decreases in contaminant concentrations. However, the applicability of stable isotope evaluations in the field depends on quantification of the extent to which bacteria fractionate specific isotopes, and an understanding of how isotope fractionation factors vary with environmental conditions and between the laboratory and the field (USEPA, 2008). At present, data concerning the *in situ* fractionation of NO_3^- isotopes in groundwater are limited and somewhat inconsistent, whereas no *in situ* fractionation factors for Cl or O have been reported for ClO_4^- biodegradation in aquifers or other natural environments.

In a previous study, we quantified the isotope fractionation of Cl and O during microbial ClO_4^- reduction by two different bacterial genera in liquid culture (Sturchio et al., 2007). Substantial isotope fractionations were observed for both elements ($\varepsilon^{18}O = -33.1 \pm 0.6$ ‰ and $\varepsilon^{37}Cl = -13.2 \pm 0.2$ ‰), the magnitudes of which were independent of bacterial type or temperature. Here we present measurements of apparent *in situ* fractionation effects for ClO_4^- (Cl and O) and NO_3^- (N and O) resulting from biodegradation in a shallow aquifer in Maryland.

7.5.2 Site Description

The *in situ* experiment was conducted in a shallow alluvial aquifer in the Coastal Plain of northeastern Maryland near the town of Elkton. This aquifer consists of silty sand and gravel from the water table (~ 1 to 1.5 m below ground surface; bgs) down to a depth of 5 m bgs, where a silty clay confining layer is present (Borden et al., 2006, 2007a). The groundwater at this site is contaminated with a mixture of ClO_4^- and chlorinated organic compounds. These chemicals leaked from a former surface impoundment used to store waste materials from the testing and manufacture of rocket motors containing NH_4ClO_4. NO_3^- is also present in the groundwater, possibly as a result of the microbial oxidation of NH_4^+ originally derived from fertilizer, NH_4ClO_4, or other sources.

In 2003, ten injection wells (2.5 cm; denoted IW-1 to IW-10) were installed on 1.5 m centers in a line perpendicular to groundwater flow, ~ 15 m downgradient of the former waste impoundment (Figure 7.21). The wells were installed to a depth of ~ 5 m using direct push methods and were screened from 1.8 to 4.9 m bgs, which spans most of the saturated zone of the shallow aquifer (Borden et al., 2007a) Three upgradient and four downgradient monitoring wells (SMW-1 to SMW-7) were also installed at this time. In October, 2003, each of the 10 injection wells received a solution of soybean oil emulsion (EOS Remediation, Inc., Raleigh, NC). Within 35 days of emulsion injection, the mean ClO_4^- concentration in the downgradient monitoring wells decreased from ~ 8.6 mg/L to 7 μg/L and the NO_3^- concentration decreased from ~ 9.5 mg/L to < 0.5 mg/L (as NO_3). Detailed results of this field demonstration are provided elsewhere (Borden et al., 2006, 2007a, 2007b)

7.5.3 Experimental Design

A single-well injection experiment to evaluate *in situ* stable isotope fractionation during ClO_4^- and NO_3^- biodegradation was conducted at IW-3 in July, 2006, nearly three years after the emulsified oil was injected into the aquifer. First, groundwater was collected from IW-3 to measure background geochemical conditions and isotopic compositions of NO_3^- and ClO_4^-. For the injection test, ~ 410 L of groundwater was extracted from upgradient well SMW-1, amended with a tracer solution of NaBr to achieve a final Br^- concentration of ~ 211 mg/L, sampled for chemical and isotopic analysis (see below), and then the remaining mixture (405 L) was injected into IW-3 at a flow rate of 30 L/min. Following injection, a peristaltic pump (Masterflex; Cole-Parmer, Chicago, IL) was used to extract water from IW-3 at eight discrete sampling times over the next 30 hr. The entry point of the tubing from the pump was placed at mid-screen depth, and groundwater was not extracted between sampling events; rather, the water was subject to natural gradient conditions during most of the test.

Prior to sample collection, pumped groundwater was passed through a field meter (YSI 556 MPS; YSI, Inc., Yellow Springs, OH) for measurement of pH, oxidation-reduction potential (ORP), conductivity, temperature, and dissolved oxygen (O_2). After these parameters were stable, groundwater samples were collected for analysis of anions (ClO_4^-, ClO_3^- Br^-, Cl^-, NO_3^-, NO_2^-), dissolved gases (Ar, N_2, O_2, CH_4), and NO^{3-} stable isotope ratios, as previously described in this report. ClO_4^- isotope samples were passed through small glass columns (13 cm length x 2.2 cm diam.; Ace Glass) containing ClO_4^--selective ion exchange resin (Purolite A-530E). Samples collected after 4.5 hr (as ClO_4^- concentrations decreased due to biodegradation) were passed directly through the resin columns in the field (4 to 30 L), whereas earlier samples (~0, 0.6, 1.5, 2.5, 4.6 hr after injection) were collected first into one or more 1L plastic bottles and then passed through similar resin columns in the laboratory. The time 0 samples were collected from the two drums used to store the upgradient water prior to injection. The bottles and resin columns used to collect ClO_4^- for isotopic analysis were preserved in the field by adding 0.05 N HCl to reduce pH to < 2.0.

7.5.4 Chemical and Stable Isotope Analyses

ClO_4^-, ClO_3^-, Br^-, Cl^-, SO_4^{2-}, and NO_2^- concentrations were measured at Shaw by ion chromatography (IC) using the methods described previously. NO_3^- was analyzed using the “denitrifier method” due to the enhanced sensitivity of this technique compared to IC (see method description below). The NO_3^- analyses were performed on the same aliquots as the NO_3^- isotope analyses. Concentrations of major dissolved gases (Ar, N_2, CH_4) were analyzed by gas chromatography and gas isotopes by continuous-flow mass spectrometry.

The quantities of ClO_4^- collected during the groundwater sampling events ranged from ~3.8 to 10 mg. The extraction, purification, and isotopic analysis of ClO_4^- collected in the field was conducted as previously described in detail in this document. The O and N isotope ratios in NO_3^- were measured at the USGS (in Reston, VA) by the "denitrifier method", in which a denitrifying bacterium (*Pseudomonas aureofaciens*) is used to convert NO_3^- to N_2O for isotopic analysis (Sigman et al., 2001; Casciotti et al., 2002). Values of $\delta^{18}O$ and $\delta^{15}N$ are reported in parts per thousand (‰), as for ClO_4^- isotope ratios, with respect to VSMOW for $\delta^{18}O$ and atmospheric N_2 (AIR) for $\delta^{15}N$. The samples were analyzed along with NO_3^- isotopic reference materials, and the data were normalized to $\delta^{18}O$ values of -27.9 ‰ for USGS34 and +25.6 ‰ for IAEA-N3 and $\delta^{15}N$ values of +4.7 ‰ for IAEA-N3 and +180.0 ‰ for USGS32 (Bohlke et al., 2003). The average reproducibilities of the normalized $\delta^{18}O$ and $\delta^{15}N$ values were approximately ± 0.3 ‰ and ± 0.2 ‰ (1σ), respectively. These analyses also yielded NO_3^- concentrations from N_2O peak areas that were calibrated against known concentrations of the isotopic reference solutions analyzed with each batch of samples, with detection limit < 0.1 μmol/L and uncertainties of ± 1-5 % (1σ) for concentrations > 2 μmol/L.

7.5.5 Calculation of Isotope Fractionation Factors

The isotope fractionation factor, α, is defined as

$$\alpha = R_A/R_B$$

where R is an isotope-amount ratio ($n(^{i}E)/n(^{j}E)$), and A and B are two substances (in the present case, ClO_4^- or NO_3^- after varying degrees of bioreduction). For O, Cl, and N compounds, R represents the isotope ratios $^{18}O/^{16}O$, $^{37}Cl/^{35}Cl$, and $^{15}N/^{14}N$, respectively. Values of α were obtained from the experimental results by assuming the exponential Rayleigh-type function

$$R/R_0 = f^{\alpha-1}$$

where R and R_0 are the O, Cl, or N isotope ratios of the residual reactant (ClO_4^- or NO_3^-) and the initial (unreacted) reactant, respectively, and f is the fraction of reactant remaining (C/C_0 = concentration at any time divided by the initial concentration). In terms of the δ values, Equation 4 can be rewritten as:

$$(\delta + 1)/(\delta_0 + 1) = f^{\alpha-1}$$

where δ represents the isotopic composition of the reactant at any value of f, and δ_0 represents the isotopic composition at $f = 1$. The value of α was obtained by linear regression of data using a logarithmic form of the previous equation:

$$\alpha\text{-}1 = \ln\,[(\delta + 1)/(\delta_0 + 1)]/\ln f$$

Isotope fractionation effects also are commonly expressed in terms of ε, where

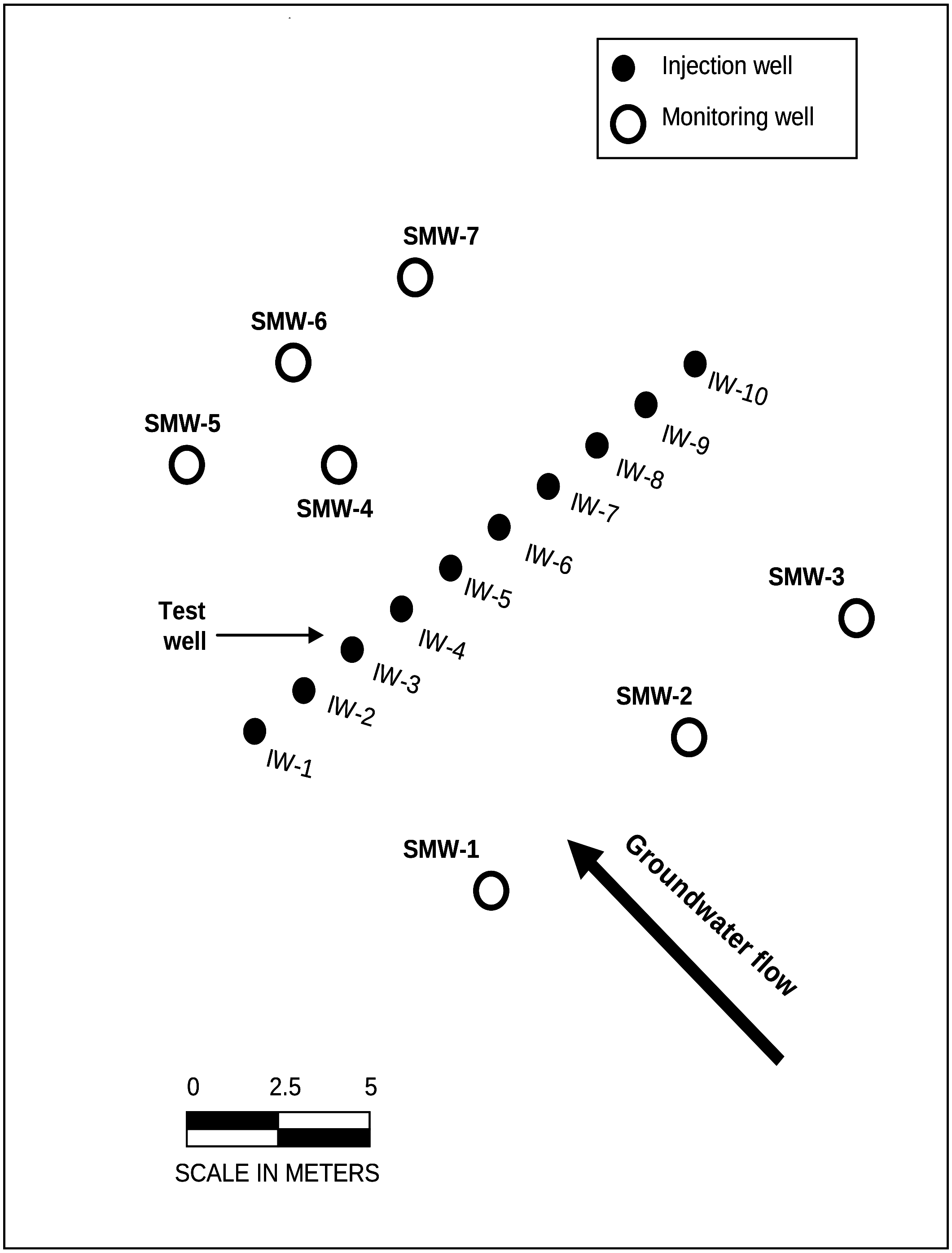
$$\varepsilon = \alpha - 1$$

with ε reported in parts per thousand (‰).

7.5.6 Data Evaluation

To calculate the chemical and isotopic effects of ClO_4^- and NO_3^- biodegradation during the *in situ* experiment, adjustments were made to the measured data to account for the dilution of the tracer Br^- with Br^--free groundwater. Two alternative models were considered: (1) assuming the Br^--free groundwater had no NO_3^- or ClO_4^-, in which case the adjusted relative concentrations were given by $f = (C/Co)_{\text{anion}}/(C/Co)_{\text{Br}}$, and (2) assuming the Br^--free groundwater had constant NO_3^- and ClO_4^- concentrations given by the "background" (pre-injection) samples, in which case a background component was subtracted from the measured anion concentration in each sample; that is, C_{anion} was replaced by $C_{\text{anion}} - C_{\text{bkg}} * [1-(C/Co)_{\text{Br}}]$. Other possibilities exist, but the data do not permit detailed evaluation of more complex scenarios. Apparent isotope effects (ε values) were calculated from analyses of samples collected during the first 6.6 hr of the test for ClO_4^- and the first 8.6 hr for NO_3^-. Accurate O and Cl isotope data could not be obtained for the 8.6 hr sample of ClO_4^-. Samples from later time points were more strongly affected by dilution and potential background contributions, which increased the uncertainty in the calculations.

Figure 7.21. Map of the Elkton, MD Study Site. Groundwater was extracted from upgradient well SMW-1 and reinjected into well IW-3.



7.5.7 Results and Discussion

The groundwater collected from upgradient well SMW-1 for reinjection into the aquifer at barrier well IW-3 had 7.4 mg/L of NO_3^- and 5.5 mg/L of ClO_4^- just prior to injection. This water was pumped from the aquifer ~ 16 hr prior to injection and stored in 2 208-L drums overnight near the injection well. Prior to injection, the average O_2 concentration was 2.9 mg/L, the ORP was – 54 mV, and the pH was 6.4. After addition of NaBr tracer, this water had a Br^- concentration of 211 mg/L.

After injection of the Br^--amended water, well IW-3 was sampled at approximately 0.6, 1.5, 2.5, 4.6, 6.6, 8.6, 23.2, 26.2, and 30.1 hr. The precise sampling time for each parameter used in the calculations is equal to the midpoint of the recorded collection time. Prior to the injection, the "background" concentrations of NO_3^- and ClO_4^- at IW-3 were 130 μg/L and 133 μg/L, respectively, and the initial oxidation-reduction potential (ORP) was - 80 mV. During the course of the 30.1 hr sampling period, the ORP in this well remained between -71 and -101 mV, and the pH was between 6.2 and 6.6. The groundwater temperature averaged $14.6 \pm 0.8^{o}C$ during the test. No electron donors or bacteria other than those in the groundwater pumped from SMW-1 were injected into the aquifer during the experiment; rather, the electron donor required for NO_3^- and ClO_4^- reduction is assumed to have been provided by the residual emulsified oil substrate that had been injected nearly three years earlier. The experimental data are presented in Table 7.7.

Data collected ~ 4 months prior to this field experiment indicated that 43 % of the carbon originally present in the emulsified oil barrier was still present within the aquifer (Borden et al., 2007b). Both ClO_4^- and NO_3^- were degraded in the aquifer during the experiment. SO_4^{2-} reduction did not occur to an appreciable extent during the test based on comparison with Br^- values, although the reduction of small quantities of SO_4^{2-} cannot be ruled out. The relative anion concentrations $(C/Co)_{anion}$, and the relative concentrations adjusted for dilution based on Br^- concentrations $[(C/Co)_{anion}/(C/Co)_{Br}]$ are shown in Fig. 7.22. The most rapid degradation of both ClO_4^- and NO_3^- occurred during the initial hours after injection. There was no apparent lag phase prior to the onset of ClO_4^- and NO_3^- biodegradation, and the processes occurred simultaneously. When normalized to Br^-

concentration to exclude dilution effects, the degradation curves of both compounds were fit by a first order rate expression ($r^2 \geq 0.98$). Assuming no background concentrations, the first order rate constants for the degradation of ClO_4^- and NO_3^- were similar at 0.18 ± 0.02 hr^{-1} ($r^2 = 0.98$) and 0.19 ± 0.01 hr^{-1} ($r^2 = 0.99$), respectively. With background concentrations taken into account, the rate constant for NO_3^- remained the same, while ClO_4^- increased slightly to 0.19 ± 0.01 hr^{-1} ($r^2 = 0.99$). The final NO_3^- concentration in the test well was 40 μg L^{-1} and the ClO_4^- concentration was 125 μg/L at the conclusion of the 30.1 hr test.

The concentration of ClO_3^- was < 1 mg/L throughout the experiment, and the increase in Cl^- during the initial 8.6 hr was approximately equal to the decrease in ClO_4^- on a molar basis, confirming that ClO_4^- was reduced to Cl^- without substantial accumulation of the ClO_3^- intermediate product. Dissolved gas analyses indicate that reduction of NO_3^- was accompanied by production of N_2, indicating denitrification was the predominant NO_3^- reduction process (though perhaps not the only one). Production of N_2 was indicated by small increases in the N_2/Ar ratios (from about 39 to 42) and the $\delta^{15}N$ values of N_2 (from about 0.9 to 1.2 ‰) between the injectate (drums) and the 6.6-h sample. The increase in N_2 (approximately 0.7-1.4 mg/L) was similar to the observed decrease in NO_3^- (1.2 mg/L as N), after adjustment for Br^- dilution. The small increase in the $\delta^{15}N$ value of total N_2 in this series is qualitatively consistent with overall isotope effects of denitrification; the non-atmospheric N_2 component in the early stages had $\delta^{15}N$ of about 4-5 ‰, compared to the initial NO_3^- value of +14 ‰.

Perchlorate reduction and denitrification occurred simultaneously in the aquifer at similar rates. For some pure cultures of ClO_4^--reducing bacteria, including *Azospira suillum,* NO_3^- has been observed to inhibit ClO_4^- reduction, presumably by negatively regulating the production of the chlorite dismutase enzyme (Coates and Achenbach, 2004). This organism preferentially biodegrades NO_3^- followed by ClO_4^- when the two anions are provided in a mixture (Chaudhuri et al., 2002). Moreover, the addition of NO_3^- during active ClO_4^- biodegradation has been observed to appreciably reduce the rate of the latter process (Farhan and Hatzinger, 2009). However, other organisms, including

Dechloromonas agitata strain CBK and strain per1ace have been observed to reduce ClO_4^- in the presence of NO_3^- (Coates and Achenbach, 2004; Chaudhuri et al., 2002; Giblin et al., 2000).

The data from this *in situ* injection experiment could indicate that the indigenous microbial community in the aquifer includes organisms capable of actively biodegrading ClO_4^- in the presence of NO_3^-. Because the extent of enzyme inhibition is frequently dependent on inhibitor concentration, it is also possible that the starting NO_3^- concentration in the aquifer was too low to have a significant effect on the key enzymes responsible for ClO_4^- reduction. For *Azospira suillum* JPLRND, a NO_3^- concentration of 31 mg/L, which is well in excess of that in the injection water in this study (7.4 mg/L), slowed but did not completely inhibit ClO_4^- reduction (Farhan and Hatzinger, 2009). Alternatively, the apparent simultaneous reduction of ClO_4^- and NO_3^- could be a result of small-scale heterogeneity with domains in which both constituents were reduced completely (see discussion below).

For the two simple mixing-model alternatives (Br dilution, Br dilution with background ClO_4^- and NO_3^-), the adjusted concentrations and isotope effects during the first 8.6 hr of the experiment were essentially indistinguishable, because the amounts of ClO_4^- and NO_3^- in the Br^--free groundwater components were less than 3 % of the amounts in the injectate components. Because background components increased in later time points and may not have remained constant, we used the Br-dilution data from the first 8.6 hr for NO_3^- and the first 6.6 hr for ClO_4^- (the 8.6 hr sample was unavailable) for calculating isotope effects (Figure 7.22).

The extents of isotope fractionation of O and Cl in ClO_4^- and O and N in NO_3^- were each proportional to the extent of biodegradation, with R^2 values ranging from ~ 0.90 for Cl and O in ClO_4^- to > 0.97 for N and O in NO_3^- (Figure 7.23). There appears to be some non-linearity in the apparent isotope effects in both compounds when all of the data from the first 8.6 hrs are plotted against $\ln(f)$, resulting in non-zero intercepts in the fit equations. Because the early data (high f values) were from the pre-injection drum samples and the first aquifer sample at 0.6 hr, it is possible the results were affected by rapid changes in the physical or biogeochemical conditions in the earliest stages of the experiment. For example, reactions in the drums and local aquifer disturbance caused by the injection could have produced different isotope effects than subsequent reactions within the aquifer under natural gradient conditions. Alternative fits excluding the injectate drum samples and the 0.6 hr well sample (i.e., 1.5 to 8.6 hr for NO_3^- and 1.5 to 6.6 hr for ClO_4^-) yielded slightly better R^2 values (ranging from 0.97 to 0.99), and slightly lower apparent ε values (for ClO_4^-, $\varepsilon^{18}O$ = -8.1 ‰ and $\varepsilon^{37}Cl$ = -3.1 ‰ and for NO_3^-, $\varepsilon^{18}O$ = -6.6 ‰ and $\varepsilon^{15}N$ = -8.0 ‰), with no change in the ratios of $\varepsilon^{18}O/\varepsilon^{37}Cl$ or $\varepsilon^{18}O/\varepsilon^{15}N$. Additional experiments and modeling would be required to determine the significance of these features, but their effects on our overall results were largely inconsequential.

Table 7.7. Experimental data from the Elkton, Maryland *in situ* degradation experiment.

Elapsed time-anions (hrs)	ClO_4^- (mg/L)	NO_3^- (mg/L)	SO_4^- (mg/L)	Br (mg/L)	Cl^- (mg/L)	$\delta^{37}Cl$ (ClO_4^-)	$\delta^{18}O$ (ClO_4^-)	$\delta^{15}N$ (NO_3^-)	$\delta^{18}O$ (NO_3^-)
Injectate[1]	5.52	7.44	32.0	211	19.6	2.5	-11.0	13.7	2.6
0.6	5.01	6.94	31.8	202	19.9	3.4	-8.4	14.7	3.5
1.5	4.10	5.64	29.6	193	20.9	5.0	-4.1	17.4	5.6
2.5	3.08	4.37	27.8	183	21.8	6.0	-2.0	19.6	7.5
4.6	1.80	2.62	25.7	169	23.0	7.7	2.2	23.4	10.6
6.6	1.21	1.48	23.4	156	24.1	8.1	3.9	27.4	13.6
8.6	0.78	0.86	20.0	136	25.0	NA[2]	NA	29.9	16.0
23.2	0.22	0.07	14.5	88.4	27.4	10.4	9.6	NA	NA
26.2	0.17	0.04	12.7	64.9	28.5	10.1	10.1	NA	NA
30.1	0.13	0.04	12.3	49.8	28.9	8.9	7.8	NA	NA
background	0.13	0.13	6.8	< 0.5	30.7	9.4	5.7	23.1	12.9

[1] Values are the averages from two drums used for injectate.

[2] NA – Data not available (see text).

Figure 7.22 (a) The relative concentrations (C/Co) of NO_3^-, ClO_4^-, SO_4^{2-}, and Br^- in well IW-3 and (b) the relative concentrations of NO_3^-, ClO_4^-, and Br^- adjusted for dilution based on Br^- concentrations $[(C/Co)_{anion}/(C/Co)_{Br}]$ assuming no NO_3^- or ClO_4^- in background water (closed symbols) or constant NO_3^- and ClO_4^- in background water (open symbols).

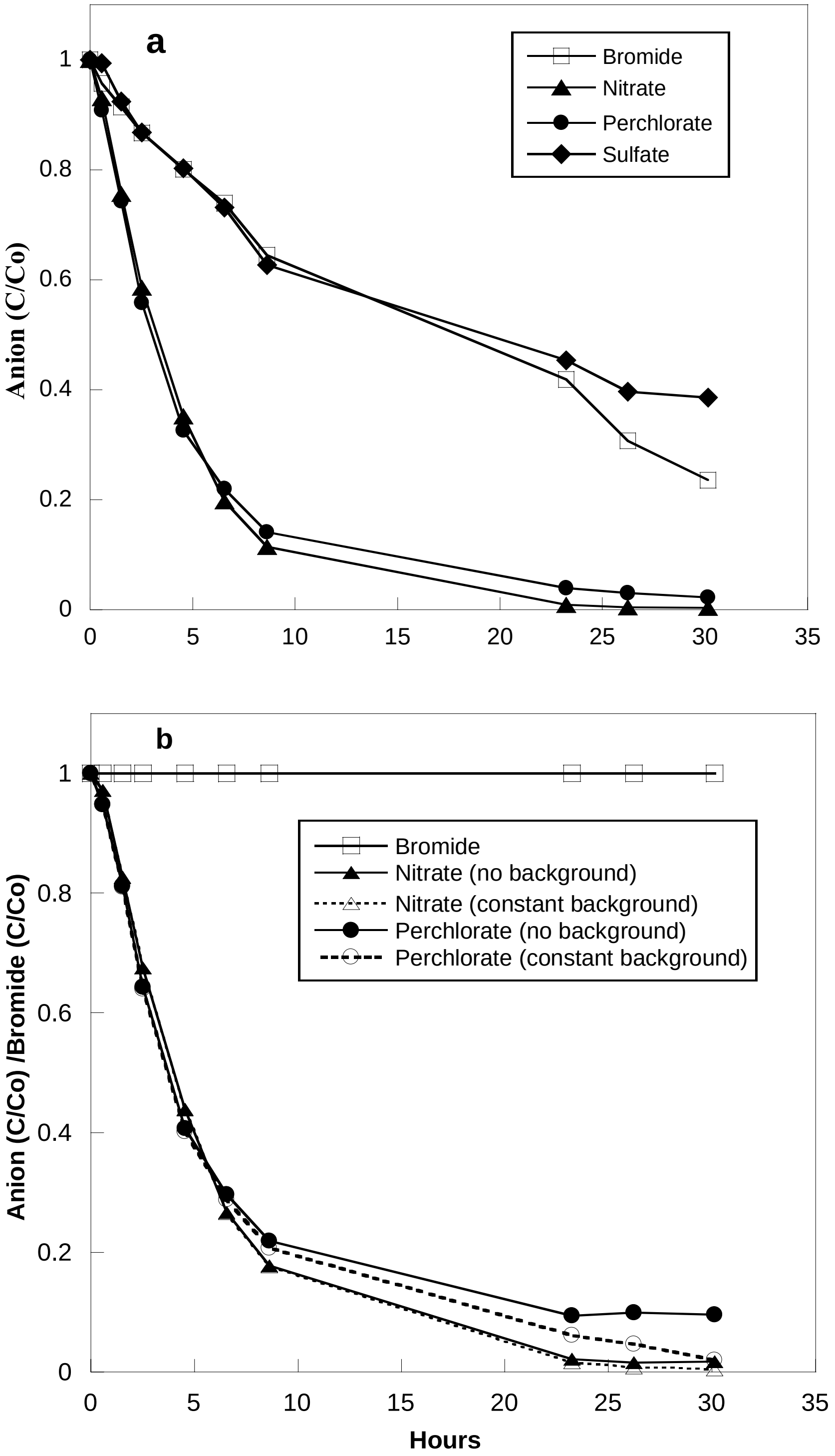
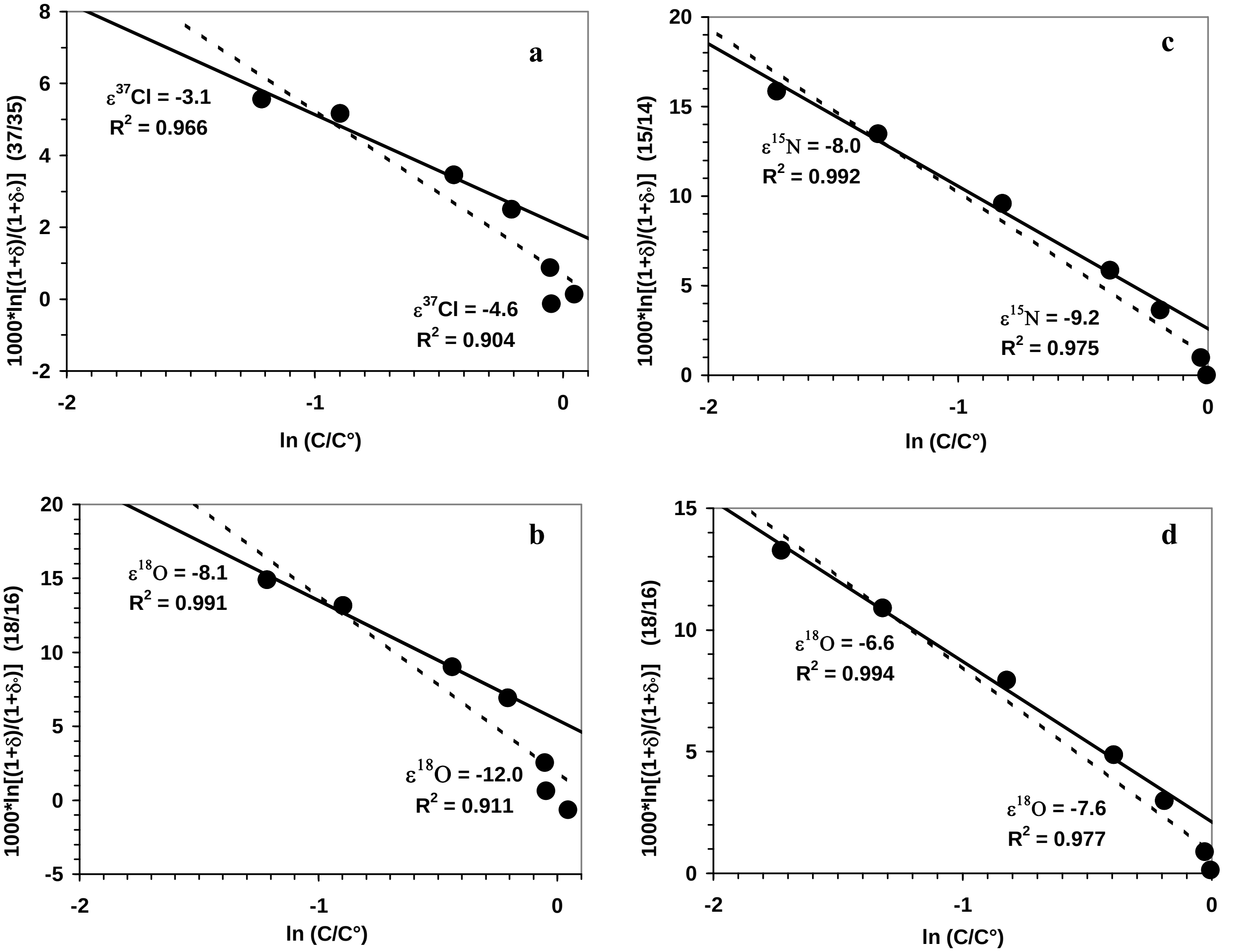


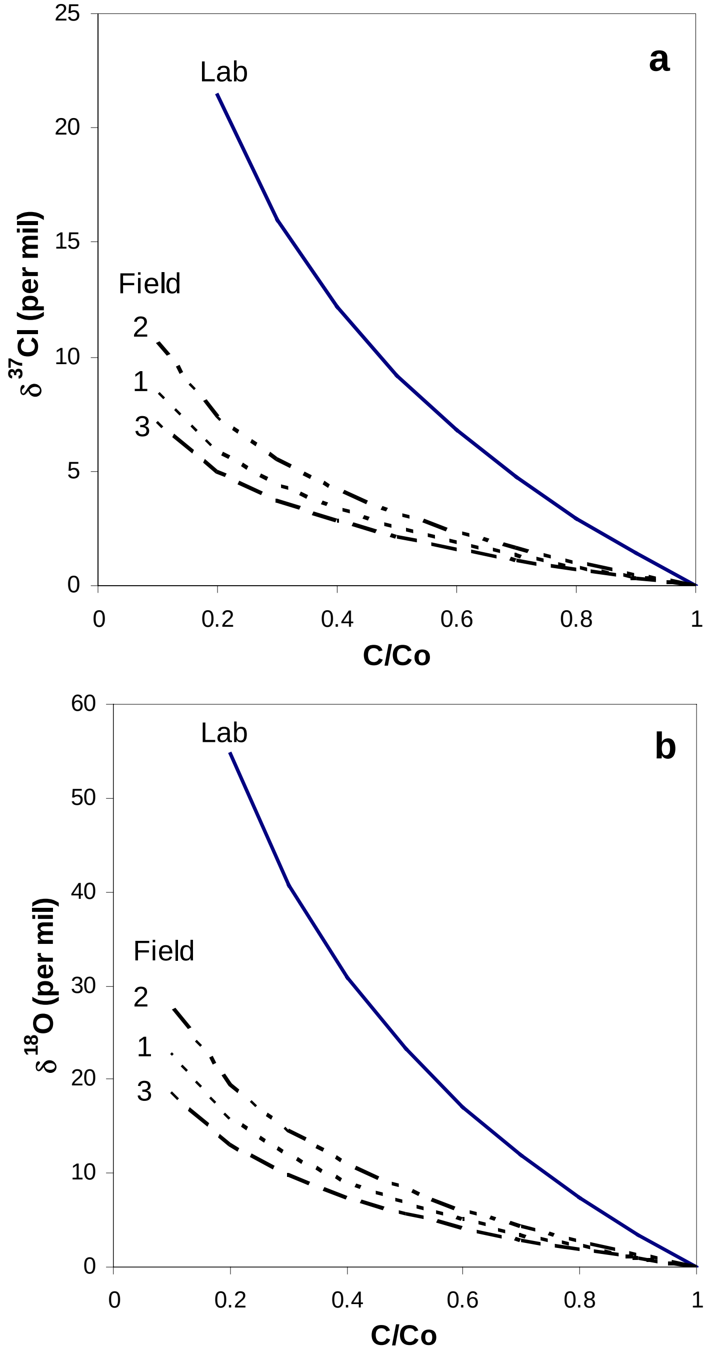
Figure 7.23. Plot of 1000*ln (1 + δ/1 + δ_o) vs ln C/C_o for (a) Cl isotopes in ClO_4^-, (b) O isotopes in ClO_4^-, (c) N isotopes in NO_3^-, and (d) O isotopes in NO_3^-. Data were adjusted to account for dilution of injected tracer solution with Br-free groundwater. The slopes of the regression lines are equal to (a) ε^{37}Cl (ClO_4^-), (b) ε^{18}O (ClO_4), (c) ε^{15}N (NO_3^-) and (d) ε^{18}O (NO_3^-). The R^2 value is given for each regression line. Two regression lines are shown for each panel: (1) dashed lines are data adjusted for dilution based on tracer Br^- concentrations for all samples collected 0-6.6 hr after injection for ClO_4^-, and 0-8.6 hr for NO_3^- and (2) solid lines are for samples collected 1.5-6.6 hr after injection for ClO_4^-, and 1.5-8.6 hr for NO_3^-.



The magnitudes of the *in situ* fractionation effects for ClO_4^- and NO_3^- both were substantially smaller than those commonly reported for homogeneous closed systems, regardless of the choice of points used to estimate the apparent *in situ* fractionation factors. For ClO_4^-, using data from 0 - 6.6 hr, the estimated values of both ε^{18}O (-12.0 ‰) and ε^{37}Cl (-4.6 ‰) in the *in situ* experiment are about 0.3-0.4 times the values reported for pure culture studies (Figure 7.23) (Sturchio et al., 2003, 2007; Coleman et al., 2003). Likewise for NO_3^-, the estimated value of ε^{15}N in the *in situ* experiment (-9.2 ‰) is between about 0.2 and 0.6 times the range of values (~ -40 ‰ to -15 ‰) reported for closed-system experiments and water-column studies of denitrification (Cline et al., 1975; Mariotti et al., 1981; Barford et al., 1999; Granger et al., 2008). The apparent ε values for both compounds would be lower by identical amounts (about 0.35 times) if compared with hypothetical values of -13 ‰ and -34 ‰ for ε^{18}O and ε^{37}Cl in ClO_4^- and -26 ‰ for ε^{15}N in NO_3^-, all of which are well within the range of most commonly reported lab values.

The relatively small apparent isotope effects in the injection experiment cannot be attributed to dilution of the tracer cloud or to mixing with background ClO_4^- and NO_3^- in the groundwater, because these effects were small and were accounted for in the calculations. Relatively small observed isotope effects in bulk samples undergoing biologically mediated redox reactions have been attributed in the past to heterogeneity caused by transport limitations at a variety of scales. This type of explanation has been given previously for small apparent isotope effects of denitrification, but no such studies have been reported for ClO_4^-. Longitudinal dispersion along ground-water flow paths can cause reduction of apparent ε values by a factor of two (Kawanishi et al., 1993; Abe et al., 2006), whereas heterogeneous flow and reaction domains can have larger effects. For example, Mariotti et al., (1988) suggest that apparent ε^{15}N values of around –5 ‰ in groundwater could indicate denitrification in poorly connected "dead-end" pores, where exchange of partially reacted NO_3^- with the external mobile fluid was limited. Similarly, Brandes and Devol, (1997) show that benthic denitrification could occur with reduced N isotope effect in the overlying water column because of limited NO_3^- exchange between the water-column and the sedimentary pore-water reaction sites. Based on direct comparison with pure culture data (see Figure 7.24), it appears that the apparent isotope fractionations for both ClO_4^- and NO_3^- at the Elkton site may have been affected to similar degrees by such processes.

Figure 7.24. Comparison of apparent isotope fractionation effects for (a) Cl and (b) O in ClO_4^- between the present field study ("Field") and previous pure culture study ("Lab") with *A. suillum* JPLRND at 10°C (Sturchio et al., 2007). For the current study, separate curves are plotted for the apparent fractionation effects based on various adjustments of the concentrations and isotope values: (1) measured values (no adjustment for dilution or background ClO_4^-) for all samples collected 0-6.6 hr after injection, (2) data adjusted for dilution based on tracer Br concentrations for all samples collected 0-6.6 hr after injection, and (3) dilution-adjusted data for samples collected 1.5-6.6 hr after injection.



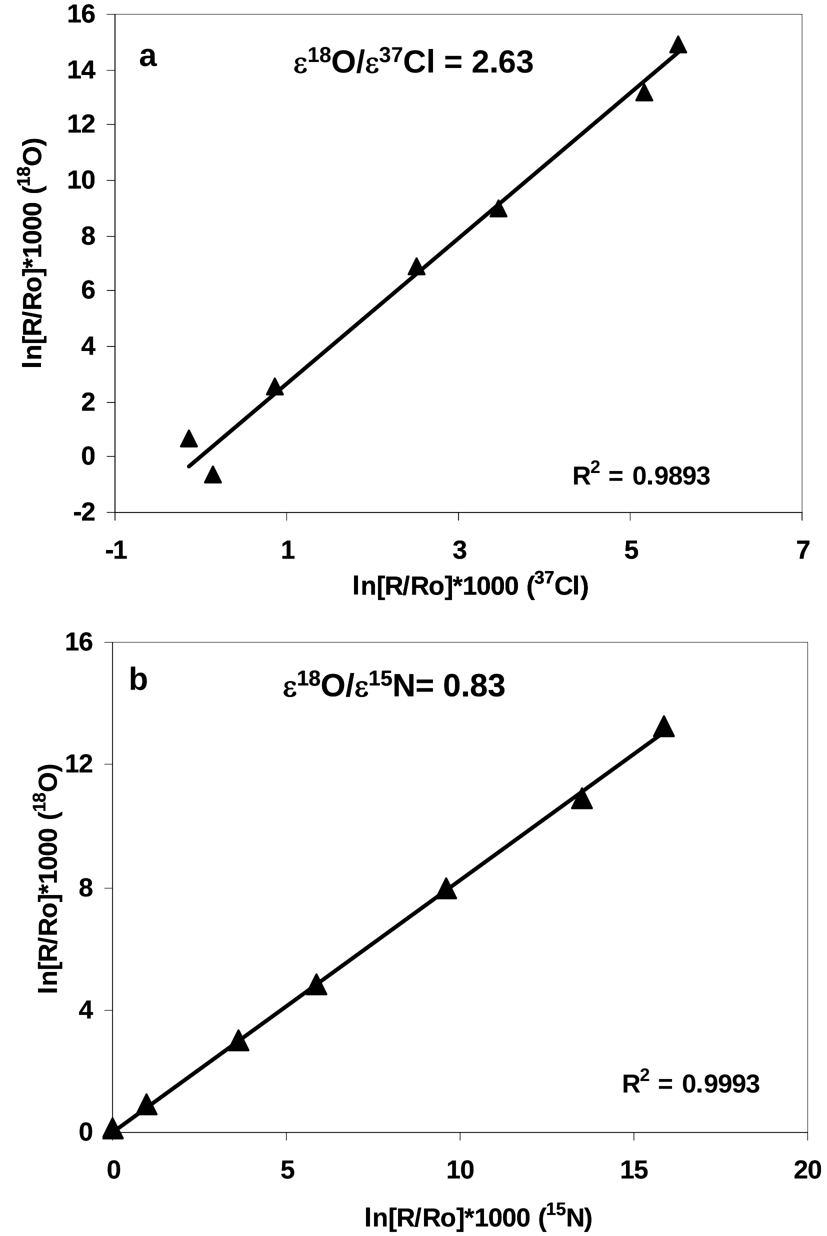
In addition to the effects of aquifer physical heterogeneity, reactions may have been limited by proximity to the remaining soybean oil substrate in the emulsified oil barrier or by the rate of generation and/or dissolution of soluble substrates from the oil (e.g., fatty acids) that were most likely utilized by the ClO_4^- and NO_3^- reducing bacteria as the electron donor for these reactions. The finite spacing and/or heterogeneous distribution or production of those substrates could contribute to the relatively small apparent isotope effects. Heterogeneity at any of these scales also may have been responsible for the apparent lack of NO_3^- inhibition of ClO_4^- reduction, which is common (though not ubiquitous) in laboratory culture studies. The same transport limitations that affected the isotopic results could have permitted local depletion of NO_3^- and reaction of ClO_4^- in partial isolation from the bulk fluid that contained higher NO_3^- concentrations.

Alternatively, it is possible that some or all of these observations could be explained by invoking different bacteria or reaction mechanisms in the different field and laboratory studies, but these possibilities cannot be evaluated fully with the available data. ClO_4^- is not readily reduced abiotically, and it does not react rapidly with typical reducing agents, such as ferrous iron, sulfite, or thiosulfate (Brown and Gu, 2006; Urbansky, 2002). ClO_4^- reduction can be mediated by some catalysts, including ruthenium(II) and titanium(III), but even these reactions are relatively slow at 25°C, with half-lives on the order of several days or longer (Brown and Gu, 2006; Epenson, 2000). Thus, we consider it unlikely that abiotic processes contributed significantly to the loss of ClO_4^- during the short period of the isotope sampling. Rapid abiotic reduction of NO_3^- also seems unlikely under the geochemical conditions present in groundwater at the site, and the production of N_2 during the test is consistent with microbial denitrification as the major reductive mechanism for NO_3^-. For NO_3^-, it is also possible that the isotope fractionations were affected by a secondary "sink" for nitrate other than denitrification (Mariotti et al., 1988; Smith et al., 1991; Granger et al., 2004). Secondary sinks (which may have lower $\varepsilon^{15}N$ values) could include either assimilatory NO_3^- uptake (i.e., utilization of NO_3-N for cell growth) or dissimilatory reduction of NO_3^- to NH_4^+, products of which could be incorporated into solid phases. These processes may have occurred, but apparently were not the major NO_3^- sinks, as indicated by N_2 data. Similar secondary sinks are not likely for ClO_4^-, which is known to be utilized biologically only as a terminal electron acceptor, with Cl^- and H_2O as final products. Physical controls (e.g., transport limitations) are considered a more likely explanation for our NO_3^- and ClO_4^- data, which exhibited almost identical fractionation patterns (Figure 7.23) and similar ε reductions compared to the most common lab data (e.g., Figure 7.24).

Unlike the magnitudes of the isotope fractionation effects (individual ε values), the relative isotope effects for the two elements within each oxyanion were nearly identical to those reported in previous studies (Figure 7.25). For example, the *in situ* ratio of $\varepsilon^{18}O/\varepsilon^{37}Cl$ for ClO_4^- was 2.63 in the aquifer, which is close to the value of 2.50 ±0.04 measured for ClO_4^- reduction by two pure cultures at varying temperatures (Sturchio et al., 2007) Similarly, the $\varepsilon^{18}O/\varepsilon^{15}N$ for NO_3^- (0.83) is within the range of 0.5 to 1.0 reported previously for denitrification in field and laboratory settings (Granger et al., 2004; Lehman et al., 2003; Bottcher et al., 1990; Sigman et al., 2005; Granger et al., 2008). For both compounds, the constant ε ratios throughout the *in situ* injection experiment indicate that O isotope exchange of the reactant with water was either constant or not important, consistent with experimental results for ClO_4^- reduction with isotopically labeled H_2O (Sturchio et al., 2007).

The ratio of $\varepsilon^{18}O/\varepsilon^{37}Cl$ in ClO_4^- (2.63) in this study is appreciably higher than the value of $\varepsilon^{18}O/\varepsilon^{15}N$ in NO_3^- (0.83). This difference in part reflects the relative mass differences of N, O, and Cl, in that the kinetic isotope effects are often proportionally larger for the lighter element in each oxyanion (Young et al., 2002). Differences in the key enzymes (and reactions) mediating the biological reduction of ClO_4^- and NO_3^- may also contribute to the different ε ratios for these two compounds. Even when acting upon a single compound, different enzymes are known to result in different ε values and ε ratios (Granger et al., 2008; Morash et al., 2002; Meckenstock et al., 2004). The fact that the pathway for bacterial ClO_4^- reduction is both simple (consisting of only two enzymes, perchlorate reductase and chlorite dismutase) and highly conserved among bacterial species (Coates and Achenbach, 2004), may account for the relatively consistent ratios of $\varepsilon^{18}O/\varepsilon^{37}Cl$ observed between pure cultures and the native microflora of an aquifer.

Figure 7.25. Plot of ln(R/R$_o$)*1000 values for (a) ^{37}Cl vs ^{18}O and (b) ^{15}N vs ^{18}O. The ratios of the fractionation effects are given for each compound.



7.5.8 Conclusions

Isotope fractionation of residual ClO_4^- and NO_3^- in groundwater samples from a tracer injection experiment provided strong qualitative evidence of *in situ* reactions (denitrification, perchlorate reduction), especially from ratios such as $(\varepsilon^{18}O/\varepsilon^{37}Cl)_{ClO4}^-$ and $(\varepsilon^{18}O/\varepsilon^{15}N)_{NO3}^-$. In fact, the ε ratios for ClO_4^- were remarkably close to those derived from pure culture studies considering the dissimilarity of the two experimental conditions (i.e., undefined microbial consortia in a sand aquifer compared to pure cultures in a homogenous laboratory salts solution). Thus, they provide evidence that ClO_4^- biodegradation occurred by the same enzymatic reaction as in the pure culture experiments. However, it is apparent from these data, as in previous studies, that the magnitudes of the individual isotope fractionation effects derived from one environment (e.g., pure cultures) could not be related quantitatively to the progress of similar reactions in other, more heterogeneous, environments (e.g., aquifers), even after adjustments for effects of dilution and mixing measured in the bulk samples. Because both compounds degraded simultaneously and exhibited similar discrepancies in apparent isotope effects, it appears likely the isotope effects were controlled largely by heterogeneity and physical limitations to transport and reaction that affected both compounds, rather than by differences in reaction mechanisms or organisms involved with the individual compounds. Effects of heterogeneity typically result in underestimation of reaction progress calculated from apparent isotope effects in the field using laboratory-determined ε values. Nevertheless, the distinctive ratios of apparent ε values indicate that biodegradation was occurring, and lower limits of the extents of degradation could be constrained provided relevant knowledge of ε values from homogeneous experiments.

7.5.9 Acknowledgement

Portions of the text and figures in Section 7.5 were previously published (Hatzinger et al., 2009) and are reprinted with permission of CSIRO Publishing. The published paper is available online (http://www.publish.csiro.au/paper/EN09008.htm).

8.0 SUMMARY AND CONCLUSIONS

The key objectives of this ESTCP project were as follows: 1) to validate the combined use of Cl and O stable isotope ratio analysis as a forensic tool to distinguish sources of ClO_4^- in groundwater, and 2) to demonstrate the isotopic techniques as a method to verify ClO_4^- biodegradation in the field. Both of these objectives were met. In addition, data gathered during this project reveal that the radioactive isotope ^{36}Cl in ClO_4^- is also a useful measure for source discrimination. This report describes isotopic techniques that can be used to discern the origin of ClO_4^- in soils and groundwater, and more specifically whether that ClO_4^- is synthetic or natural. These techniques determine the relative abundances of the stable isotopes of chlorine (^{37}Cl and ^{35}Cl) and oxygen (^{18}O, ^{17}O, and ^{16}O) in ClO_4^- using IRMS and the radioactive isotope ^{36}Cl using AMS. Taken together, these measurements on the ClO_4^- ion (which provide four independent quantities) can be used to distinguish natural from synthetic ClO_4^- sources, to discriminate different types of natural ClO_4^-, and to detect ClO_4^- biodegradation in the environment. Other isotopic, chemical, and hydrogeologic techniques that can be applied in conjunction with the Cl and O isotopic analyses of ClO_4^- to provide supporting data for forensic studies are also described. The results of forensic studies at four separate sites are presented as is the application of the technique for documenting *in situ* biodegradation at one field location. Moreover, this project has resulted in the description and isotopic characterization of natural ClO_4^- occurring in various regions of the U.S. This information provides a foundation for understanding both the possible mechanisms of formation of natural ClO_4^-, and the processes that may impact its fate and distribution in soils and groundwater.

A summary of the results and conclusions from this ESTCP project is summarized below:

1. Perchlorate (ClO_4^-) has both synthetic and natural sources, each of which contributes to its occurrence in soils and groundwater. Typical analytical methods for determining ClO_4^- concentrations do not provide direct information on its potential origin.

2. A new forensic approach for ClO_4^- has been developed, based on measurements of the stable isotopes of chlorine (^{37}Cl and ^{35}Cl) and oxygen (^{18}O, ^{17}O, and ^{16}O), and a radioactive chlorine isotope (^{36}Cl) in ClO_4^-. The basic steps in this approach are as follows:

    - Sample collection using ion exchange (IX) columns to trap mg quantities of ClO_4^- from groundwater or soil extracts;
    - Extraction and purification of ClO_4^- from IX columns;
    - Verification of sample purity via Raman spectroscopy and/or ion chromatography;
    - Analysis of stable O isotopes in ClO_4^- by IRMS;
    - Analysis of stable Cl isotopes in ClO_4^- by IRMS; and
    - Analysis of ^{36}Cl by AMS.

3. The data gained from these isotopic analyses can be used to distinguish natural from synthetic ClO_4^- in both source materials and environmental samples. Key isotopic characteristics of different types of ClO_4^- are as follows, based on current published results (see Appendix A, Table A-1):

    - Synthetic ClO_4^- produced by electrochemical reaction is characterized by (1) a mean $\delta^{37}Cl$ value (with respect to SMOC) of 0.6 ‰ and exhibits little variation among samples (-3.1 to +1.6 ‰), (2) more variable $\delta^{18}O$ values (with respect to VSMOW) ranging from -24.8 to -12.5 ‰, and (3) $\Delta^{17}O$ values near 0 ‰, consistent with mass-dependent isotopic fractionation of O during ClO_4^- synthesis. This material also is characterized by low $^{36}Cl/Cl$ values (^{36}Cl mole fractions) of 0×10^{-15} to 40×10^{-15}.

    - Natural ClO_4^- from caliche deposits in the Atacama Desert of Chile, and nitrate fertilizers derived from this material, have reported $\delta^{37}Cl$ values ranging from -14.5 ‰ to -11.8 ‰, with a mean value more than 10 ‰ lower than that of synthetic ClO_4^-. Reported $\delta^{18}O$ values of Atacama ClO_4^- (-24.8

‰ to -4.2 ‰) exhibit substantial overlap with the δ^{18}O values of synthetic ClO_4^-, but the Atacama ClO_4^- is characterized by substantially elevated values of Δ^{17}O (+4.2 to +9.6 ‰), indicating non-mass-dependent isotope effects or precursors contributed to its formation, most likely during atmospheric generation. This natural ClO_4^- has slightly elevated ^{36}Cl/Cl values (22×10^{-15} to 590×10^{-15}) compared to synthetic ClO_4^-.

- Natural ClO_4^- from the southwestern U.S. varies somewhat by location and environment. Samples collected from a large area of the Southern High Plains (SHP) and the Middle Rio Grande Basin (MRGB) are similar isotopically, with δ^{37}Cl values ranging from +3.1 to +5.0 ‰, δ^{18}O values ranging from +0.6 to +3.8 ‰, and Δ^{17}O values ranging from +0.3 to +1.3 ‰. Some samples from the arid Lower Umatilla Basin (LUB) of northeastern OR also were similar isotopically to the SHP and MRGB samples, except that their Δ^{17}O values were somewhat higher (+1.7 to +2.9 ‰). The data indicate that indigenous natural ClO_4^- in the western US (represented by samples from the SHP, MRGB, and LUB) is distinguishable from both Chilean ClO_4^- and synthetic ClO_4^- when all relevant stable isotope ratios are considered.

- Natural ClO_4^- samples from caliche deposits in and around Death Valley, California have lower δ^{37}Cl values (-0.8 to -3.7 ‰) and much higher Δ^{17}O values (+ 8.6 to +18.4 ‰) compared to the SHP, MRGB, and LUB samples. Interestingly, however, all of the SHP, MRGB, LUB, and Death Valley samples analyzed to date are characterized by substantially elevated ^{36}Cl/Cl values (3130×10^{-15} to $28{,}800 \times 10^{-15}$) compared to those of synthetic or Chilean ClO_4^-. Overall, the SHP, LUB, MRGB, and Death Valley samples can be considered together as U.S. indigenous sources and, even though there are substantial ranges in the individual isotope ratios, this indigenous grouping is isotopically distinct from synthetic and Chilean ClO_4^- when all relevant isotope ratios are considered.

4. Experiments to date indicate that post depositional modification by biodegradation causes a reproducible fractionation factor ratio between O and Cl isotopes in ClO_4^- ($\varepsilon^{18}O/\varepsilon^{37}Cl = 2.5$) that is roughly perpendicular to the area in which mixtures of synthetic and Chilean ClO_4^- plot in dual isotope plots. Thus, biodegradation will not obscure differences between these two major sources, when considered with the large differences in $^{36}Cl/Cl$ and(or) $\Delta^{17}O$ values (which will not change appreciably during biodegradation). Biodegradation is also unlikely to lead to lead to errors in source delineation among indigenous U.S. sources and synthetic or Chilean sources of ClO_4^- when all relevant parameters are considered.

5. In addition to Cl and O isotopes of ClO_4^-, there are a large number of supporting methods/analyses available as forensic lines of evidence to help identify sources of ClO_4^- (or other contaminants) in a groundwater environment. These analyses include basic field parameters, stable H, O, N, and S isotopes in H_2O, NO_3^-, and SO_4^{2-}, concentrations of anions, dissolved gases, and trace elements, and groundwater dating. The use of these methods in conjunction with Cl and O isotopic analyses of ClO_4^- is recommended in studies to identify the origin of ClO_4^- in groundwater.

6. The currently defined ranges of isotopic compositions characteristic of different ClO_4^- sources may evolve as more samples are analyzed, but these data already have proven useful for identifying ClO_4^- sources in a number of groundwater studies and we expect additional data will further enhance the value of this approach for ClO_4^- forensic applications.

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Appendix A: Stable Isotope Data for Perchlorate Sources

TABLE A-1. CHLORINE AND OXYGEN ISOTOPIC COMPOSITIONS OF PERCHLORATE SOURCE SAMPLES

Sample Identification	ClO_4 Salt	Sample Description	δ^{37}Cl (‰)	δ^{18}O (‰)	Δ^{17}O (‰)[10]
SYNTHETIC					
Laboratory Reagents	$NaClO_4$	Mallinckrodt lot # 1190KHJJ[1]	+1.2	-16.2	+0.01
	$KClO_4$	Baker Analyzed lot # 45155[1]	+1.1	-24.8	+0.01
	$NaClO_4.H_2O$	Aldrich lot # 00722CG[1]	+1.3	-16.1	+0.12
	$KClO_4$	Sigma lot # 60K3451[1]	+0.5	-16.3	n.a.[4]
	$NaClO_4$	Sigma lot # 111K1334[1]	+1.0	-17.6	n.a.
	$KClO_4$	Hummel-Croton[1]	+0.4	-12.5	n.a.
	$NaClO_4.H_2O$	EM lot # SX0693-2[1]	-3.1	-17.2	+0.08
	$KClO_4$	General Chem. Co. lot # 13[1]	+0.6	-19.1	+0.00
	$RbClO_4$	Aldrich lot # AN00625LZ[1]	+1.3	-16.4	+0.11
	$CsClO_4$	Aldrich lot # LI09119JI[1]	+1.6	-16.6	-0.04
	$CsClO_4$	Aldrich lot # 02407AS[1]	+0.6	-16.9	+0.00
	$HClO_4$	Baker 9656-1, lot # 146358[1]	n.a.	-14.6	+0.01
	$KClO_4$	Aldrich, lot # 11921HO[1]	+0.6	-17.0	+0.00
	$KClO_4$	Allied Chemicals[2]	n.a.	-19.9	-0.06
	$KClO_4$	Aldrich[2]	n.a.	-17.8	-0.12
	$NaClO_4$	EM-Science[2]	n.a.	-17.3	-0.06
	$NaClO_4$	Fisher Scientific[2]	n.a.	-19.5	-0.20
	$AgClO_4$	Aldrich[2]	n.a.	-17.3	-0.10
Manufactured ClO_4^-	$NaClO_4$	American Pacific Co. (N3300401)[1]	+0.4	-22.3	-0.01
	$KClO_4$	American Pacific Co. (P0900402)[1]	+0.4	-21.5	+0.07
	NH_4ClO_4	American Pacific Co. (A2000433)[1]	+0.4	-21.3	n.a.
	$NaClO_3$	Western Electrochemical Co. (TO403E)[1]	+1.1	n.a.	+0.06
	$NaClO_4$	Western Electrochemical Co. (TO403B)[1]	+0.9	-20.4	+0.00
Commercial	$CsClO_4$	Fireworks – UMD Sample 1[3]	+0.7	-19.1	+0.09
	$CsClO_4$	Fireworks – UMD Sample 2[3]	+0.1	-19.6	+0.07
	$CsClO_4$	Taiwanese sample[4]	-0.5	-16.1	+ 0.00
	$CsClO_4$	Flare – UMD Sample 3[3]	+0.1	-13.1	+0.13
	$RbClO_4$	Flare – Orion Safety products.[4]	-0.8	-12.4	+0.03
	$CsClO_4$	Defol 5 - Chlorate defoliant[5]	+ 0.6	-17.5	-0.04
	$CsClO_4$	Poly-Foliant 5 – Chlorate defoliant[5]	+0.6	-17.9	-0.14

Commercial	$RbClO_4$	Pyrodex gunpowder[4]	+0.2	-14.5	-0.02
	$CsClO_4$	Clorox bleach[6]	+14.3	-55.9	-0.3
	$CsClO_4$	Commercial bleach[7]	+9.3	-83.2	-0.2
NATURAL					
Chilean ClO_4^-	$KClO_4$	Commercial Hoffman fertilizer[1]	-13.7	-8.4	+8.95
	$CsClO_4$	Commercial Hoffman fertilizer[1]	-14.5	-9.3	+8.93
	$CsClO_4$	Atacama, Chile evaporite (AT-74-1) [1]	-11.8	-4.2	+9.57
	$CsClO_4$	SQM-7791 fertilizer (RSIL N7791) [1]	-14.2	-7.6	+9.25
	$CsClO_4$	Atacama (AT-24-1) [2]	n.a.	-4.6	+9.6
	$CsClO_4$	Atacama (AT-74-1) [2]	n.a.	-4.5	+9.6
	$KClO_4$	Atacama (AT-75-1) [2]	n.a.	-24.8	+4.2
	$CsClO_4$	Commercial Hoffman fertilizer[2]	n.a.	-9.0	+8.8
Chilean ClO_4 *(Con't)*	$CsClO_4$	Atacama – well water[8]	-12.9	-7.6	+9.3
	$CsClO_4$	P1[8]	-14.3	-10.5	+8.1
	$CsClO_4$	P2[8]	-13.6	-6.7	+9.2
	$CsClO_4$	P3[8]	-11.8	-5.7	+8.8
	$CsClO_4$	P4[8]	n.a.	-7.8	+8.5
	$CsClO_4$	GJ01[8]	-12.5	-5.2	+9.4
	$CsClO_4$	J-470[8]	-12.5	-5.6	+8.8
Southern High Plains Groundwater	$CsClO_4$	Well - MW2A[8]	+4.2	+1.0	+0.3
	$CsClO_4$	Well - MW2B[8]	+3.7	+1.4	+0.3
	$NaClO_4$	Well - MW3A[8]	+5.0	+2.2	+0.3
	$CsClO_4$	Well - MW3B[8]	+4.1	+2.4	+0.3
	$CsClO_4$	Well - GW2[8]	+5.0	+3.8	+0.2
	$CsClO_4$	Well - BW2[8]	+4.5	+0.6	+0.6
	$NaClO_4$	Well - JTY1[8]	+5.1	+2.7	+0.5
	$HClO_4$	Well - KJ1[8]	+4.5	+4.8	+0.8
	$CsClO_4$	Well - RR-8[8]	+3.1	+1.5	+1.2
	$CsClO_4$	Well – RR-16[8]	+3.6	+1.9	+1.3
	$CsClO_4$	Well TTU-G1S[1]	+6.2	+4.7	+0.4
	$CsClO_4$	Well TTU-M3L[1]	+5.1	+2.5	+0.5
Southern High Plains Vadose Zone		SHP-V[8]	+3.7	+2.1	+0.8

Death Valley Caliche	$CsClO_4$	Confidence Hills 1[8]	-0.8	+2.9	+8.6
	$CsClO_4$	Confidence Hills 2[8]	-3.8	+7.2	+12.8
	$CsClO_4$	Saratoga Hills[8]	-1.4	+6.4	+10.9
	$CsClO_4$	Zabriskie[8]	-3.7	+26.1	+18.4

[1] Data from Sturchio et al., (2006).

[2] Data from Bao and Gu, (2004).

[3] Samples collected at the University of Massachusetts, Dartmouth (UMD) after fireworks display .

[4] Samples obtained by Baohua Gu from local retailers in Knoxville, TN.

[5] Commercially available chlorate herbicides.

[6] Aged Clorox bleach sample obtained from Peter Philbrook, USEPA.

[7] Commercial dairy bleach sample obtained from Greg Harvey, USAF.

[8] Data from Jackson et al., (2010).

[9] n.a. - data “not available”.

[10] $\Delta^{17}O$ calculated according to Eq 5.6 in this document: $\mathit{\Delta}^{17}O$ (‰) = $[(1 + \delta^{17}O) / (1 + \delta^{18}O)^{0.525}] - 1$.

Appendix B: Occurrence and Potential Sources of Perchlorate Releases to the Environment as of April, 2003 (Mayer, 2003)

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE RELEASES TO THE ENVIRONMENT as of APRIL, 2003. [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc. ppb
AL	Redstone Army Arsenal - NASA Marshall Space Flight Huntsville, AL	Propellant Manufacturing, Testing, Research, Disposal	Monitoring Well Springs/Seeps	19,000 37
AL	Unregulated Contaminant Monitoring Rule (UCMR) data Escambia County, AL	Unknown	Public Water Supply	8.9
AZ	Apache Nitrogen Products Benson, AZ	Explosives Manufacturing	Monitoring Well	670
AZ	Aerodyne Gila River Ind. Res., Chandler, AZ	Propellant Testing	Monitoring Well	18
AZ	Davis Monthan AFB Tucson, AZ	Explosives/ Propellant Disposal	Soil	--
AZ	Unidynamics Phoenix Inc. Phoenix Goodyear Airport Goodyear, AZ	Explosives/Ordnance Manufacturing	Public Water Supply Well Monitoring Well	65 80
AZ	Unidynamics Phoenix Inc. White Tanks Disposal Area Maricopa County, AZ	Explosives/ Ordnance Disposal	Soil	--
AZ	Universal Propulsion Phoenix, AZ	Rocket Manufacturing	Soil	--
AR	Atlantic Research East Camden, AR	Rocket Manufacturing Disposal - Open burn/ Open detonation	Monitoring Well Surface Water Soil	640,000 12,500 --
CA	Aerojet General Rancho Cordova, CA	Rocket Manufacturing	Public Water Supply Well Monitoring Well	260 640,000
CA	Alpha Explosives Lincoln, CA	Explosives Manufacturing	Monitoring Well Reported in Surface Water	67,000
CA	Boeing/ Rocketdyne, NASA at Santa Susana Field Lab USDOE Santa Susana, CA	Rocket Research, Testing and Production	Monitoring Well	750
CA	Casmalia Resources Casmalia, CA	Hazardous Waste Management Facility	Monitoring Well	58
CA	El Toro Marine Corps Air Station Orange County, CA	Explosives Disposal	Monitoring Well	380
CA	Edwards AFB Jet Propulsion Lab, North Base Edwards, CA	Rocket Research	Monitoring Well	300

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE RELEASES TO THE ENVIRONMENT as of APRIL, 2003. [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc ppb
CA	Lawrence Livermore National Laboratory Site 300 Tracy, CA	U.S. Dept. of Energy Explosives Research	Monitoring Well	84
CA	Lockheed Propulsion Upper Santa Ana Valley Redlands, CA	Rocket Manufacturing	Public Water Supply Well	87
CA	NASA - Jet Propulsion Lab Pasadena, CA	Rocket Research	Public Water Supply Well	54
CA	Olin Safety Flare Morgan Hill, CA	Flare Manufacturing	Public Water Supply Well Monitoring Well	15 167
CA	Rancho Cordova Test Site (Affects Mather AFB) Rancho Cordova, CA	Boeing/ McDonnell Douglas Rocket Testing	Public Water Supply Well Monitoring Well	120 1800
CA	Rialto-Colton Plume Rialto, CA	Fireworks Facility Flare Manufacturing Rocket Research and Manufacturing	Public Water Supply Well	811
CA	San Fernando Valley Glendale, CA	Grand Central Rocket ? Rocket Manufacturing	Monitoring Well	13
CA	San Gabriel Valley Baldwin Park, CA	Aerojet Rocket Manufacturing	Public Water Supply Well Monitoring Well	159 2,180
CA	San Nicholas Island Ventura County, CA	U.S. Navy Firing Range	Public Water Supply (Springs)	12
CA	Stringfellow Superfund Site Glen Avon, CA	Hazardous Waste Disposal Facility	Monitoring Well Private Well	682,000 37
CA	UTC (United Technologies) San Jose, CA	Rocket Testing	Monitoring Well	180,000
CA	Whittaker-Bermite Ordnance Santa Clarita, CA	Ordnance Manufacturing	Public Water Supply Well	47
CA	Whittaker Ordinance Hollister, CA	Ordnance Manufacturing	Private Well Monitoring Well	810 88
CO	Pueblo Chemical Depot Pueblo, CO	Munition Demobilizing Open burn/ Open detonation	Monitoring Well	180
GA	Unregulated Contaminant Monitoring Rule (UCMR) data Houston County, GA	Unknown	Public Water Supply	5.2
GA	Unregulated Contaminant Monitoring Rule (UCMR) data Oconee County, GA	Unknown	Public Water Supply	38

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE RELEASES TO THE ENVIRONMENT as of APRIL, 2003 [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc. ppb
IA	Ewart, IA	Unknown source	Livestock Well	29
IA	Hills, IA	Unknown source	Private Well	30
IA	Iowa Army Ammunition Plant Middleton, IA	Propellant handling	Monitoring Well	9
IA	Napier, IA	Agriculture(?)	Private Well	11
KS	Herington, KS	Ammunition Facility	Monitoring Well	9
MD	Aberdeen Proving Grounds Aberdeen, MD	Field Training - Pyrotechnics and Explosives	Public Water Supply Well Monitoring Well/ Hydropunch	5 24
MD	Naval Surface Warfare Center Indian Head, MD	Propellant Handling	Waste Discharge to Surface Water	>1,000
MD	White Oak Fed. Research Center (Naval Surface Warfare Center) White Oak, MD	Propellant Handling	Monitoring Well/ Hydropunch	798
MD	Unregulated Contaminant Monitoring Rule (UCMR) data Hagerstown, MD	Unknown	Public Water Supply	4
MA	Massachusetts Military Res. Barnstable County, MA	Disposal - Open burn/ Open detonation	Monitoring Well	100
MN	Unregulated Contaminant Monitoring Rule (UCMR) data New Brighton, MN	Unknown	Public Water Supply	4.5
MN	Unregulated Contaminant Monitoring Rule (UCMR) data Northfield, MN	Unknown	Public Water Supply	6
MO	ICI Explosives Joplin, MO	Explosives Facility	Monitoring Well	107,000
MO	Lake City Army Amm. Plant Independence, MO	Propellant Handling	Monitoring Well	70
NE	Lewiston, NE	Agricultural Chemical Facility	Shallow Private Well	5
NE	Mead, NE	Fireworks Facility	Monitoring Well	24
NV	Boeing/Rocketdyne near Reno, NV	Propellant Testing	Monitoring Well	400
NV	Kerr-McGee/BMI Henderson, NV	Perchlorate Manufacturing	Public Water Supply Monitoring Well Surface Water	24 3,700,000 120,000
NV	PEPCON Henderson, NV	Perchlorate Manufacturing	Monitoring Well	600,000

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE RELEASES TO THE ENVIRONMENT as of APRIL, 2003. [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc. ppb
NJ	Unregulated Contaminant Monitoring Rule (UCMR) data Middlesex County, NJ	Unknown	Public Water Supply	7
NJ	Picatinny Arsenal Morris County, NJ	Munitions Handling	Monitoring Well	627
NM	Cannon AFB Clovis, NM	Explosives Disposal	Public Water Supply	46
NM	New Mexico American Water Co Clovis, NM	Unknown	Public Water Supply Well	5.8
NM	Deming, NM	Agricultural	Public Water Supply Well	20
NM	Des Moines, NM	Agricultural	Public Water Supply Well	4.5
NM	Fort Wingate Depot Activity Gallup, NM	Explosives Disposal	Monitoring Well Soil	2,860 --
NM	Holloman AFB Alamogordo, NM	Rocket Testing	Monitoring Well Seasonal Surface Water Soil	40 16,000 --
NM	Los Alamos National Lab Los Alamos, NM	U.S. Dept of Energy Lab Chemicals	Public Water Supply Well Monitoring Well Deep Borehole Water	3 220 1,662
NM	Melrose Air Force Range Melrose, NM	Explosives	Public Water Supply Well	40.7
NM	Mountain View Albuquerque South Valley, NM	Agricultural	Public Water Supply Well	4.8
NM	White Sands Missile Range White Sands, NM	Rocket Testing	Monitoring Well Soil	21,000 --
NY	Unregulated Contaminant Monitoring Rule (UCMR) data Bethpage, NY	Unknown	Public Water Supply	5
NY	Unregulated Contaminant Monitoring Rule (UCMR) data Plainview, NY	Unknown	Public Water Supply	11
NY	Westhampton Suffolk County, NY	Unknown Source(s), Possibly Agricultural	Public Water Supply Well Monitoring Well	16 3,370
NY	Yaphank Suffolk County, NY	Fireworks	Private Well Monitoring Well	26 122
NC	Unregulated Contaminant Monitoring Rule (UCMR) data Nash County, NC	Unknown	Public Water Supply	5.8
OR	Umatilla Army Depot, Ammunition Demolition Activity Hermiston, OR	Munitions Disposal OB/OD	Monitoring Well	10

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE RELEASES TO THE ENVIRONMENT as of APRIL, 2003. [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc. ppb
OR	Elf Atochem Portland, OR	Perchlorate Manufacturing	Monitoring Well	1000
PA	Unregulated Contaminant Monitoring Rule (UCMR) data Berks County, PA	Unknown	Public Water Supply	4
PA	Unregulated Contaminant Monitoring Rule (UCMR) data Crawford County, PA	Unknown	Public Water Supply	33
PA	Unregulated Contaminant Monitoring Rule (UCMR) data Huntingdon County, PA	Unknown	Public Water Supply	6.7
PA	Unregulated Contaminant Monitoring Rule (UCMR) data Lancaster County, PA	Unknown	Public Water Supply	12
TX	Andrews County, TX	Unknown Source(s)	Public Water Supply Well	15.8
TX	Dawson County, TX	Unknown Source(s)	Public Water Supply Well Private Well	26 58.8
TX	Ector County, TX	Unknown Source(s)	Public Water Supply Well	5
TX	Gaines County, TX	Unknown Source(s)	Public Water Supply Well Private Well	27 30
TX	Glasscock County, TX	Unknown Source(s)	Public Water Supply Well Private Well	1.1* 3* *estimated
TX	Howard County, TX	Unknown Source(s)	Public Water Supply Well Private Well	1.4* 26 *estimated
TX	Unregulated Contaminant Monitoring Rule (UCMR) data Kleburg County, TX	Unknown Source	Public Water Supply Well	4.5
TX	Unregulated Contaminant Monitoring Rule (UCMR) data Hockley County, TX	(s)Improper Cathodic Protection	Elevated Storage Tank	32
TX	Lone Star Army Ammunition Plant Texarkana, TX	Propellant and Munitions Handling	Monitoring Well Surface Water Soil	23 6 --
TX	Longhorn Army Ammunition Depot Karnak, TX	Propellant Handling	Monitoring Well Reported in Surface Water Soil	169,000 -- --
TX	Martin County, TX	Unknown Source(s)	Public Water Supply Well Private Well	32 19.1

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.

OCCURRENCE AND POTENTIAL SOURCES OF PERCHLORATE RELEASES TO THE ENVIRONMENT as of APRIL, 2003. [a]

State	Location	Suspected Source	Type of Contamination	Max. Conc. ppb
TX	McGregor Naval Weapons Plant McGregor, TX	Propellant Handling	Monitoring Well Reported in Surface Water Soil	91,000 – --
TX	Midland County, TX	Unknown Source(s)	Public Water Supply Well	46
TX	PANTEX Plant (USDOE) Amarillo, TX	Explosives	Monitoring Well	340
TX	Red River Army Depot Texarkana, TX	Propellant Handling	Monitoring Well	80
UT	Alliant Tech Systems Magna, UT	Rocket Manufacturing	Public Water Supply Well	16
UT	Thiokol Promontory, UT	Rocket Manufacturing	Water Supply Well (Inactive)	42
VA	Unregulated Contaminant Monitoring Rule (UCMR) data Accomack County, VA	Unknown	Public Water Supply	4.3
WA	Camp Bonneville near Vancouver, WA	Explosives/Propellant OB/OD Disposal	Monitoring Wells	200
WA	Unregulated Contaminant Monitoring Rule (UCMR) data Lakewood, Pierce County, WA	Unknown	Public Water Supply	6
WA	Unregulated Contaminant Monitoring Rule (UCMR) data Puyallup, Pierce County, WA	Unknown	Public Water Supply	8
WV	Allegheny Ballistics Lab Rocket Center, WV	Rocket Research, Production, OB/OD	Surface Discharge of Groundwater Extraction	400

(a) - Information from Mayer (2003). All reports have been confirmed by federal, state or county. Soil concentrations are not listed.

Appendix C: More Detailed Information on Natural Perchlorate and Forensic Studies

This appendix contains manuscripts and supporting information published during the course of this ESTCP project. All manuscripts are reprinted with permission of the American Chemical Society.

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Atacama Perchlorate as an Agricultural Contaminant in Groundwater: Isotopic and Chronologic Evidence from Long Island, New York

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Perchlorate (ClO_4^-) is a common groundwater constituent with both synthetic and natural sources. A potentially important source of ClO_4^- is past agricultural application of ClO_4^--bearing natural NO_3^- fertilizer imported from the Atacama Desert, Chile, but evidence for this has been largely circumstantial. Here we report ClO_4^- stable isotope data ($\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$), along with other supporting chemical and isotopic environmental tracer data, to document groundwater ClO_4^- contamination sources and history in parts of Long Island, New York. Sampled groundwaters were oxic and ClO_4^- apparently was not affected by biodegradation within the aquifers. Synthetic ClO_4^- was indicated by the isotopic method in groundwater near a fireworks disposal site at a former missile base. Atacama ClO_4^- was indicated in agricultural and urbanizing areas in groundwaters with apparent ages >20 years. In an agricultural area, ClO_4^- concentrations and ClO_4^-/NO_3^- ratios increased with groundwater age, possibly because of decreasing application rates of Atacama NO_3^- fertilizers and/or decreasing ClO_4^- concentrations in Atacama NO_3^- fertilizers in recent years. Because ClO_4^-/NO_3^- ratios of Atacama NO_3^- fertilizers imported in the past ($\sim 2 \times 10^{-3}$ mol mol^{-1}) were much higher than the ClO_4^-/NO_3^- ratio of recommended drinking-water limits (7×10^{-5} mol mol^{-1} in New York), ClO_4^- could exceed drinking-water limits even where NO_3^- does not, and where Atacama NO_3^- was only a minor source of N. Groundwater ClO_4^- with distinctive isotopic composition was a sensitive indicator of past Atacama NO_3^- fertilizer use on Long Island and may be common in other areas that received NO_3^- fertilizers from the late 19th century through the 20th century.

Introduction

Perchlorate (ClO_4^-) in drinking water or food can cause health problems by interfering with iodide uptake and hormone production in the thyroid gland (*1*). Recommended limits for ClO_4^- concentrations in drinking water in the USA range from about 1 to 25 μg L^{-1} (10−250 nmol L^{-1}), reflecting uncertainty about the harmful exposure level. Perchlorate is a component of solid rocket fuels and explosives, and these products and their manufacturing facilities are well-known sources of local ClO_4^- contamination. Other synthetic sources of ClO_4^- include fireworks, road flares, chlorate herbicides, and bleach products, but the extent of their influence on groundwater is largely unknown. In addition, ClO_4^- is a minor component of natural NO_3^--rich salt deposits in the Atacama Desert in Chile, which have been refined and distributed worldwide as NO_3^- fertilizer products (mostly $NaNO_3$). Atacama NO_3^- fertilizer has been imported to the USA since the late 1800s. Although manufactured sources of N fertilizer have been more important globally since the middle 1900s, Atacama NO_3^- is still used locally on some crops, including tobacco, cotton, vegetables, and fruit trees including citrus (*2*), and it is a common component of "organic" fertilizers. ClO_4^- also is present in atmospheric deposition (*3*), and natural accumulations of ClO_4^- presumed to be of atmospheric origin are common in desert soils of the southwestern USA (*4*). Groundwater concentrations of nonsynthetic ClO_4^- of the order of 10−1000 nmol L^{-1} or more could result from historical Atacama NO_3^- fertilizer use or from evaporative enrichment of atmospheric deposition in arid regions (*2, 5, 6*), but it may be difficult to distinguish these and other sources of ClO_4^- on the basis of chemical and hydrologic evidence alone. Recent studies indicate ClO_4^- from different natural and synthetic sources has distinctive Cl and O isotopic compositions (*7*−*9*), but field studies of these differences are just beginning and they have not been explored systematically in diverse groundwater settings.

The objectives of the current study were to test the applicability of Cl and O isotopes as source indicators of groundwater ClO_4^- in the humid eastern USA, and to determine sources of ClO_4^- affecting groundwater usability in Suffolk County, eastern Long Island, New York. Groundwater is the sole source of public water supply and a carefully protected resource in Suffolk County. Perchlorate is present in groundwater in many locations on Long Island (*10*) and some important public water supplies are being treated to remove ClO_4^- at substantial cost, based on a New York State drinking-water guidance level of 5 μg L^{-1} (50 nmol L^{-1}). Various potential sources of ClO_4^- are present, including agriculture (past or present), fireworks manufacture and use, military bases including missile storage and launch facilities, road-flare runoff, and lawn fertilizer, among others.

Experimental Section

Sample Locations. Groundwater containing ClO_4^- was collected from three different areas in Suffolk County (Figure 1a), each representing a different land use and/or water use. The DL transect (North Fork area, near Cutchogue) consisted of three clusters of three observation wells (5.1 cm diameter, 1.5 m screened interval) in a northwest-southeast array across the middle of the North Fork Peninsula (Figure 1b). Land use in this area in 2006−2007 was largely agricultural, with turf grass, corn, grapes, and potatoes as important crops. The DL wells were screened within the surficial upper glacial aquifer, which consists of Pleistocene moraine and outwash sediments dominated by brownish sand and gravel with local

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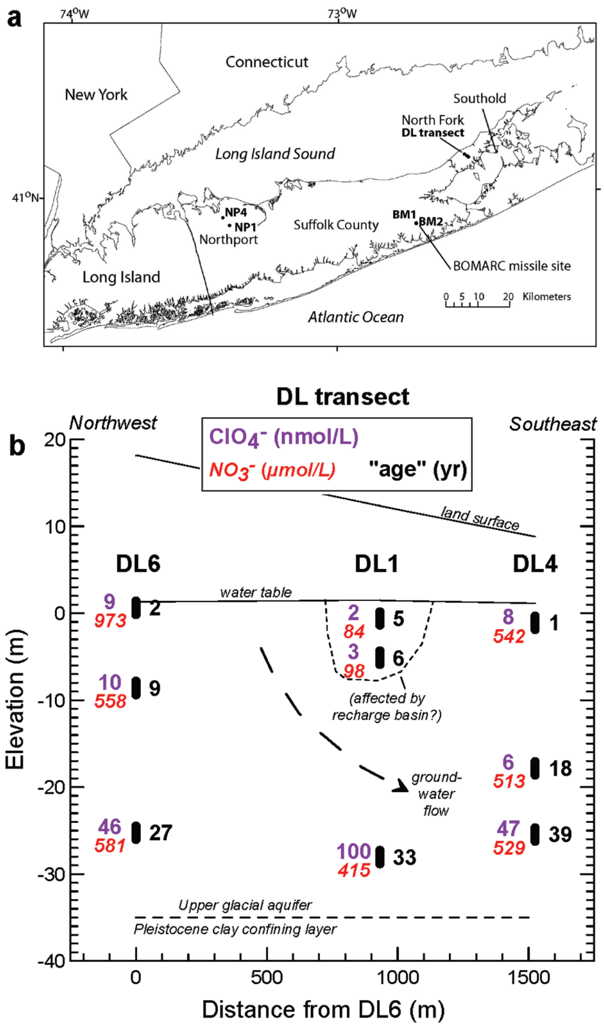

FIGURE 1. (a) Map of Long Island, New York, showing locations of samples. (b) Vertical profile of the DL groundwater transect in 2007 showing well screens (vertical bars), ClO_4^- and NO_3^- concentrations, and composite mean apparent groundwater ages.

silt and clay (*11*). The deepest well screens were a short distance above a lower confining unit, which begins at approximately −35 to −31 m elevation (*12*) and consists of Pleistocene glacial-lake clay, silt, and sand.

Two samples were obtained from observation wells (BM1, BM2) at a former BOMARC missile site near Westhampton (Figure 1a). The BOMARC (Boeing and Michigan Aerospace Research Center) missile program at this site was active between 1957 and 1969 (http://www.dmna.state.ny.us/forts/fortsQ_S/suffolkBOMARC.htm) and included the first version of the BOMARC missile, the CIM-10A, which was powered in part by liquid-fuel booster rockets; available data do not indicate deployment of the CIM-10B with solid-fuel rockets. At the time of this study (2006−2008), this site was used by Suffolk County as a police training facility and included a weapons firing range and fireworks disposal pit. The general direction of groundwater flow was from north to south. Both sampled wells were upgradient from the former missile silos and downgradient from the firing range and fireworks disposal pit.

Two samples were obtained from large-volume production wells (NP1, NP4) in the Northport area (Figure 1a). This was an important farming region prior to the 1950s, and some vegetable and sod farms still existed in the area in 2007, but the majority of the land was residential at the time of this study. The screened intervals of these wells (NP1 = 117 ± 9 m, NP4 = 92 ± 9 m below the water table) were in the Magothy aquifer, which underlies the upper glacial aquifer.

Sample Collection and Analyses. Samples were collected for isotopic analysis of ClO_4^-, NO_3^-, and SO_4^{2-}, along with major and minor element chemistry, major dissolved gases (Ar, N_2, O_2, and CH_4), and atmospheric environmental tracers (^3H, ^3He, SF_6, and chlorofluorocarbons (CFCs)) to determine the timing of ClO_4^- infiltration and its relation to other natural and anthropogenic constituents, as illustrated previously in studies of agricultural NO_3^- (*13*−*15*). Samples were collected mainly between December 2006 and January 2007. DL transect wells were resampled in December 2007 to April 2008 for dissolved gases, including SF_6 and CFCs. ClO_4^- was analyzed by IC/MS/MS at Texas Tech University (*3*). ClO_4^- for isotopic analysis was collected on Purolite A530E selective ion-exchange resin columns and then recovered, purified, and analyzed as described previously (*7*−*9*, *16*). Shallow DL wells were not analyzed for ClO_4^- isotopes because of low concentrations. Analytical methods and results for most constituents are summarized in the Supporting Information.

Results and Discussion

Distribution and Isotopic Composition of Perchlorate. Perchlorate was present in all samples (>1 nmol L^{-1}) and some concentrations exceeded the New York drinking-water guidance level of 50 nmol L^{-1} (5 μg L^{-1}) (Table 1). The highest concentrations by far were from the BOMARC site (BM1 = 43 400 nmol L^{-1}, BM2 = 3550 nmol L^{-1}), where fireworks disposal and military activities were potential sources. In the DL transect, ClO_4^- concentrations were relatively high in the deepest wells (46−100 nmol L^{-1}) and lower in the shallower wells (2−10 nmol L^{-1}). Production wells in the Northport area (NP1, NP4) had relatively high ClO_4^- concentrations (84−112 nmol L^{-1}).

Previous studies indicate $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ values of ClO_4^- (defined in Table 1) are related to the environment and process of ClO_4^- formation (*7*−*9*). Distinctive isotopic signatures have been documented for (1) synthetic ClO_4^- formed commercially by electrolytic oxidation of NaCl brine, (2) natural ClO_4^- accumulated with NO_3^- in the Atacama Desert and distributed as a component of natural NO_3^- fertilizer, and (3) other natural sources in the southwestern USA (Figure 2). The $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ values of Long Island ClO_4^- fall into 2 distinct groups (Table 1, Figure 2): the BOMARC wells plot within the synthetic ClO_4^- ranges, whereas the NP production wells and the deep DL transect wells plot within the Atacama ClO_4^- ranges. There is no clear isotopic evidence for ClO_4^- biodegradation, which is consistent with other data indicating the sampled groundwaters were oxic and not denitrified (see below).

At the BOMARC site, the synthetic ClO_4^- isotopic signature was associated with unusually high ClO_4^- concentrations, relatively low NO_3^- concentrations, and young apparent groundwater ages (1−2 years; see below). Sample BM1 (adjacent to a fireworks disposal pit) had anomalously high concentrations of K, Sr, and Sb, which are common constituents of fireworks, used for color and brightness (*17*). Although various local sources of synthetic ClO_4^- may be present at this former missile site, leaching of unexploded fireworks is supported by proximity of the upgradient well (BM1) to a fireworks disposal pit and association of ClO_4^- with trace elements that are common constituents of fireworks.

At the DL and NP sites, the Atacama ClO_4^- isotopic signature was associated with relatively high concentrations of NO_3^- and locally with other constituents including Ca, Mg, Cl^-, and SO_4^{2-}, indicating recharge beneath agricultural (or horticultural) land receiving various types of fertilizers (see below). No other ClO_4^- sources reported to date have

TABLE 1. Selected Data for Groundwater Samples (Extracted from Table S1 in the Supporting Information)[a]

well	depth BWT (m)	GW age (years)	NO_3^- (μM)	ClO_4^- (nM)	ClO_4^- $\delta^{37}Cl$ (‰)	ClO_4^- $\delta^{18}O$ (‰)	ClO_4^- $\Delta^{17}O$ (‰)
BM1	11.6	2	97	43400	0.2	−16.7	0.1
BM2	2.1	1	72	3550	0.2	−17.7	−0.1
NP1	117.0	35	792	112.1	−12.5	−3.0	9.4
NP4	92.0	41 ± 4	336	84.3	−13.2	−8.2	7.9
DL6s	0.6	2 ± 2	973	8.7	na	na	na
DL6m	9.8	9 ± 3	558	10.2	na	na	na
DL6d	26.5	27 ± 5	581	45.8	−12.6	−6.0	8.4
DL1s	2.1	5 ± 8	84	1.5	na	na	na
DL1m	6.7	6 ± 3	98	3.4	na	na	na
DL1d	29.5	33 ± 3	415	99.6	−14.0	−6.1	8.2
DL4s	2.2	1 ± 4	542	7.7	na	na	na
DL4m	19.0	18 ± 3	513	5.8	na	na	na
DL4d	26.6	39 ± 1	529	46.6	−12.9	−1.6	10.2

[a] DL well clusters are designated shallow (s), medium (m), and deep (d). Depth BWT = depth below water table, middle of well screen. Mean and standard deviation of composite apparent groundwater (GW) ages are from various combinations of techniques (no ± if single technique, see Table S1 and Figure S4 in the Supporting Information). $\mu M = \mu mol\ L^{-1}$; $nM = nmol\ L^{-1} = 10^{-3}\ \mu mol\ L^{-1}$. Stable isotope data are reported as follows (see the Supporting Information for calibration data) (*8, 42*): $\delta^{37}Cl = [n(^{37}Cl)/n(^{35}Cl)]_{sample}/[n(^{37}Cl)/n(^{35}Cl)]_{SMOC} - 1$; $\delta^{18}O = [n(^{18}O)/n(^{16}O)]_{sample}/[n(^{18}O)/n(^{16}O)]_{VSMOW} - 1$; $\Delta^{17}O = [(1 + \delta^{17}O)/(1 + \delta^{18}O)^{0.525}] - 1$; values given in parts per thousand (‰).

the distinctive combination of low $\delta^{37}Cl$, low $\delta^{18}O$, and high $\Delta^{17}O$ that characterize the Atacama ClO_4^-. High $\Delta^{17}O$ values in both ClO_4^- and NO_3^- from the Atacama Desert and a few other hyper-arid environments have been interpreted as a result of photochemical reactions involving O_3, leading to the conclusion that those salts represent long-term accumulations of atmospheric deposition (*7, 18*). Other studies indicate NO_3^- and ClO_4^- isotopic compositions of Atacama NO_3^- fertilizer products typically were similar to those of the natural salt deposits from which they were produced (*7–9, 18, 19*). The distinctive ClO_4^- isotopic signature apparently was not altered substantially by plants, soils, or aquifer interactions during transport from fields to wells in Suffolk County (Figure 2).

Dissolved Gases, Recharge Conditions, and Redox Status of Groundwater. Concentrations of Ne, Ar, N_2, O_2, and CH_4 were used to assess recharge conditions (needed for groundwater dating) and subsequent redox reactions that might have affected ClO_4^- stability in the aquifer. Mean concentrations (± 1σ) of Ne, Ar, and N_2 were 0.0106 ± 0.0009 (n = 11), 18.0 ± 0.3 (n = 22), and 709 ± 23 (n = 22) $\mu mol\ L^{-1}$, respectively. These data were compared to hypothetical aqueous concentrations in equilibrium with air at the water table to derive estimates of recharge temperature, concentrations of excess air trapped and dissolved during recharge, and concentrations of excess N_2 that might have been produced in the saturated zone by denitrification (*13, 15*) (see the Supporting Information). Apparent recharge temperatures and concentrations of excess air were 10.8 ± 0.7 °C and 2.3 ± 0.7 cm^3-STP L^{-1} when calculated from Ne+Ar data (n = 10), and 10.0 ± 0.7 °C and 1.8 ± 0.7 cm^3-STP L^{-1} when calculated from Ar+N_2 data (n = 22), assuming excess air was dissolved without fractionation. Concentrations of excess N_2 were undetectable (−14 ± 11 $\mu mol\ L^{-1}$) when calculated from all three gases (assuming Ne+Ar recharge conditions). $\delta^{15}N$ values of dissolved N_2 (mean = +0.68 ± 0.07%, n = 22) were consistent with dissolved atmospheric N_2 (i. e., no discernible excess nonatmospheric N_2). Concentrations of O_2 ranged from about 240 to 350 $\mu mol\ L^{-1}$ (mean = 294 ± 32, n = 22), about 65–97% of the maximum recharge values (360–370 $\mu mol\ L^{-1}$) based on the Ne, Ar, and N_2 data. All CH_4 concentrations were <0.1 $\mu mol\ L^{-1}$. In summary, combined evidence from dissolved gas data indicates the sampled aquifers were oxic and denitrification within the saturated zone was minimal (e.g., affected <5% of the NO_3^- in the DL transect). Because microbial ClO_4^- reduction occurs mainly in suboxic conditions and commonly is inhibited by NO_3^- (*20, 21*), these data indicate that microbial ClO_4^- reduction in the sampled parts of the saturated zone was unlikely and ClO_4^- concentrations and isotopic signatures likely reflect initial values at the time of recharge.

Groundwater Ages and Fluxes. Groundwater dating provided information needed to evaluate recharge fluxes and possible decade-scale historical changes in recharge chemistry. Apparent recharge dates and ages of groundwater samples (representing time spent in the saturated zone after isolation from air during recharge) were estimated from concentrations of various atmospheric environmental tracers ^3H−^3He, SF_6, CFC11, CFC12, and CFC113, as summarized previously (*22*) (see the Supporting Information). Apparent recharge dates and ages derived individually from different tracers were discordant in some cases because (1) apparent CFC recharge dates after 1990 had large uncertainties caused by peaking atmospheric concentrations, (2) apparent SF_6 dates before 1985 may have been affected by low-level background concentrations or contamination, (3) some tracers were contaminated locally (e.g., CFCs in production wells), and (4) some samples probably were mixtures of waters with varying ages. After selection of data based on these criteria (see the Supporting Information), we estimated a composite mean apparent age for each well, with results ranging from 1 to 41 years and typical uncertainties of the order of 2–5 years (Table 1).

At the DL transect, apparent groundwater ages ranged from 1 to 39 years and increased with depth (Figure 1b), consistent with distributed recharge (*23*). The mean recharge rate was estimated by fitting the DL data with an exponential age-depth model (*23*) with saturated thickness of 37 m and porosity of 0.30 (*24*) (see Figure S5 in the Supporting Information). Results of multiple fits with different data subsets yielded a mean recharge rate of 0. 50 ± 0. 05 m $year^{-1}$. This is about 44% of the mean annual precipitation (1.14 m $year^{-1}$) and similar to a previously estimated recharge rate (0.56 ± 0.05 m $year^{-1}$) based on physical measurements and meteorological data in the North Fork area (*24, 25*).

At the NP production wells, composite apparent groundwater ages derived from CFCs and ^3H−^3He were 35 and 41 years, but the well screens were relatively deep below the water table and would imply unrealistic recharge rates if they represented undisturbed aquifer conditions. Low ^3H concentration at NP4 (1.6 TU) and high rate of pumping from these and other wells in this area indicate these samples probably were mixtures of young and old water and the age profiles may have been disturbed. Nevertheless, despite

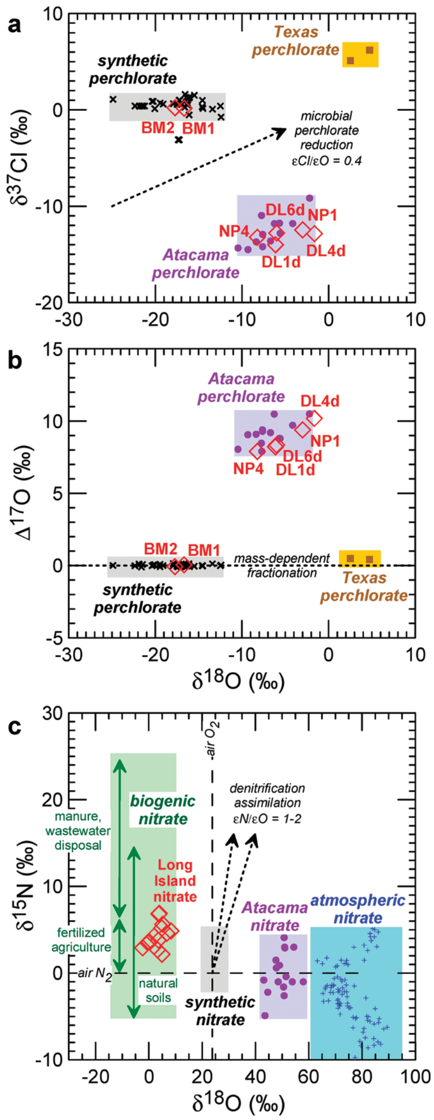

FIGURE 2. Summary of isotope data for ClO_4^- and NO_3^- in groundwater samples (Table 1 and Table S1 in the Supporting Information), compared with major known sources (modified, with additional data, from refs *8, 18, 30*) and bioreduction trends (*42*−*44*). Texas perchlorate is believed to be natural (*6*), but with isotopic composition different from Atacama perchlorate (*8*).

various uncertainties, the combined results of groundwater dating indicate ClO_4^- and other constituents were present in recharge in varying amounts over a period of about 40 years or more.

Agricultural Chemicals in Groundwater. Elevated ClO_4^- concentrations were associated with NO_3^- and other chemicals commonly enriched in agricultural recharge, including Ca, Mg, Cl^-, and SO_4^{2-} (Figure 3 and Figure S6 in the Supporting Information). Two wells (DL1s, DL1m) near a partially wooded recharge basin had low concentrations of ClO_4^-, NO_3^-, and other major solutes and are considered to represent diluted or nonagricultural recharge. Because Long Island is surrounded by ocean, elevated salt concentrations in groundwater could be related to mixing with marine fluids at depth, or to locally high concentrations of marine salts in atmospheric deposition. For comparison with possible recharge values, concentrations of selected constituents in local precipitation were multiplied by 2.3 (= precipitation/recharge) to account for evapotranspiration, and again by 2.0 to represent hypothetical contributions from dry deposition (see Table S2 in the Supporting Information). Potential concentrations of Cl^-, SO_4^{2-}, and dissolved inorganic N ($NH_4^+ + NO_3^-$) for atmospheric recharge components were similar to the lowest values in our groundwater samples, whereas most samples were relatively enriched in Cl^-, SO_4^{2-}, and NO_3^-, along with Ca and Mg, in proportions that were different from those of seawater (Figure 3). Road salts and local deposition of marine aerosols near the coast could be responsible for some elevated Na and Cl^- concentrations. Marine aerosols probably were not a major cause of high Ca and SO_4^{2-} concentrations because of their much larger enrichments and because $\delta^{34}S[SO_4^{2-}]$ values (+1 to +8 ‰) were lower than that of seawater (+21‰) (see the Supporting Information).

The same chemicals enriched in some of our samples (NO_3^-, Cl^-, SO_4^{2-}, Ca, and Mg) were interpreted previously to have agricultural sources on Long Island, based on statistical analyses of groundwater chemistry and land use (*26*−*28*). Similar enrichments (with the exception of SO_4^{2-}) have been attributed to agricultural effects in other mid-Atlantic aquifers (*14, 29*). The isotopic composition of NO_3^- was consistent with nitrification in aerated soils (Figure 2c), and similar to those of high-NO_3^- groundwater beneath fertilized agricultural areas elsewhere in the eastern USA (*30*). Therefore, we interpret these constituents as evidence for agricultural inputs, including N fertilizer in various forms, Ca−Mg−carbonate commonly used to neutralize acidity, possibly some KCl as a source of K, and S or SO_4^{2-} (e. g., $CaSO_4$, $[NH_4]_2SO_4$) to fertilize potatoes, improve soil texture, combat fungi, or regulate acidity in vineyards. The pesticide aldicarb, applied to control golden nematode and Colorado potato beetle from 1975−1979, was reported in shallow groundwater near the DL transect in the late 1970s and 1980s (*12*).

Concentrations of NO_3^- in DL wells (excluding DL1s and DL1m) ranged from 415 to 973 μmol L^{-1}. Combined with the estimated recharge rate (0.50 m $year^{-1}$), these data indicate NO_3^- recharge fluxes of 0.21−0.49 mol m^{-2} $year^{-1}$ (2.9−6.8 g m^{-2} $year^{-1}$). Agricultural land-use data (*31*) combined with N-loading data (*32*) indicate the mean application rate of fertilizer N on cropland in Suffolk County was approximately 24 ± 4 g $m^{-2}year^{-1}$ from 1987 to 2001. The fraction of that applied agricultural N load that hypothetically could account for the range of DL recharge NO_3^- fluxes (12−28%) is within range of fractional NO_3^- infiltration losses estimated by similar methods in other well-drained agricultural areas in the eastern USA (*14, 33*). Thus, although spatial variations are to be expected, and temporal loading variations may not be reflected precisely in recharge history, our estimated NO_3^- recharge fluxes are consistent with agricultural effects in the region.

For ClO_4^-, estimated recharge fluxes indicated by DL wells (excluding DL1s and DL1m) were 0.29−5.0 × 10^{-5} mol m^{-2} $year^{-1}$ (0.29−5.0 × 10^{-3} g m^{-2} $year^{-1}$). In arid regions, high evapotranspiration factors and(or) redissolution of accumulated salts in the unsaturated zone could yield concentrations of atmospheric anions including ClO_4^- as high as those observed in DL and NP groundwaters (*5, 34*). However, the low evapotranspiration factors and high recharge rates on Long Island are not consistent with this mechanism for concentrating natural atmospheric deposition, which typically has $ClO_4^- < 2$ nmol L^{-1} (*3, 35*). Although correlations between ClO_4^- and other agriculture-related constituents are poor (Figure 3), observed concentrations and fluxes of ClO_4^-, and co-occurrence of ClO_4^- with other agricultural constituents, are consistent with ClO_4^- isotope data indicating an agricultural (or horticultural) source for ClO_4^- in DL and NP samples (see below).

Selected fertilizers used on Long Island around the time of this study had ClO_4^- concentrations ranging from about

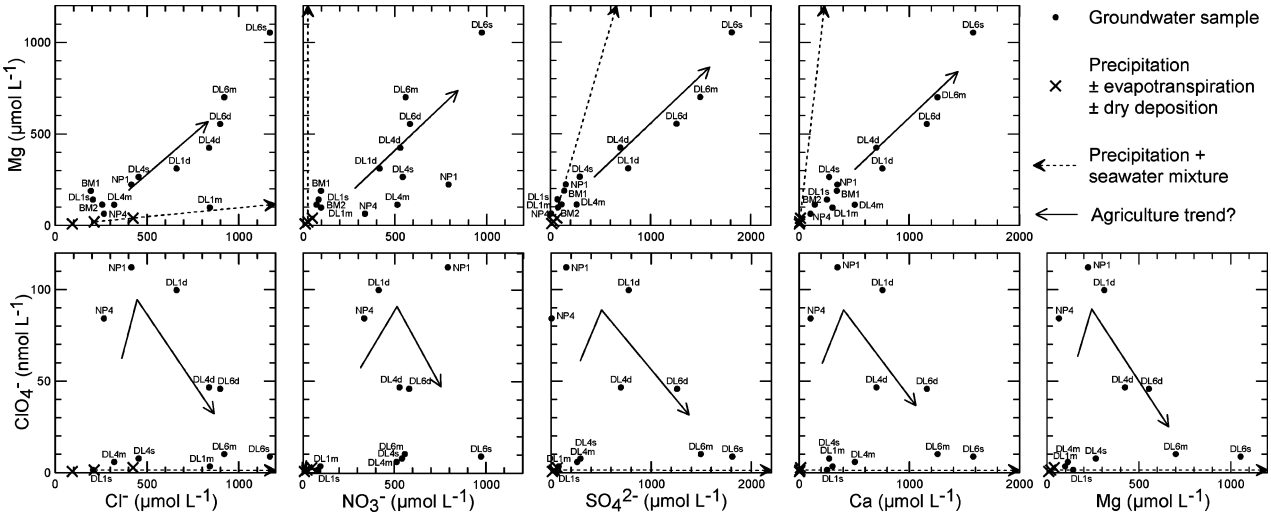

FIGURE 3. Concentrations of ClO_4^- and other selected constituents in groundwater. Dotted arrows indicate hypothetical mixtures of atmospheric deposition and seawater. Solid arrows indicate generalized hypothetical trends related to increasing overall agricultural effects on groundwater chemistry. ClO_4^- concentrations are high in samples with moderate agricultural impacts.

0.001 to 9 mg kg^{-1} (see Table S3 in the Supporting Information). Relatively high concentrations were in dried plant material ("kelp" product) and some other organic fertilizers, some of which may have included Atacama NO_3^- components. Sources like these could be responsible for some groundwater ClO_4^-, but only if applied at relatively high rates, as their ClO_4^- concentrations are orders of magnitude lower than those of Atacama $NaNO_3$ imported in the past (~1400−4000 mg kg^{-1}; see Table S3 in the Supporting Information). Inconsistent reports of ClO_4^- in natural KCl and other evaporite salts have not been fully resolved, but ClO_4^-/Cl^- ratios in some common KCl fertilizer products are too low to account for the ClO_4^- in our samples (*36*−*39*) (see Table S3 in the Supporting Information). Our data do not indicate a correlation between ClO_4^- and either K or Cl^- in Long Island groundwater.

Relation between Perchlorate and Nitrate in Agricultural Recharge. Although ClO_4^- isotope data indicate an Atacama source for groundwater ClO_4^- in some areas, NO_3^- isotope data do not indicate an Atacama source for the NO_3^- (Figure 2). This apparent discrepancy can be explained by a combination of two factors: (1) Atacama NO_3^- was only a small fraction of total applied N fertilizer, and (2) Atacama NO_3^- may have been largely assimilated and replaced in recharging groundwater with new biogenic NO_3^- formed in agricultural soils, whereas Atacama ClO_4^- may have been recharged without being replaced or lost substantially by processes resulting in isotopic alteration. Replacement of Atacama NO_3^- with biogenic NO_3^- in soils would be consistent with observations elsewhere, indicating the distinctive O isotopic composition of atmospheric NO_3^- is preserved only in hyper-arid environments and lost where more biologically active soils exist (*18, 19*). In some environments, therefore, the existence and isotopic composition of ClO_4^- may be more reliable indicators of atmospheric deposition or Atacama NO_3^- fertilizer use than the existence or isotopic composition of NO_3^-.

Hypothetical concentrations of Atacama NO_3^- that potentially could be associated with observed groundwater ClO_4^- can be estimated by comparing concentrations and ClO_4^-/NO_3^- ratios of groundwaters and Atacama NO_3^- fertilizers. If ClO_4^- in older NP and DL groundwaters (>20 years, 46−112 nmol L^{-1}) was derived from Atacama NO_3^- fertilizer with a ClO_4^-/NO_3^- mole ratio of 2×10^{-3} (see Table S3 in the Supporting Information), then the maximum concentration of NO_3^- from that source would be around 23−56 μmol L^{-1}, and corresponding maximum Atacama N recharge fluxes would be around 0.011−0.028 mol m^{-2} $year^{-1}$. Compared individually by sample, these Atacama NO_3^- fluxes would equal 4−12% of estimated total NO_3^- in recharge. Compared to county-level loading data, the amount of Atacama fertilizer N needed to account for the ClO_4^- would be only about 0.7−1.6% of total N applied per unit area of cropland. Conversely, if all applied fertilizer N was Atacama NO_3^-, then hypothetical ClO_4^- concentrations could have been as high as 670−1580 nmol L^{-1} (67−157 μg L^{-1}) if based on recharge N data, or 6850 nmol L^{-1} (682 μg L^{-1}) if based on county-level cropland loading data. These comparisons would need to be modified if ClO_4^- was removed permanently by plants or microbial processes in soils. Nevertheless, they are consistent with Atacama NO_3^- N being only a minor source of the total NO_3^- N, and they illustrate the potential for small amounts of Atacama NO_3^- fertilizer to have contaminated large amounts of groundwater with ClO_4^- in the past.

Dated Long Island groundwaters provide a record of decreasing ClO_4^- and relatively constant or slightly increasing NO_3^- in recharge between about 1966 and 2006 (Figure 4). An upward decrease in ClO_4^- concentrations in DL groundwater could indicate either (1) decreasing proportion of Atacama NO_3^- with constant ClO_4^- concentration in applied N fertilizer mixtures, or (2) constant application rates of both Atacama NO_3^- and other N fertilizers during a period when ClO_4^- concentrations in Atacama NO_3^- fertilizer decreased. Compared to the mean molar ratio of ClO_4^-/NO_3^- in Atacama NO_3^- ores and fertilizer products imported in the 20th century (~2×10^{-3}), some reports indicate the refining process was changed around 2000 to reduce ClO_4^- concentrations in NO_3^- fertilizer product by about 1 order of magnitude (*40*). A statement from a major manufacturer in 2001 indicates new $NaNO_3$ product should have $ClO_4^- < 100$ mg kg^{-1} ($ClO_4^-/NO_3^- < 8.5 \times 10^{-5}$ mol mol^{-1}) (*2*). The ClO_4^- concentrations and ClO_4^-/NO_3^- ratios in recharge represented by our samples apparently decreased around 20−30 years ago (Figure 4), before the announced decrease in Atacama fertilizer ClO_4^- content. Therefore, we interpret our data as indicating a decreasing application rate of Atacama NO_3^- fertilizer with pre-2000 ClO_4^- concentrations, which may or may not have been followed by post-2000 low-ClO_4^- Atacama fertilizer. Continued use of Atacama fertilizer with $ClO_4^- <$ 100 μg kg^{-1} at past application rates presumably would lower the groundwater-recharge concentrations further.

The groundwater recharge trends of decreasing ClO_4^- and relatively constant or slightly increasing NO_3^- concentrations

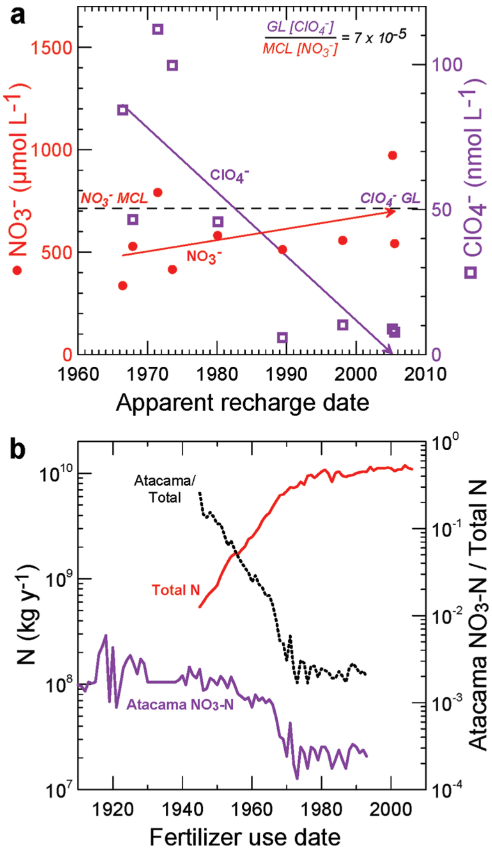

FIGURE 4. Trends related to changing agricultural inputs. (a) ClO_4^- and NO_3^- concentrations in dated groundwaters, compared to EPA NO_3^- maximum contaminant level (MCL) and New York ClO_4^- guidance level (GL). Data are from Northport (NP wells) and North Fork (DL transect, minus DL1s and DL1m). (b) Records of national (USA) Atacama NO_3^- and total N fertilizer use (*2, 45, 46*).

between 1966 and 2006 (Figure 4A) resemble qualitatively the national trends of Atacama and non-Atacama N fertilizer use in the USA (Figure 4B). Production wells 200−300 m southwest of the DL transect produced water with $ClO_4^- \approx$ 20−60 nmol L^{-1} from open intervals approximately 26−33 m below the land surface (Suffolk County Water Authority data from 2005−2006), possibly representing the gradient between low and high ClO_4^- in the DL profile. Northport data also indicate relatively high ClO_4^- concentrations in groundwaters several decades old, recharged when land use was more agricultural than at present. Wells screened in high-ClO_4^- zones in areas like these may experience decreasing ClO_4^- concentrations in the future as younger low-ClO_4^- groundwater moves downward, although large and variable pumping rates could disturb these patterns. Atacama ClO_4^- may be common in other oxic aquifers underlying areas with agricultural histories ranging from the late 19th century through the 20th century. Groundwaters in such areas could exhibit varying trends of Atacama ClO_4^- concentrations with depth and groundwater age, in many cases accompanied by decreasing NO_3^- concentrations with age (*41*).

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Note Added in Proof

In this paper, "solutes introduced into the hydrologic environment as a result of man's activities are referred to as contaminants, regardless of whether or not the concentrations reach levels that cause significant degradation of water quality" (*47*).

Supporting Information Available

Brief description of analytical methods, summary of data, interpretation of dissolved gases and atmospheric environmental tracers, description of NO_3^- and SO_4^{2-} isotope results, and additional tables and figures cited in the paper (Tables S1−S3 and Figures S1−S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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SUPPORTING INFORMATION

Atacama perchlorate as an agricultural contaminant in ground water: Isotopic and chronologic evidence from Long Island, New York, USA

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SUPPORTING INFORMATION

Sample collection and analyses

Groundwater samples were collected mainly between December 2006 and January 2007 using a portable submersible pump (Grundfos) for observation wells at DL transect and BOMARC, and permanently installed vertical turbine pumps for the NP production wells. DL transect wells were re-sampled in December 2007 to April 2008 for dissolved gases, including SF_6 and CFCs. Samples for major and minor element chemistry were filtered in the field and analyzed at the U.S. Geological Survey (USGS), Reston, VA. Cations and trace elements were analyzed by inductively coupled plasma mass spectrometry (ICPMS); major anions were analyzed by ion chromatography (IC). High ClO_4^- concentrations (samples BM1, BM2) were measured by IC at Shaw Environmental [1]; all others were measured by IC/MS/MS at Texas Tech University [2]. Major dissolved gas samples were collected in serum bottles, preserved with KOH, and analyzed at USGS for Ar, N_2, O_2, and CH_4 by gas chromatography (http://water.usgs.gov/lab/) and $\delta^{15}N$ of N_2 by continuous-flow isotope-ratio mass spectrometry [3].

Samples for ClO_4^- isotopic analysis were collected by pumping water through cartridges containing Purolite A530E anion exchange resin (approximately 1-2 L/min), then extracted, purified, and analyzed as described previously [4-7]. ClO_4^- was eluted from the resins with HCl+$FeCl_3$, precipitated as $CsClO_4$, purified, and tested for purity by Raman spectroscopy at Oak Ridge National Laboratory (ORNL). Aliquots of $CsClO_4$ were decomposed at 650°C to produce O_2 for $\delta^{18}O$ and $\delta^{17}O$ analysis at USGS in Reston, VA. CsCl from decomposition was converted to CH_3Cl for $\delta^{37}Cl$ analysis at the University of Illinois at Chicago (UIC). Stable isotope analyses of H_2O, NO_3^-, and SO_4^{2-} were done by isotope-ratio mass spectrometry at USGS in Reston, VA. H_2O was equilibrated with H_2 and CO_2 for measurement of δ^2H and $\delta^{18}O$, respectively [8] (http://isotopes.usgs.gov/). NO_3^- was reduced bacterially (*Pseudomonas aureofaciens*) to N_2O for simultaneous $\delta^{15}N$ and $\delta^{18}O$ analysis [9, 10]. SO_4^{2-} was precipitated as $BaSO_4$, which was converted to SO_2 and CO for measurement of $\delta^{34}S$ and $\delta^{18}O$, respectively [11, 12]. Co-precipitation of NO_3^- with $BaSO_4$ was quantified by measuring the amount of N_2 in the CO during $\delta^{18}O$ analysis, giving estimates of the fraction of total O derived from NO_3^- ($z[O_{NO3}]$) [13], but adjustments to SO_4^{2-} $\delta^{18}O$ values were not made because $\delta^{18}O$ values of NO_3^- and SO_4^{2-} were similar and adjustments were small. Isotopic reference materials were prepared and analyzed as samples, and data were normalized to the following values:[1, 5, 12, 14]:

For $\delta^{18}O$: -27.9 ‰ (USGS34 KNO_3), +26.7 ‰ (IAEA-NO3 $NaNO_3$), +57.5 ‰ (USGS35 $NaNO_3$), +8.6 ‰ (NBS127 $BaSO_4$), -17.0 ‰ (USGS37 $KClO_4$), +52.5 ‰ (USGS38 $KClO_4$)
For $\delta^{17}O$: -8.96 ‰ (USGS37 $KClO_4$), +102.5 ‰ (USGS38 $KClO_4$)
For $\delta^{37}Cl$: 0.0 ‰ (seawater Cl), +0.6 ‰ (USGS37 $KClO_4$), -87.2 ‰ (USGS38 $KClO_4$)
For $\delta^{15}N$: +4.7 ‰ (IAEA-NO3 $NaNO_3$), +180.0 ‰ (USGS32 KNO_3)
For $\delta^{35}S$: +0.5 ‰ (IAEA-SO5 $BaSO_4$), +21.1 ‰ (NBS127 $BaSO_4$)

Samples were collected for ground-water dating based on ^3H-^3He, SF_6, and chlorofluorocarbons (CFC11 = $CFCl_3$, CFC12 = CF_2Cl_2, CFC113 = $C_2F_3Cl_3$) as described previously [15-18](http://water.usgs.gov/lab/). SF_6 and CFC analyses were done by purge and trap gas chromatography with electron capture detection at USGS in Reston, Virginia; ^3H was analyzed by electrolytic enrichment and scintillation counting at USGS in Menlo Park, California; He and Ne isotopes were analyzed by mass spectrometry at Lamont-Doherty Earth Observatory, Palisades, New York.

Interpretation of dissolved gases and atmospheric environmental tracers

Concentrations of dissolved atmospheric gases (Ne, Ar, N_2) were used to estimate groundwater recharge temperatures (temperatures when last in equilibrium with unsaturated-zone air), concentrations of excess air (dissolved air in excess of the equilibrium concentration, attributed to incorporation of trapped air following recharge events), and concentrations of excess N_2 (reaction product of denitrification accumulated during reaction within the saturated zone), as described previously [19-23], using published solubility data [24, 25]. Calculated equilibration temperatures and concentrations of unfractionated excess air were slightly different when evaluated separately from Ne+Ar data and from Ar+N_2 data, assuming non-atmospheric N_2 was negligible (Figure S1). Applying the Ne+Ar derived temperatures and excess air values to all three gases resulted in slightly negative but insignificant calculated concentrations of excess N_2 for most samples (mean = -14 ± 11 μmol L^{-1}). The reasons for the minor discrepancies and slightly negative excess N_2 values are not known, but could include other types of excess air fractionation during recharge and(or) subsequent artifacts of sampling, handling, or analysis. Similar but generally smaller bias has been reported elsewhere based on similar datasets [21, 26]. All three gases can be made to fit a partial equilibrium (CE) model for fractionated excess air [27], but only with more variable and in some cases unrealistic temperatures (12 to 25°C) or excess air quantities. Additional noble gas data (e.g., Kr, Xe) and additional modeling might help to resolve these discrepancies. Nevertheless, the estimated recharge temperatures were indistinguishable from the long-term mean annual air temperature (10.4°C) at nearby Bridgehampton, New York (http://www.worldclimate.com/cgi-bin/grid.pl?gr=N40W072). Calculations of equilibrium partial pressures (atmospheric mixing ratios) of CFC11, CFC12, CFC113, SF_6, and He used to interpret ground-water ages were done by using the temperature and excess air values derived from Ar+N_2, which were measured simultaneously in the same samples, whereas Ne+Ar were measured by different methods in samples collected differently. Calculated concentrations of $^3He_{tritiogenic}$ and ^3H-^3He ages were insensitive to this choice of temperature basis.

Apart from potential sampling and analysis artifacts, different ground-water dating methods have a variety of limitations related to their respective atmospheric concentration histories (Figure S2), local and regional sources of contamination, variable transport through the unsaturated zone, dispersion within the aquifer, or mixing at the well screen. Given a set of concentrations for individual tracers in different samples (Table S1), we evaluated some of these issues by using tracer-tracer plots (Figure S3). These plots were used to compare sample data with hypothetical curves representing various expectations for ground-water samples that have discrete ages or age mixtures, as determined using spreadsheet mixing models [28]. In most cases, the different tracers appear to indicate approximately similar ages for the ground-water samples; that is, they plot relatively close to the solid curves representing the loci of values representing concordant discrete sample ages. In addition, the tracer-tracer plots reveal several types of anomalies that affect the interpretation of ground-water ages:

(1) Some samples have concentrations of one or more trace gases that exceed maximum values expected from normal atmospheric equilibrium and excess air. For example, CFC11 concentrations in the BOMARC wells and several others are elevated by as much as 30 %. CFC113 exceeds expected concentrations by more than 2 orders of magnitude at BOMARC and NP1. CFC12 exceeds expected concentrations by at least 20 % at NP1. Possible sources of contamination include local atmospheric or wastewater sources and artifacts of pumps or tubing.

(2) SF_6 appears to be relatively enriched slightly in some of the older samples, possibly because of local surface sources in the past or because of in situ sources in the aquifer [18]. Discrepancies also could result from the samples being mixtures of waters of different ages, as

indicated by the broken curves in Figure S3. Mixing and dispersion are more likely to have affected the deep samples because of longer flow paths and compression of isochrons with depth in the aquifer. However, application of a simple dispersion model to the data did not improve overall consistency between SF_6, CFC, and $^3H/^3He$ results.

(3) The two shallowest samples in the DL transect have measured $\delta^3He < 0$, yielding $^3H/^3H^o$ ratios > 1 and ^3H-^3He ages < 0 yr. As most of the analyzed samples also yielded slightly negative calculated values of radiogenic (terrigenic) ^4He, it is considered likely that these anomalies are related to fractionation of gases during recharge, sampling, or handling, as indicated also by the small discrepancies between apparent equilibration temperatures for different gas pairs (see above).

(4) Many samples plot in clusters near the modern values for CFC11, CFC12, and CFC113. Because the concentrations of these gases changed relatively slowly and peaked in the atmosphere between about 1990 and 2005 (Figure S2), there is not much variation in their concentrations in ground waters that recharged during that time period and small variations or errors in recharge temperatures can cause large uncertainties in derived ground-water ages.

Composite mean apparent ages were derived from tracer data that were judged to be relatively reliable in each sample, as follows (Table S1, Figure S4):

(1) For CFC11, we eliminated samples that plot above the curves in Figure 3A (contaminated?), and we eliminated apparent recharge dates after about 1990 because of uncertainty and ambiguity related to slow change and reversal in atmospheric concentrations and uncertainties in recharge temperatures.

(2) For CFC12, we eliminated NP1 and BM1 (contaminated), and we eliminated apparent recharge dates after about 1990 because of uncertainty and ambiguity related to slow change and reversal in atmospheric concentrations and uncertainties in recharge temperatures. At BM2, the CFC12 concentration could be consistent with recharge in either 1997 or 2007, the latter being consistent with the ^3H-^3He age of 1 yr.

(3) For CFC113, we eliminated apparent recharge dates after about 1990 because of uncertainty and ambiguity related to slow change and reversal in atmospheric concentrations and uncertainties in recharge temperatures.

(4) For SF_6, we eliminated apparent recharge dates before about 1985 because of possible low-level contamination or natural sources [18]. The relatively low number of SF_6 data for samples collected in 2007 is related to poor sealing of the sample bottles, which resulted in partial SF_6 loss into bubbles that formed during storage and were lost when samples were prepared for analysis (i.e., apparent ages were older than they should have been). These samples were eliminated on the basis of measured bubble sizes.

(5) For ^3H-^3He, we used all available data. For DL4d, we combined the measured value of δ^3He with estimated concentrations of He and Ne (assumed to be equal to those of DL4m).

In the absence of a solute transport model, it is not possible to evaluate these data fully; nevertheless, composite mean apparent ages were used to construct a vertical age profile and estimate recharge rate in the vicinity of the DL transect (Figure S5), as illustrated in previous studies of relatively homogeneous, transmissive, unconsolidated aquifers elsewhere [29-32]. The composite apparent age profile was fit to an exponential age gradient [33, 34]:

$$t_i = (n*Z/r)*\ln[Z/(Z-z_i)],$$

where n = porosity (0.30 [35]), Z = saturated-zone thickness (37 m between the water table and lower confining unit), t_i = composite mean apparent age of a sample, z_i = depth of a sample below the water table, and r = recharge rate (unknown). This equation was modified by adding an age intercept value (t_0 = the apparent age at the water table) to permit best fits of age profiles with possible minor systematic bias. The mean difference between composite apparent ages (Figure S5) and ages calculated with this equation was minimized by using Microsoft Excel Solver (Excel 2003) to estimate optimum recharge values (r) and age intercept values (t_0). A result for the full set of composite apparent ages was r = 0.52 m yr^{-1} and t_o = 2.4 yr. In this case, the mean difference between apparent and calculated ages was 2.0 yr and the median difference was 0.8 yr. An alternative fit to the composite apparent ages with t_o fixed at 0 yielded r = 0.48 m yr^{--1} with mean and median differences of 2.7 and 1.5 yr. Independent fits to the ^3H-^3He data alone yielded r = 0.44 m yr^{-1} and t_0 = -2.0 yr with mean and median differences of 4.1 and 3.8 yr; or r = 0.47 m yr^{-1} and t_0 = 0 yr with mean and median differences of 4.4 and 4.3 yr. Eliminating the 3 shallow wells from the fits did not alter these results significantly. Given uncertainty in the choice of models and uncertainty (instability) in the individual Solver fits caused in part by the small dataset, we assumed an average DL recharge rate of 0.50 m yr^{-1} for converting chemical concentrations to recharge fluxes. Uncertainty in this estimate could be of the order of ± 10 % or more, but is difficult to quantify as it could be related to (1) local variations in recharge rates, (2) local or regional anomalies in atmospheric CFC and SF_6 concentrations, (3) mixing (dispersion) or other sources of error in the estimated ages, (4) variations in the saturated thickness of the aquifer or other properties that could affect the simple exponential model, and (5) sampling artifacts or analytical errors. Improved estimates might be obtained by aquifer flow simulations accounting for dispersion and optimized to fit the tracer concentrations, rather than the apparent ages. Our recharge estimates are not significantly different from a value of 0.56 m yr^{-1} estimated from precipitation records in the North Fork area [35], assuming recharge in a given year was equal to 82 % of precipitation from October 15 to May 15, based on previous physical measurements in the unsaturated zone (± 9 % in the original publication [36]). Another previous estimate was 50 % of annual precipitation [37]. Irrigation pumps were present near the DL transect, but total pumpage in the North Fork area was estimated to be only about 4.5 % of the recharge rate [35].

The mean measured concentration of ^3H in shallow ground waters with composite apparent ages less than 20 yr was 4.8 ± 0.4 TU (n = 8). This is interpreted to be close to the mean value for “modern” meteoric water (precipitated between about 1980 and 2007, collected and analyzed in 2007) near the coast of eastern Long Island. This value is similar to modern values estimated for coastal areas of the Delmarva Peninsula in Maryland and Delaware [38, 39] but significantly lower than recorded values at Boston [40] (R.L. Michel, USGS, written communication, 2008). We interpret these data as indicating relative ^3H depletion near the shoreline, on barrier islands, and in estuaries of the mid-Atlantic region caused by local exchange or mixing with low ^3H oceanic moisture. Based on our data, we applied a factor of 0.76 to the Boston ^3H record in precipitation to represent local meteoric water values in eastern Long Island (Figure S2).

^3H concentrations significantly higher than modern (e.g., NP1 at 9.6 TU) indicate components from the thermonuclear bomb test peak in precipitation ^3H between about 1954 and 1975, whereas relatively low concentrations (e.g., NP4 at 1.6 TU, DL1d at 2.8 TU) indicate components precipitated before 1954. Given the 5-12 m thickness of the unsaturated zone at the BOMARC and DL sites, and greater thicknesses at the Northport sites, there may have been differences between the time of precipitation and the time of recharge for individual parcels of water. Nevertheless, H_2O fluxes were high, and measured ^3H concentrations and calculated initial ^3H concentrations ($^3H° = {}^3H + {}^3He_{tritiogenic}$) generally were consistent with the apparent ^3H-^3He ages and other atmospheric environmental tracers, given various sources of uncertainty. Unsaturated-zone transport is considered less likely to affect the interpretation of the gas tracers substantially.

For some of the wells, tracer-tracer plots (Figure S3) indicate samples may have been mixtures of ground waters with a range of ages. The clearest example is production well NP4, which had ^{3}H < modern, but elevated concentrations of CFCs and SF_6, indicating a mixture of pre-bomb and post-bomb water. These data, plus the relatively large screened interval and depth of this well indicate young ground water probably was drawn down from above by intensive pumping in the area of the well. Other samples most likely to contain mixtures include DL1d and DL4d, both of which plot below the ^{3}H bomb peak in Figure S3. These wells were screened near the lower boundary of the upper glacial aquifer, where age gradients were likely to be steep and effects of vertical dispersion in the aquifer and mixing in the well screen were likely to be relatively strong.

Atmospheric concentrations of CFCs and SF_6 may have been elevated above hemispheric average values because of concentrated sources in major metropolitan areas like New York City [41-43]. For example, analyses of soil gases indicate the atmospheric concentration of SF_6 in eastern Long Island could have been higher than the baseline hemispheric value by around 12 ± 4 % (data from 2001-2002) [43]. Our data were not adjusted for these potential differences, which are poorly known and may have varied over time.

Isotopic composition of nitrate and sulfate

δ^{15}N values of NO_3^- range from +2.3 ‰ to +6.9 ‰ and δ^{18}O values of NO_3^- range from –2.3 ‰ to +8.3 ‰ (Table S1). Though variations are substantial, these data are generally consistent with nitrification as a major source of NO_3^- and similar to values reported for ground-water NO_3^- beneath fertilized agricultural land elsewhere in the eastern US [e.g., 44]. In the North Fork area (DL transect), δ^{15}N values tend to increase with depth and ground-water age. Because these samples do not seem to have been affected by denitrification in the saturated zone, the downward increase in δ^{15}N may be attributed to an overall change in the mean δ^{15}N value of recharging NO_3^- over time. Kreitler et al. [45] report that ground-water NO_3^- in Suffolk County, mostly from the North Fork area, had a mean δ^{15}N value of +5.3 ‰ (range +3 to +9 ‰) in the 1970's. Flipse and Bonner [46] report a similar mean (+6.2 ‰) for ground-water NO_3^- collected in 1978 beneath North Fork potato fields that received 166-245 kg/ha of N in the form of both NO_3^- and reduced N. Those historical δ^{15}N data are similar to our values for the deeper ground waters with apparent recharge dates from 1966 to 1982.

δ^{34}S values of SO_4^{2-} range from 1.1 to 7.6 ‰ (mean = 5.7 ± 1.9 ‰, n=10) and δ^{18}O values of SO_4^{2-} range from 4.2 to 9.4 ‰ (mean = 7.8 ± 1.9 ‰, n=10) (Table S1). The δ^{34}S values are similar to those of continental atmospheric SO_4^{2-}, and within the range of S and SO_4^{2-} fertilizers from various sources, but significantly lower than the modern seawater value of +21.1 ‰ [14, 47, 48]. The δ^{18}O values are within the range of atmospheric, fertilizer, and seawater values, but higher than those typical of SO_4^{2-} produced by sulfide oxidation in soils and aquifers [48, 49]. Combined SO_4^{2-} isotope data are consistent with some combination of atmospheric and fertilizer-derived S.

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Table S1. Data summary

sample	local ID S-#	USGS station ID	lat N degrees	long W degrees	land surface elev m	water table elev m	mid-screen elev m	± screen elev m	depth BWT m	sample date	Cl^- µM	Br µM	NO_3^- µM	SO_4^{2-} µM	ClO_4^- µM	Na µM	K µM	Ca µM	Mg µM	Si µM
BM1	113014	405014072405101	40.8372	72.6809	13.7	4.0	-7.6	1.5	11.6	12/6/2006	194	0	97	136	*43.4389*	171	328	343	189	81
BM2	116209	405007072405001	40.8354	72.6807	13.7	2.1	0.0	1.5	2.1	39057.00	256	0	72	109	*3.5495*	150	64	142	113	90
NP1	35939	405140073190801	40.8608	73.3178	52.1	17.2	-99.8	9.3	117.0	12/7/2006	415	1	792	151	0.1121	467	35	348	223	140
NP4	115702	405259073203101	40.8830	73.3420	92.7	10.4	-81.5	9.3	92.0	12/7/2006	266	0	336	4	0.0843	282	19	104	64	118
DL6s		410138072303001	41.0274	72.5078	18.2	1.3	0.6	0.8	0.6	4/9/2007	1168	-1	973	1809	0.0087	524	128	1579	1053	215
DL6m		410138072302801	41.0274	72.5078	18.1	1.2	-8.6	0.8	9.8	12/14/2006	920	-1	558	1494	0.0102	380	72	1255	700	206
DL6d	120404	410138072303101	41.0274	72.0578	18.2	1.3	-25.3	0.8	26.5	12/13/2006	898	-1	581	1257	0.0458	605	67	1159	554	248
DL1s		410121072295701	41.0226	72.4992	12.4	1.5	-0.6	0.8	2.1	1/18/2007	206	0	84	69	0.0015	234	54	253	141	152
DL1m		410121072295702	41.0225	72.4992	12.4	1.5	-5.1	0.8	6.7	1/12/2007	842	0	98	75	0.0034	565	114	302	98	120
DL1d	124060	410120072295901	41.0225	72.4992	12.3	1.5	-28.1	0.8	29.5	12/14/2006	660	1	415	774	0.0996	573	46	755	311	222
DL4s		410108072293701	41.0191	72.4938	8.8	1.1	-1.1	0.8	2.2	1/9/2007	455	1	542	292	0.0077	369	37	272	265	151
DL4m		410110072293701	41.0196	72.4938	8.8	1.2	-17.8	0.8	19.0	12/13/2006	321	1	513	259	0.0058	305	46	506	113	208
DL4d	124131	410108072294001	41.1907	72.4938	8.8	1.2	-25.5	0.8	26.6	12/12/2006	837	1	529	696	0.0466	631	41	701	424	260
										12/13/2006					0.0469					
											negative concentrations are "less than"									
DL6s2		410138072303001	41.0274	72.5078	18.2	1.3	0.6	0.8	0.6	1/8/2008	na	na	na	na	na	na	na	na	na	na
DL6m2		410138072302801	41.0274	72.5078	18.1	1.2	-8.6	0.8	9.8	1/8/2008	na	na	na	na	na	na	na	na	na	na
DL6d2	120404	410138072303101	41.0274	72.0578	18.2	1.3	-25.3	0.8	26.5	1/8/2008	na	na	na	na	na	na	na	na	na	na
DL1s2		410121072295701	41.0226	72.4992	12.4	1.5	-0.6	0.8	2.1	4/10/2008	na	na	na	na	na	na	na	na	na	na
DL1m2		410121072295702	41.0225	72.4992	12.4	1.5	-5.1	0.8	6.7	4/10/2008	na	na	na	na	na	na	na	na	na	na
DL1d2	124060	410120072295901	41.0225	72.4992	12.3	1.5	-28.1	0.8	29.5	4/9/2008	na	na	na	na	na	na	na	na	na	na
DL4s2		410108072293701	41.0191	72.4938	8.8	1.1	-1.1	0.8	2.2	4/9/2008	na	na	na	na	na	na	na	na	na	na
DL4m2		410110072293701	41.0196	72.4938	8.8	1.2	-17.8	0.8	19.0	1/10/2008	na	na	na	na	na	na	na	na	na	na
DL4d2	124131	410108072294001	41.1907	72.4938	8.8	1.2	-25.5	0.8	26.6	1/10/2008	na	na	na	na	na	na	na	na	na	na

Table S1

sample	Ag µM	Al µM	As µM	B µM	Ba µM	Cd µM	Co µM	Cr µM	Cu µM	Fe µM	Li µM	Mn µM	Mo µM	Ni µM	Pb µM	Rb µM	Sb µM	Se µM	Sr µM	U µM	V µM	Zn µM
BM1	0.00	0.07	0.00	1.94	0.10	0.00	-0.0008	-0.02	0.01	-0.36	-0.14	0.02	0.014	0.01	0.0014	0.06	0.11	-0.01	15.29	0.00	0.00	0.02
BM2	0.00	0.15	0.00	-1.85	0.07	0.00	-0.0008	-0.02	0.00	-0.36	-0.14	0.11	0.003	0.02	-0.0002	0.02	0.00	-0.01	1.54	0.00	0.00	0.05
NP1	0.00	-0.04	0.00	-1.85	0.17	0.00	0.0011	0.06	0.34	-0.36	-0.14	0.01	0.001	0.02	0.0022	0.02	0.00	0.01	0.91	0.00	0.00	0.06
NP4	0.00	-0.04	0.00	-1.85	0.08	0.00	0.0039	-0.02	0.12	-0.36	-0.14	0.02	-0.001	0.02	0.0016	0.01	0.00	-0.01	0.29	0.00	0.00	0.21
DL6s	0.00	1.52	0.00	7.22	0.13	0.00	0.0020	-0.02	0.03	-0.36	-0.14	1.73	0.002	0.07	0.0002	0.06	0.00	-0.01	1.62	0.00	0.00	0.37
DL6m	0.00	7.93	0.00	7.31	0.15	0.00	0.0012	-0.02	0.03	-0.36	-0.14	0.24	-0.001	0.03	-0.0002	0.05	0.00	-0.01	1.22	0.00	0.00	0.04
DL6d	0.00	0.07	0.00	4.07	0.27	0.00	0.0126	-0.02	0.02	-0.36	-0.14	0.02	-0.001	0.03	-0.0002	0.03	0.00	-0.01	0.93	0.00	0.00	0.06
DL1s	0.00	0.07	0.00	-1.85	0.07	0.00	-0.0008	-0.02	0.00	-0.36	-0.14	0.01	0.002	0.01	-0.0002	0.03	0.00	-0.01	0.41	0.00	0.00	-0.02
DL1m	0.00	-0.04	0.00	-1.85	0.25	0.00	0.0012	-0.02	0.00	-0.36	-0.14	1.56	0.003	0.01	-0.0002	0.04	0.00	-0.01	0.62	0.00	0.01	-0.02
DL1d	0.00	0.04	0.00	2.22	0.35	0.00	-0.0008	-0.02	0.01	-0.36	-0.14	0.02	0.001	0.02	0.0004	0.01	0.00	-0.01	1.61	0.00	0.00	0.03
DL4s	0.00	20.35	0.00	2.68	0.13	0.00	0.0056	-0.02	0.01	-0.36	-0.14	1.15	-0.001	0.01	0.0003	0.02	0.00	-0.01	0.38	0.00	0.00	0.03
DL4m	0.00	0.07	0.00	5.37	0.26	0.00	0.0023	-0.02	0.01	-0.36	-0.14	0.91	-0.001	0.01	-0.0002	0.04	0.00	-0.01	0.93	0.00	0.00	0.02
DL4d	0.00	0.19	0.00	-1.85	0.34	0.00	0.0013	-0.02	0.01	-0.36	-0.14	0.01	-0.001	0.02	-0.0002	0.01	0.00	-0.01	1.70	0.00	0.00	0.03
DL6s2	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
DL6m2	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
DL6d2	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
DL1s2	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
DL1m2	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
DL1d2	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
DL4s2	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
DL4m2	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na
DL4d2	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na	na

Table S1

sample	ClO_4^- $\delta^{37}Cl$ ‰	ClO_4^- $\delta^{18}O$ ‰	ClO_4^- $\Delta^{17}O$ ‰	SO_4^{2-} $\delta^{34}S$ ‰	SO_4^{2-} $\delta^{18}O$ ‰	NO_3^- $\delta^{15}N$ ‰	NO_3^- $\delta^{18}O$ ‰	RCUL O_2 µM ave	±	n	RCUL CH_4 µM ave	±	n	RCUL Ar µM ave	±	n	RCUL N_2 µM ave	±	n	RSIL N_2 $\delta^{15}N_2$ ave	±	n
BM1	0.2	-16.7	0.1	na	na	4.9	8.3	349	1	2	0.0000	0.0000	2	17.76	0.03	2	687	2	2	0.77	0.01	2
BM2	0.2	-17.7	-0.1	5.7	6.6	2.2	4.9	340	4	2	0.0000	0.0000	2	17.81	0.28	2	701	17	2	0.69	0.00	2
NP1	-12.5	-3.0	9.4	7.3	4.2	6.8	3.8	331	1	2	0.0000	0.0000	2	18.17	0.07	2	730	7	2	0.70	0.01	2
NP4	-13.2	-8.2	7.9	na	na	3.8	3.6	338	1	2	0.0000	0.0000	2	18.66	0.04	2	744	1	2	0.81	0.01	2
DL6s	na	na	na	7.6	8.9	2.7	3.3	325	5	2	0.0000	0.0000	2	18.00	0.29	2	726	19	2	0.58	0.02	2
DL6m	na	na	na	6.9	9.3	3.6	0.2	283	2	2	0.0000	0.0000	2	17.43	0.14	2	674	8	2	0.70	0.02	2
DL6d	-12.6	-6.0	8.4	6.8	9.0	4.3	2.0	278	1	2	0.0000	0.0000	2	17.59	0.15	2	681	8	2	0.72	0.05	2
DL1s	na	na	na	na	na	2.9	-2.3	254	2	2	0.0000	0.0000	2	18.40	0.05	2	754	6	2	0.68	0.05	2
DL1m	na	na	na	1.1	4.6	4.6	6.7	241	3	2	0.0000	0.0000	2	17.98	0.18	2	709	12	2	0.65	0.00	2
DL1d	-14.0	-6.1	8.2	4.2	9.4	5.6	5.2	285	0	2	0.0000	0.0000	2	17.94	0.07	2	694	5	2	0.72	0.07	2
DL4s	na	na	na	6.0	8.4	3.5	-0.4	267	2	2	0.0000	0.0000	2	18.04	0.13	2	720	8	2	0.56	0.04	2
DL4m	na	na	na	6.3	8.9	6.9	3.9	275	3	2	0.0000	0.0000	2	17.65	0.09	2	686	3	2	0.64	0.04	2
DL4d	-12.9	-1.6	10.2	5.0	8.4	5.2	4.9	273	1	2	0.0000	0.0000	2	17.82	0.01	2	683	2	2	0.75	0.01	2
DL6s2	na	na	na	na	na	na	na	321	1	2	0.0000	0.0000	2	17.29	0.08	2	681	0	2	0.80	0.01	2
DL6m2	na	na	na	na	na	na	na	310	1	2	0.0000	0.0000	2	17.96	0.00	2	704	5	2	0.69	0.06	2
DL6d2	na	na	na	na	na	na	na	294	5	2	0.0000	0.0000	2	18.03	0.17	2	705	10	2	0.67	0.01	2
DL1s2	na	na	na	na	na	na	na	308	2	2	0.0000	0.0000	2	17.69	0.18	2	704	12	2	0.58	0.01	2
DL1m2	na	na	na	na	na	na	na	297	5	2	0.0000	0.0000	2	18.10	0.23	2	739	19	2	0.59	0.06	2
DL1d2	na	na	na	na	na	na	na	291	2	2	0.0000	0.0000	2	18.29	0.05	2	721	1	2	0.67	0.04	2
DL4s2	na	na	na	na	na	na	na	227	7	2	0.0000	0.0000	2	18.28	0.26	2	736	16	2	0.64	0.06	2
DL4m2	na	na	na	na	na	na	na	291	4	2	0.0000	0.0000	2	18.00	0.10	2	708	7	2	0.60	0.00	2
DL4d2	na	na	na	na	na	na	na	289	1	2	0.0000	0.0000	2	18.28	0.03	2	707	5	2	0.71	0.02	2

Table S1	LDEO	LDEO	USGS	USGS	LDEO	LDEO	select	LDEO	LDEO	LDEO	LDEO	RCUL	RCUL	RCUL	RCUL	RCUL	RCUL	RCUL	RCUL
	MS	**MS**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**	**H2O**
sample	**He**	**Ne**	**^{3}H**	**^{3}H**	**^{3}H**	**^{3}H**	**^{3}H**	**δ^3He**	**^{3}He[trit]**	**^{3}H°**	**^{3}H/^{3}H°**	**CFC11**	**CFC11**	**CFC12**	**CFC12**	**CFC113**	**CFC113**	***SF_6***	***SF_6***
	µM	**µM**	**TU**	**TU**	**TU**	**TU**	**TU**	**%**	**TU**	**TU**	**TU**	**pM**		**pM**		**pM**		**fM**	
				±		±	ave					ave	±	ave	±	ave	±	ave	±
BM1	0.00241	0.0103	5.39	0.26	5.75	0.12	5.57	1.52	0.66	6.23	0.89	7.5955	0.6682	3.6355	0.0205	357.97	1.8618	na	
BM2	0.00251	0.0110	4.95	0.26	4.67	0.09	4.81	-0.32	0.32	5.13	0.94	7.8325	0.1718	2.9365	0.0078	111.9	0.5438	na	
NP1	0.00269	0.0120	9.50	0.40	9.02	0.18	9.26	174.85	58.92	68.18	0.14	5.9945	0.1195	4.7215	0.1591	182.06	2.9819	na	
NP4	0.00265	na	1.64	0.20	1.96	0.18	1.80	35.3	12.11	13.91	0.13	0.9233	0.0393	0.2347	0.0284	0.0313	0.0186	0.20	0.03
DL6s	0.00205	0.0083	4.60	0.30	na		4.60	-0.56	-0.04	4.56	1.01	5.8553	0.5297	2.7057	0.0448	0.4433	0.0031	na	
DL6m	0.00238	0.0105	4.70	0.30	4.68	0.09	4.69	13.35	4.38	9.07	0.52	7.206	0.206	2.7877	0.275	0.451	0.0131	1.76	
DL6d	0.00255	0.0105	4.50	0.30	4.44	0.22	4.47	52.17	16.85	21.32	0.21	5.1103	0.2348	1.865	0.0223	0.2937	0.014	na	
DL1s	0.00281	0.0115	4.78	0.25	na		4.78	-3.59	-0.89	3.89	1.23	6.5063	1.938	2.7557	0.0348	0.569	0.2021	na	
DL1m	0.00250	0.0104	4.25	0.28	na		4.25	1.32	0.78	5.03	0.84	4.761	0.0184	2.7775	0.0276	0.457	0.0014	na	
DL1d	0.00245	0.0105	2.82	0.22	3.51	0.13	3.16	44.62	14.04	17.20	0.18	2.261	0.0745	0.8387	0.0708	0.082	0.0095	na	
DL4s	0.00252	0.0109	4.31	0.24	na		4.31	-2.82	-0.52	3.79	1.14	4.454	0.0396	2.554	0.0099	0.44	0.0071	na	
DL4m	0.00245	0.0107	5.15	0.26	5.27	0.11	5.21	41.06	12.96	18.17	0.29							1.29	0.00
DL4d	na	na	5.30	0.30	5.23	0.11	5.27	128.61	*39.70*	*44.97*	*0.12*	1.255	0.059	0.619	0.233	0.0317	0.01	na	
									DL4d 3He is based on estimated He and Ne concentrations*										
DL6s2	na	na	na	na	na	na	na	na	na	na	na	4.7432	0.0081	2.8178	0.0414	0.459	0.0141	2.38	0.04
DL6m2	na	na	na	na	na	na	na	na	na	na	na	4.9995	0.0831	2.8721	0.0072	0.4798	0.0015	2.41	
DL6d2	na	na	na	na	na	na	na	na	na	na	na	2.1807	0.0198	1.3236	0.0095	0.163	6E-05	0.89	0.03
DL1s2	na	na	na	na	na	na	na	na	na	na	na	5.04	0.0263	2.8251	0.0032	0.4725	0.0027	1.70	
DL1m2	na	na	na	na	na	na	na	na	na	na	na	5.0902	0.0249	2.916	0.0049	0.4861	0.0018	2.33	
DL1d2	na	na	na	na	na	na	na	na	na	na	na	1.5089	0.0268	0.9907	0.0091	0.1337	0.0027	0.90	0.00
DL4s2	na	na	na	na	na	na	na	na	na	na	na	4.4442	0.0683	2.8829	0.0858	0.4541	0.007	2.70	0.09
DL4m2	na	na	na	na	na	na	na	na	na	na	na	4.5156	0.099	2.4046	0.0126	0.3086	0.0045	1.32	0.21
DL4d2	na	na	na	na	na	na	na	na	na	na	na	0.7754	0.009	0.5591	0.0137	0.0408	0.0009	0.45	0.01

Table S1 **sample**	RCUL **H2O CFC11 pptv** ave	**H2O CFC11** ±	RCUL **H2O CFC12 pptv** ave	**H2O CFC12** ±	RCUL **H2O CFC113 pptv** ave	**H2O CFC11** ±	RCUL **H2O *SF_6* pptv** ave	**H2O *SF_6*** ±	calc **H2O ^{3}H-^{3}He age**	calc **H2O CFC11 age** ave	calc **H2O CFC12 age** ave	calc **H2O CFC113 age** ave	*select* ***H2O SF_6 age*** ave	calc **H2O ^{3}H-^{3}He date**	calc **H2O CFC11 date** ave	calc **H2O CFC12 date** ave	calc **H2O CFC113 date** ave	*calc* **H2O SF_6 date** ave
BM1	357	31	656	4	54151	282	na		2.0	contam	contam	contam		2005	contam	contam	contam	na
BM2	379	8	541	1	17402	85	na		1.1	contam	*10*	contam		2006	contam	*1997*	contam	na
NP1	287	6	859	29	27924	457	na		35.5	contam	contam	contam		1971	contam	contam	contam	na
NP4	41	2	40	5	4.5	2.6	0.38	0.05	36.4	40	46	40	33	1971	1967	1961	1967	1974
DL6s	290	26	507	8	70.5	0.5	na		-0.2	17	16	18		2007	1990	1991	1989	na
DL6m	354	10	523	52	71.5	2.1	4.11		11.7	contam	17	18	9	1995	contam	1990	1989	1998
DL6d	247	11	344	4	45.7	2.2	na		27.8	19	25	22		1979	1988	1982	1985	na
DL1s	317	94	506	6	88.6	31.5	na		-3.7	20	16	18		2011	1988	1991	1989	na
DL1m	226	1	503	5	69.6	0.2	na		3.0	21	16	18		2004	1986	1991	1989	na
DL1d	104	3	148	13	12.1	1.4	na		30.1	33	36	32		1977	1974	1971	1975	na
DL4s	215	2	468	2	68.2	1.1	na		-2.3	22	19	18		2009	1985	1988	1989	na
DL4m							2.91	0.00	22.2	na	na	na	14	1985	na	na	na	1993
DL4d	58	3	110	41	4.7	1.5	na		*38.1*	37	39	39		*1969*	1970	1968	1968	na
											BM2 CFC12 age could be 0				*BM2 CFC12 date could be 2007*			
DL6s2	245	0	551	8	76.8	2.4	5.43	0.09	-0.2	21	7	18	4	2007	1988	2002	1990	2004
DL6m2	236	4	517	1	72.6	0.2	5.17		11.7	21	16	19	6	1995	1987	1992	1990	2003
DL6d2	101	1	236	2	24.3	0.0	1.92	0.07	27.8	35	33	28	20	1979	1974	1976	1981	1988
									0.0					0				
DL1s2	253	1	536	1	76.4	0.4	3.64		-3.7	20	12	18	13	2011	1988	1996	1990	1996
DL1m2	255	1	549	1	78.0	0.3	4.56		3.0	20	6	18	9	2004	1989	2003	1991	2000
DL1d2	69	1	173	2	19.5	0.4	1.86	0.00	30.1	37	36	30	21	1977	1971	1973	1979	1987
									0.0					0				
DL4s2	212	3	521	16	69.2	1.1	5.34	0.17	-2.3	23	15	19	5	2009	1985	1993	1989	2003
DL4m2	213	5	433	2	46.6	0.7	2.80	0.45	22.2	23	21	23	16	1985	1985	1987	1986	1992
DL4d2	34	0	95	2	5.8	0.1	0.95	0.03	38.1	42	41	38	27	1969	1967	1967	1970	1981

Table S1 **sample**	comp **H2O age yr** ave	comp **H2O age ±**	**basis**	**select H2O age yr**	**select H2O age ±**	**basis**	**select H2O date**
BM1	2		3He	**2**		**3He**	**2004**
BM2	1		3He	**1**		**3He**	**2005**
NP1	35		3He	**35**		**3He**	**1971**
NP4	41	4	3He,11a,12a,113a	**41**	**4**	**3He,11a,12a,113a**	**1966**
DL6s	0		3He	**2**	**2**	**3He,SF6b**	**2005**
DL6m	11	1	3He,SF6a	**9**	**3**	**3He,SF6ab**	**1998**
DL6d	23	3	3He,11a,12a,113a	**27**	**5**	**3He,11ab,12ab,113ab**	**1980**
DL1s	-4		3He	**5**	**8**	**3He,SF6b**	**2002**
DL1m	3		3He	**6**	**3**	**3He,SF6b**	**2001**
DL1d	33	2	3He,11a,12a,113a	**33**	**3**	**3He,11ab,12ab,113ab**	**1973**
DL4s	-2		3He	**1**	**4**	**3He,SF6b**	**2005**
DL4m	18	4	3He,SF6a	**18**	**3**	**3He,SF6ab**	**1989**
DL4d	38	1	3He,11a,12a,113a	**39**	**1**	**3He,11ab,12ab,113ab**	**1967**
DL6s2	4		SF6				
DL6m2	9	3	3He,SF6b				
DL6d2	31	3	3He,11b,12b,113b				
DL1s2	5	8	3He,SF6b				
DL1m2	6	3	3He,SF6b				
DL1d2	33	3	3He,11b,12b,113b				
DL4s2	1	4	3He,SF6b				
DL4m2	19	3	3He,SF6b				
DL4d2	40	2	3He,11b,12b,113b				

Table S2. Concentrations and ratios of selected constituents in seawater and North Fork precipitation.

Parameter	Seawater µM	Precipitation µM
Cl^-	558460	93.30
SO_4^{2-}	28890	13.50
NO_3^-	nd	11.20
NH_4^+	nd	5.94
Na^+	479200	79.10
K^+	10440	nd
Mg^{2+}	54310	8.72
Ca^{2+}	10340	2.83
SO_4^{2-}/Cl	0.0517	0.1447
$[NO_3^-+NH_4^+]/Cl$	nd	0.1837
Na/Cl	0.8581	0.8478
K/Cl	0.0187	nd
Mg/Cl	0.0972	0.0935
Ca/Cl	0.0185	0.0303
$Mg/\ SO_4^{2-}$	1.8799	0.6459
$Ca/\ SO_4^{2-}$	0.3579	0.2096

Seawater data are from [50].

Precipitation data are means of the annual precipitation-weighted concentrations for 2004, 2005, and 2006 at site NY96, Southold, New York) [51].

nd = no data

Table S3. Perchlorate concentrations in selected solid fertilizer products

Product	**ClO_4^- (mg kg^{-1})**	**ClO_4^-/X mol mol^{-1}**	**Source of data[1]**
Long Island fertilizers, 2006		**ClO_4^-/N**	
“organic fertilizer” (contains Atacama NO_3^-?)	9		[52]
Thorvin “kelp” (vegetable farm, Northport)	0.82		this study (STL)
“Iceland kelp” (Ascophyllum nodosum, Thorvin distributor, Northport)	0.36		this study (TTU)
“Maine kelp” (Thorvin distributor, Northport)	0.29		this study (TTU)
NPK 20-20-20 (vineyard farm, Cutchogue)	0.015		this study (STL)
“paramagnetic rock” (vegetable farm, Northport)	0.006		this study (STL)
Harmony chicken compost (vineyard, Cutchogue)	0.003		this study (STL)
Ammonium nitrate (farm, Riverhead, NY)	0.001		this study (STL)
Atacama nitrate		**ClO_4^-/N**	
Unprocessed NO_3^- ore (1932-1967)		2.8×10^{-3}	[53, 54]
$NaNO_3$ refined pellets from Chile (before 1990) [Chile 375]	2130	1.8×10^{-3}	this study
$NaNO_3$ fertilizer samples (before 2001)	1900-4000	$1.6\text{-}3.4 \times 10^{-3}$	[55]
$NaNO_3$ fertilizer samples (before 2001)	1450-2080	$1.2\text{-}1.8 \times 10^{-3}$	[56]
$NaNO_3$ industrial-grade pellets from SQM North America (2003) [RSIL N7791]	2375	2.0×10^{-3}	this study (TTU)
$NaNO_3$ high-purity chips from Chile (2001) (non-commercial?) [USGS35]	260	2.2×10^{-4}	this study (TTU)
$NaNO_3$ reported target for SQM product (beginning in 2001)	≤ 100	$\leq 8.5 \times 10^{-5}$	[55, 57]
Miscellaneous		**ClO_4^-/N**	
Grow More 13-0-44 (~KNO_3) (New Jersey, 2004)	257	2.8×10^{-4}	this study (Shaw)
North Country 10-0-0 (New Jersey, 2004)[2]	55	7.7×10^{-5}	this study (Shaw)
North Country 5-3-4 (New Jersey, 2004)	2.2	6.2×10^{-6}	this study (Shaw)
Champion 12.5-0-45 (~KNO_3) (New Jersey, 2004)	26	2.9×10^{-5}	this study (Shaw)
		ClO_4^-/Cl^-	
Milford “potash” (KCl), Delaware	< 0.005	$< 4 \times 10^{-9}$	this study (TTU)

[1] STL = analysis by IC/MS/MS at Severn Trent Laboratory, Inc.; TTU = analysis by IC/MS/MS at Texas Tech University; Shaw = analysis by ion chromatography at Shaw Environmental, Inc.

[2] May contain Atacama nitrate (North Country website, January 2009)

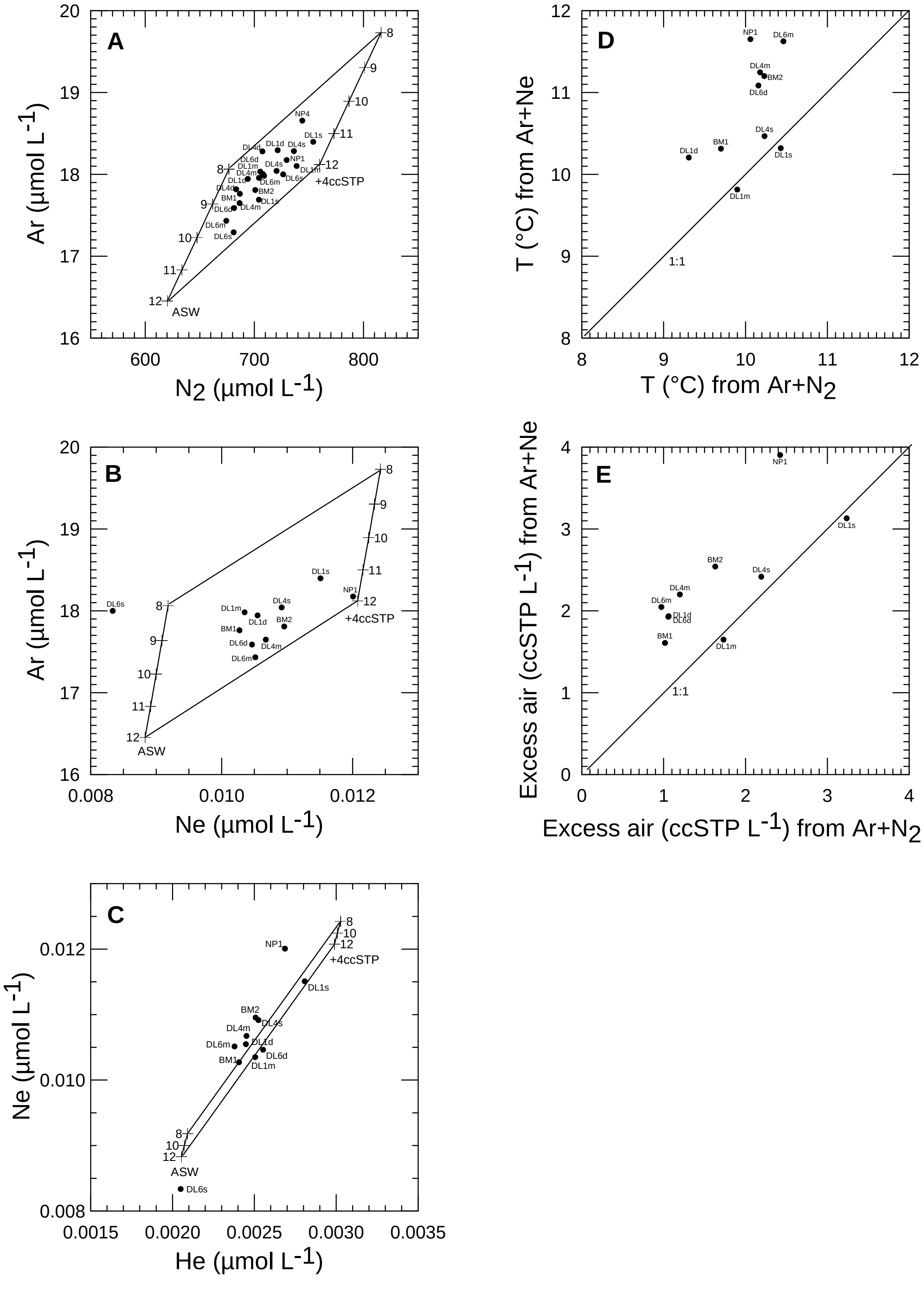

Figure S1. Dissolved gas data. [A-C] Concentrations of He, Ne, Ar, and N_2 compared with atmospheric saturation values. [D-E] Calculated air-water equilibrium temperatures and excess air concentrations, based on Ne+Ar data or Ar+N_2 data. Air-water equilibrium concentrations were calculated from solubility data [24, 25]. Excess air was assumed to be unfractionated.

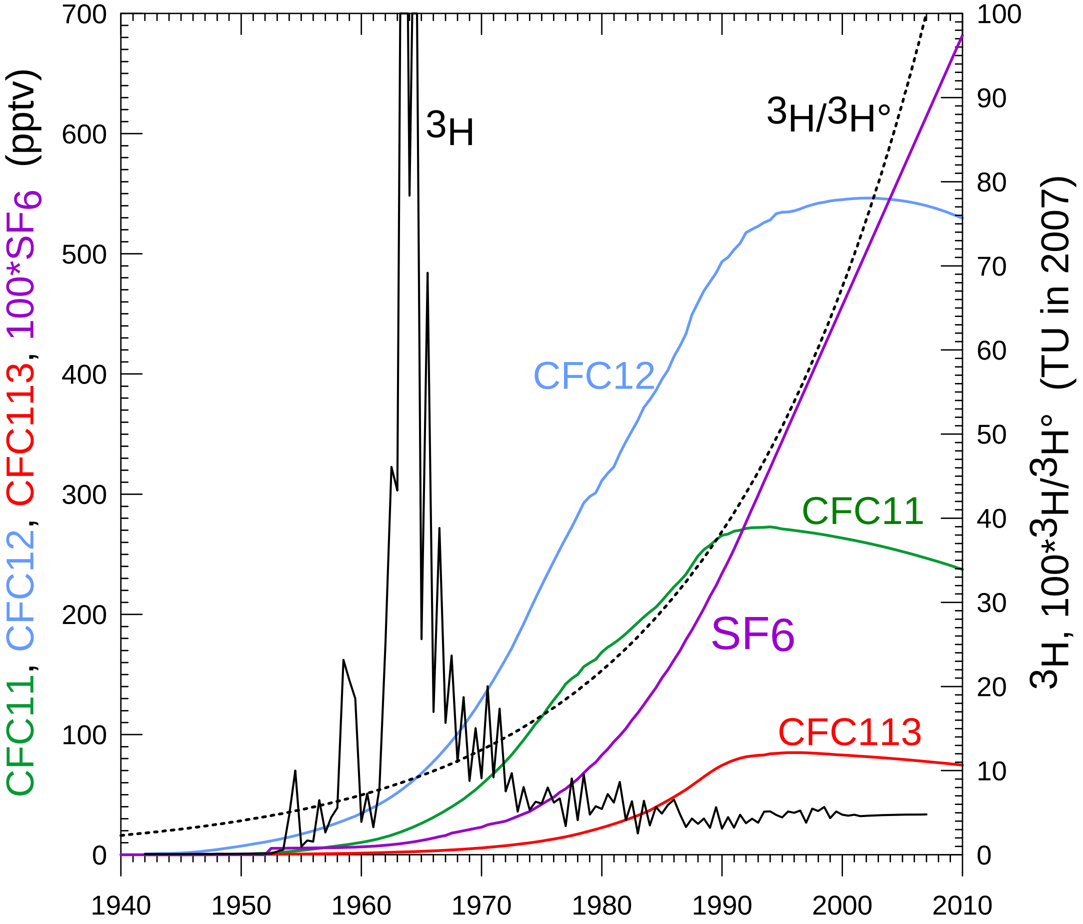

Figure S2. Atmospheric environmental tracers used for ground-water dating. Concentrations of CFCs and SF_6 (mixing ratios in parts per trillion [10^{-12}] by volume) are from mid-latitude northern hemisphere compilations by E. Busenberg, USGS (http://water.usgs.gov/lab/). The record of ^3H in Suffolk County recharge was estimated as follows: Measurements at Boston (1963-1986) were combined with data from Ottawa (before 1963) and Vienna (after 1986) after adjustments based on correlations for overlapping periods [40] (R.L. Michel, USGS, written communication, 2008), then that combined record was multiplied by 0.76 to give a mean value of 4.8 tritium units (TU) for decayed samples recharged since 1981 (this study). The ratio $^3H/^3H°$ expected from closed-system decay in precipitation samples collected in 2007 is shown for comparison.

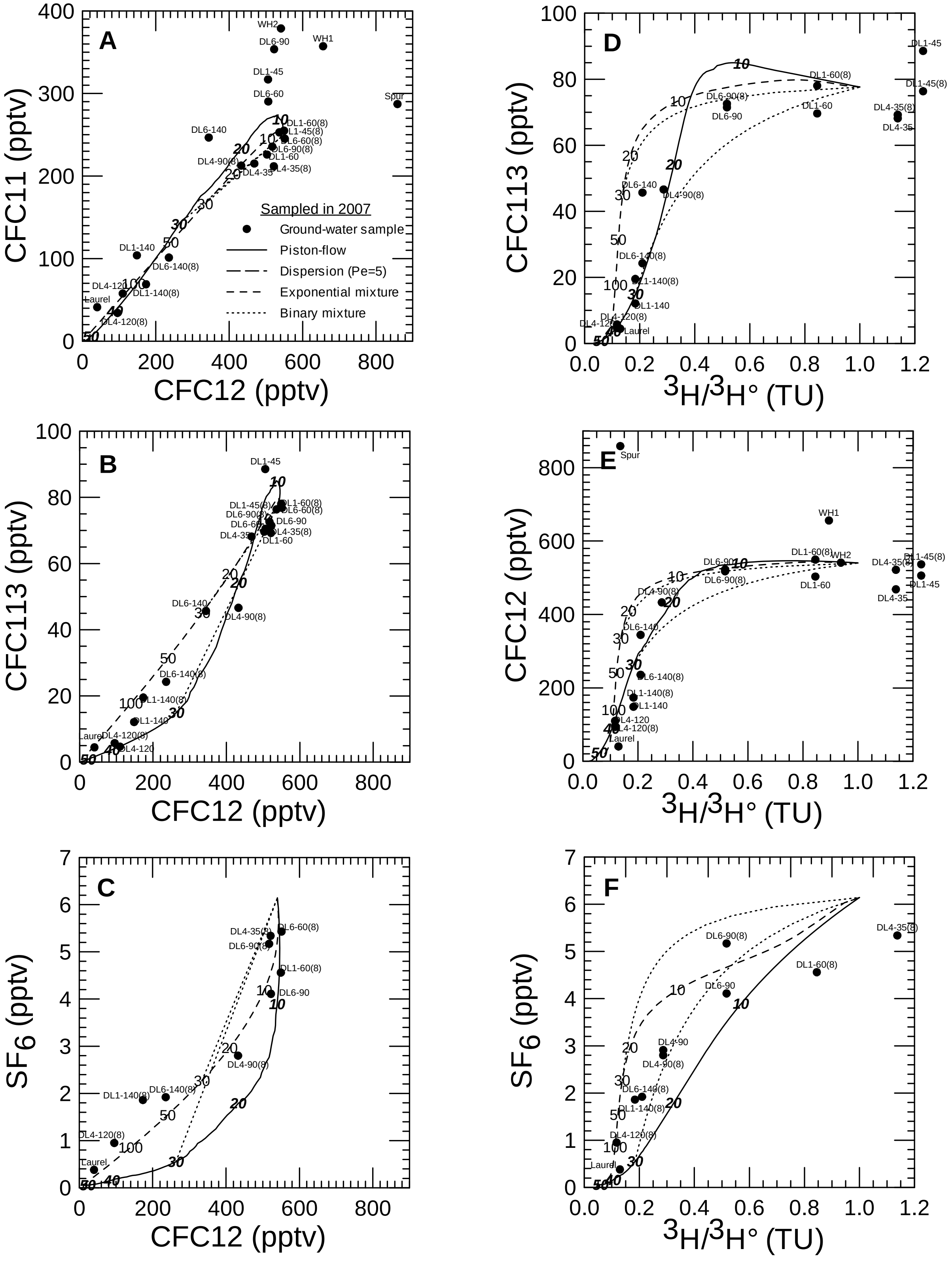

Figure S3. Tracer-tracer plots for atmospheric environmental tracers. Concentrations in samples compared to concentrations expected based on simple mixing models.

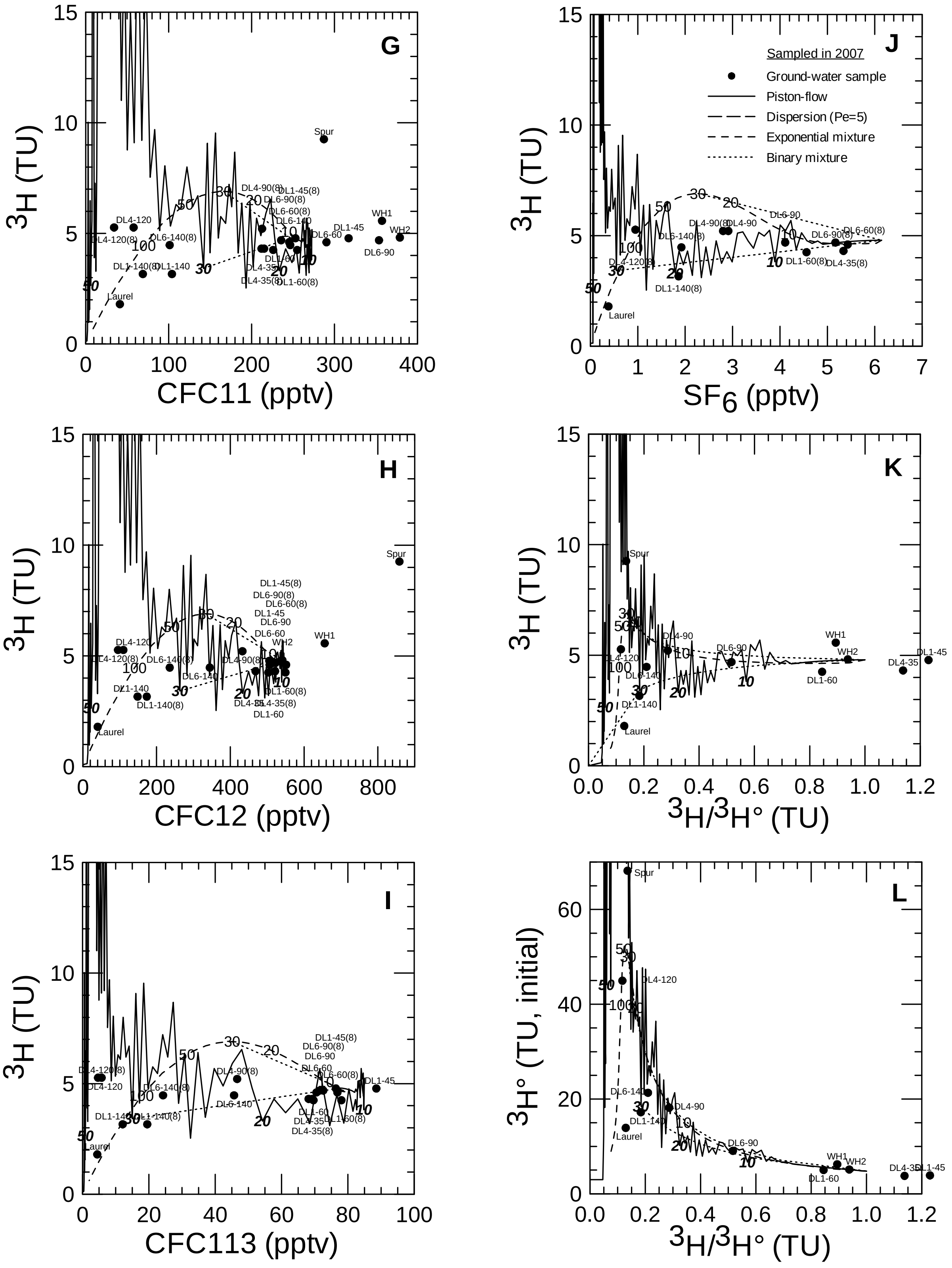

Figure S3 (continued). Tracer-tracer plots for atmospheric environmental tracers. Concentrations in samples compared to concentrations expected based on simple mixing models.

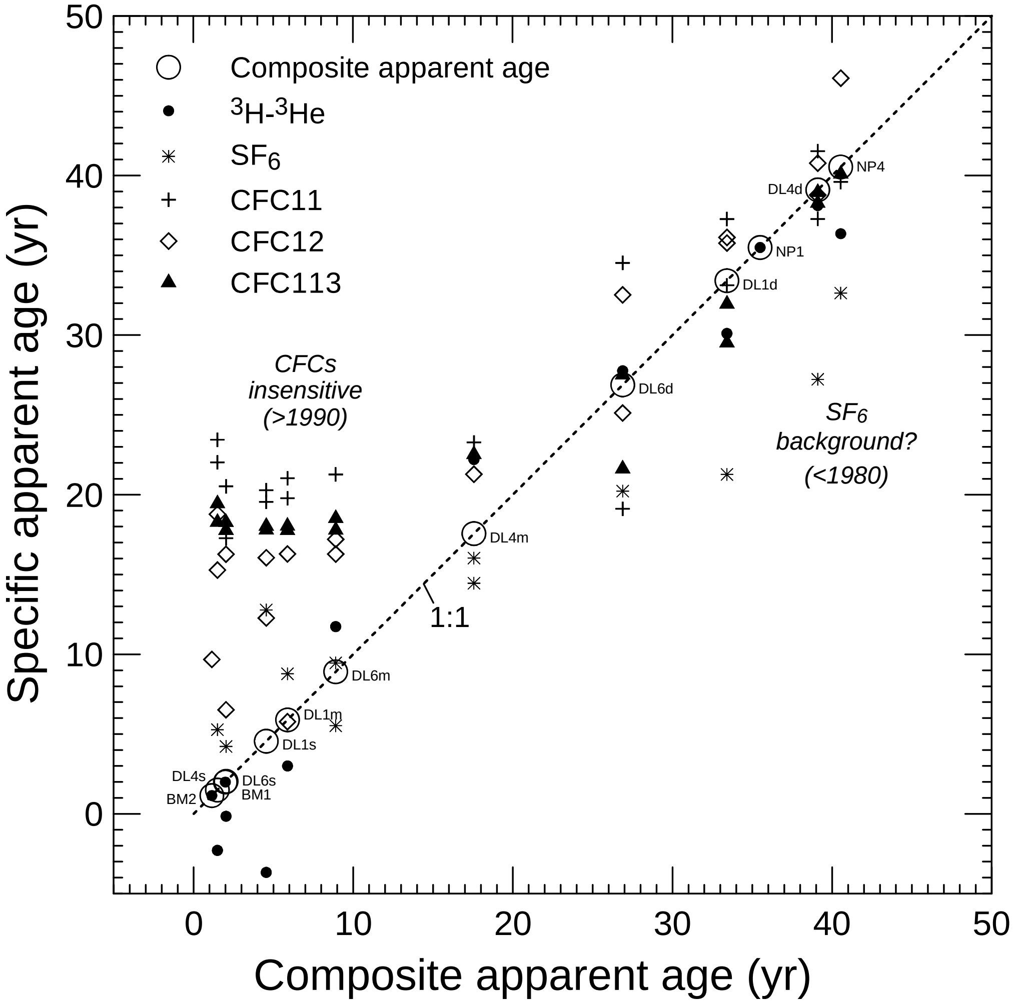

Figure S4. Apparent ground-water ages derived from specific atmospheric environmental tracers, compared with selected composite apparent ages (Table S1). Areas outlined by dashed lines indicate data that were not included in the composites. Persistent low concentrations of SF$_6$ yielding anomalously young ages in old waters may represent minor natural background or artificial sample contamination. Apparent ages from CFCs have large uncertainties after about 1990 because changes in atmospheric concentrations were relatively small.

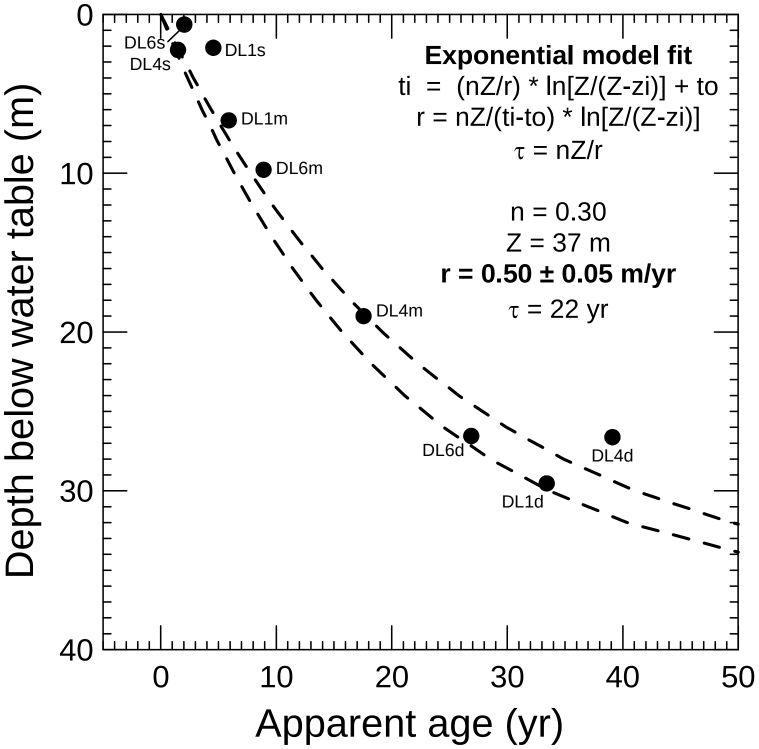

Figure S5. Distribution of composite apparent ages of ground-water samples with depth below the water table in the DL transect. Composite apparent ages are from Table S1 and Figure S4. Dashed curves are exponential age gradients representing a range of best fits to the apparent age profile, using equations and parameters indicated (see text).

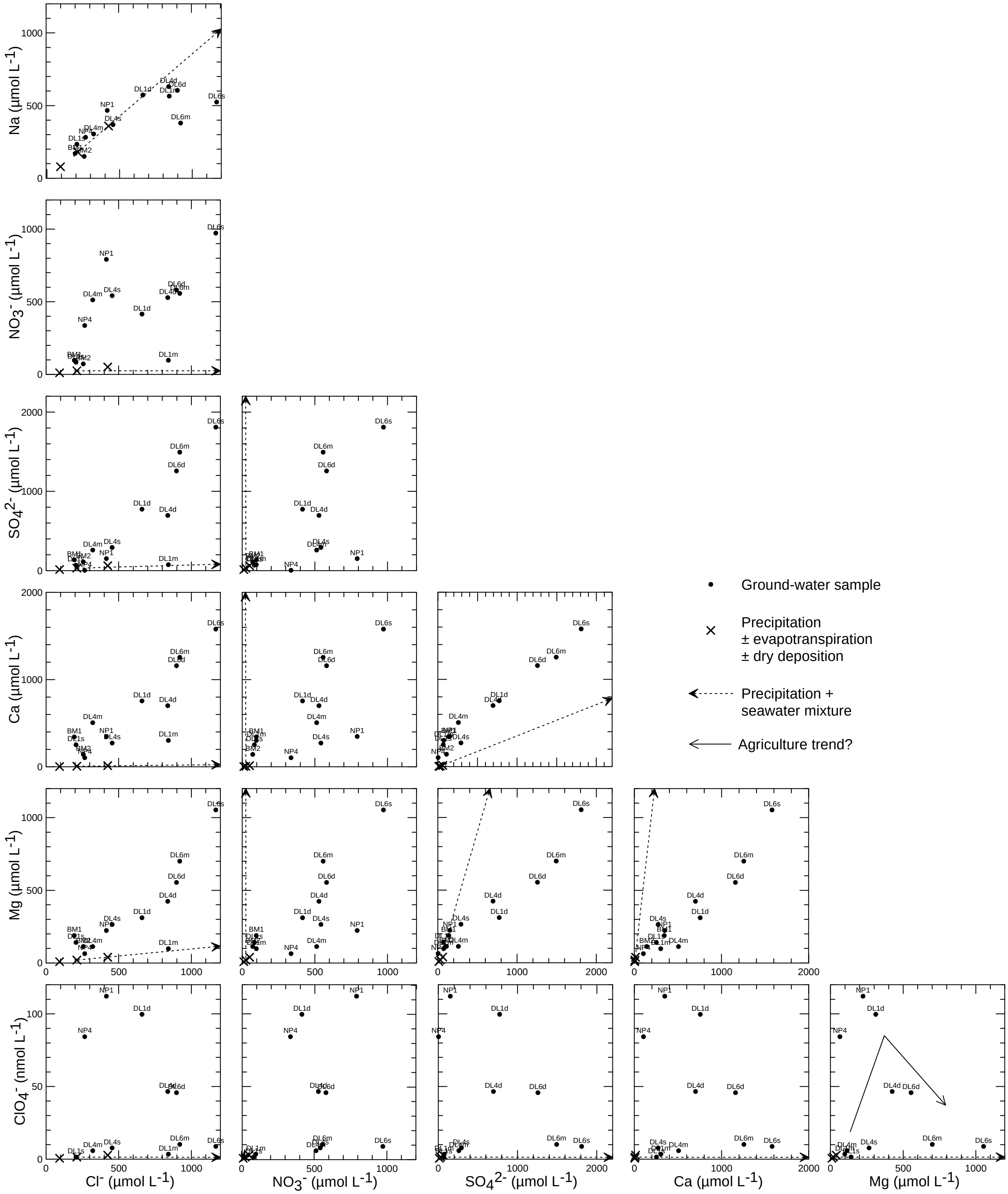

Figure S6. Selected constituents possibly related to agricultural land use. Dashed lines indicate hypothetical mixtures of atmospheric deposition and seawater. Alternative concentrations for atmospheric deposition are (1) measured values in precipitation (wet deposition); (2) 2.3 times the precipitation values, accounting for evapotranspiration indicated by the ground-water recharge rate at the DL transect; and (3) 4.6 times the precipitation values, accounting for evapotranspiration and an uncertain contribution from dry deposition (Table S2).

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Isotopic Composition and Origin of Indigenous Natural Perchlorate and Co-Occurring Nitrate in the Southwestern United States

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Perchlorate (ClO_4^-) has been detected widely in groundwater and soils of the southwestern United States. Much of this ClO_4^- appears to be natural, and it may have accumulated largely through wet and dry atmospheric deposition. This study evaluates the isotopic composition of natural ClO_4^- indigenous to the southwestern U.S. Stable isotope ratios were measured in ClO_4^- ($\delta^{18}O$, $\Delta^{17}O$, $\delta^{37}Cl$) and associated NO_3^- ($\delta^{18}O$, $\Delta^{17}O$, $\delta^{15}N$) in groundwater from the southern High Plains (SHP) of Texas and New Mexico and the Middle Rio Grande Basin (MRGB) in New Mexico, from unsaturated subsoil in the SHP, and from NO_3^--rich surface caliche deposits near Death Valley, California. The data indicate natural ClO_4^- in the southwestern U.S. has a wide range of isotopic compositions that are distinct from those reported previously for natural ClO_4^- from the Atacama Desert of Chile as well as all known synthetic ClO_4^-. ClO_4^- in Death Valley caliche has a range of high $\Delta^{17}O$ values (+8.6 to +18.4 ‰), overlapping and extending the Atacama range, indicating at least partial atmospheric formation via reaction with ozone (O_3). However, the Death Valley $\delta^{37}Cl$ values (−3.1 to −0.8 ‰) and $\delta^{18}O$ values (+2.9 to +26.1‰) are higher than those of Atacama ClO_4^-. In contrast, ClO_4^- from western Texas and New Mexico has much lower $\Delta^{17}O$ (+0.3 to +1.3‰), with relatively high $\delta^{37}Cl$ (+3.4 to +5.1 ‰) and $\delta^{18}O$ (+0.5 to +4.8 ‰), indicating either that this material was not primarily generated with O_3 as a reactant or that the ClO_4^- was affected by postdepositional O isotope exchange. High $\Delta^{17}O$ values in ClO_4^- (Atacama and Death Valley) are associated with high $\Delta^{17}O$ values in NO_3^-, indicating that both compounds preserve characteristics of O_3-related atmospheric production in hyper-arid settings, whereas both compounds have low $\Delta^{17}O$ values in less arid settings. Although $\Delta^{17}O$ variations in terrestrial NO_3^- can be attributed to mixing of atmospheric (high $\Delta^{17}O$) and biogenic (low $\Delta^{17}O$) NO_3^-, variations in $\Delta^{17}O$ of terrestrial ClO_4^- are not readily explained in the same way. This study provides important new constraints for identifying natural sources of ClO_4^- in different environments by multicomponent isotopic characteristics, while presenting the possibilities of divergent ClO_4^- formation mechanisms and(or) ClO_4^- isotopic exchange in biologically active environments.

Introduction

Perchlorate (ClO_4^-) is a common contaminant in water, soils, and plants, with potential toxic effects on thyroid function. Concerns about ClO_4^- in drinking water and food products have increased since the late 1990s. Because a large amount of synthetic ClO_4^- is used as an oxidant in solid propellants, its distribution initially was considered to be limited primarily to select military installations, aerospace facilities, and a small number of ClO_4^- manufacturing sites (*1*). However, during the past decade, it has become apparent that ClO_4^- is much more widely distributed in the environment than previously thought, and that a variety of natural and anthropogenic sources may contribute to its ubiquity. Major documented sources of ClO_4^- distributed in the environment by human activities include (1) electrochemically produced salts used as oxidants in solid rockets, air-bags, fireworks, flares, munitions, and other industrial products; (2) hypochlorite and chlorate salts, which contain ClO_4^- as a minor constituent; and (3) natural NO_3^--rich caliche salt deposits containing ClO_4^- from the Atacama Desert in Chile, which have been imported to the U.S. and elsewhere, primarily for use as fertilizer (*2*, *3*).

Natural ClO_4^- that is unrelated to the Atacama source has now been detected widely in groundwater and soils in the southwestern United States (U.S.). This "indigenous" ClO_4^- has been described in groundwater beneath a large area (155 000 km^2) of the southern High Plains (SHP) of Texas and New Mexico (*4*), in groundwater of Holocene and Pleistocene age in the Middle Rio Grande Basin (MRGB) in New Mexico (*5*), and in premodern (mainly Holocene) atmospherically deposited salt accumulations in the vadose zone throughout the arid southwestern U.S (*6*). Perchlorate is also ubiquitous in precipitation (*7*) and was detected (>40 ng L^{-1}) in more than 55% of groundwater samples in a national survey of wells presumed to be minimally impacted by human activities (*8*). Given the widespread occurrence and potential regulatory importance of natural ClO_4^-, its origins and distinguishing characteristics (e.g., isotopic composition) are receiving increased attention, but remain poorly understood. Additional data are required to establish the isotopic characteristics and origin (or origins) of natural ClO_4^- in the diverse environments in which it has been identified.

Stable isotope ratio analysis of Cl and O in ClO_4^- has been used to distinguish anthropogenic ClO_4^- from Atacama-derived natural ClO_4^- in source materials and groundwaters (*9*–*11*). Electrochemically produced ClO_4^- has relatively well-constrained $\delta^{37}Cl$ values (−3 to +2 ‰), more variable $\delta^{18}O$ values (−25 to −13 ‰), likely reflecting variations in the source water and fraction of O lost during production, and $\Delta^{17}O$ values that are consistent with mass-dependent fractionation of O isotopes ($\Delta^{17}O = 0.0 \pm 0.1$ ‰) (*10*–*12*) (see definitions in Table 1). In contrast, Atacama ClO_4^- from saline caliche deposits and imported Chilean nitrate fertilizers has isotopic compositions ($\delta^{37}Cl = -15$ to -12 ‰; $\delta^{18}O = -25$ to -3 ‰ and $\Delta^{17}O = +4$ to $+11$ ‰) that are distinct from those of synthetic perchlorate. Elevated $\Delta^{17}O$ values in ClO_4^-

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10.1021/es903802j

TABLE 1. Selected Chemical and Isotopic Data for Caliche-Type Salts in Unconsolidated Surficial Material from the Atacama Desert in Chile and the Death Valley Clay Hills Region of the Mojave Desert in California

		concentration				ClO_4^- isotopes			NO_3^- isotopes		
site	nonsoluble fraction	ClO_4^-	Cl^-	NO_3^--N	SO_4^{-2}	$\delta^{37}Cl^d$	$\delta^{18}O^b$	$\Delta^{17}O^e$	$\delta^{15}N^c$	$\delta^{18}O^b$	$\Delta^{17}O^e$
Death Valley	%	mg kg^{-1}		g kg^{-1}			‰			‰	
Confidence Hills 1	NA	0.25	320	1.8	72	−0.81	+2.9	+8.6	+3.4	+25.0	+7.9
Confidence Hills 2	49	0.85	180	5.5	100	−3.1	+7.2	+12.8	−1.0	+34.5	+12.7
Saratoga Hills	78	0.95	63	5.9	23	−1.4	+6.4	+10.9	−0.1	+43.6	+15.5
Bully Hill	62	0.82	80	28	6.5	NA	NA	NA	+5.1	+20.9	+7.2
Zabriskie	64	1.7	140	4.4	39	−3.7	+26.1	+18.4	+3.4	+32.8	+10.8
Atacama											
P1	42	243	80	12	57	−14.3	−10.5	+8.1	+0.2	+55.5	18.4
P2	50	328	456	44	84	−13.6	−6.7	+9.2	+0.6	+52.8	+17.3
P3	13	113	50	15	51	−11.8	−5.7	+8.8	−2.5	+55.9	+20.7
P4	51	132	61	22	51	NA	−7.8	+8.5	−2.1	+56.5	+20.7
GJ01	NA	5.4	6	1.2	13	−12.5	−5.2	+9.4	−0.2	+55.3	+20.7
UIC 24 (J-470)	NA	220	127	66	20	−12.8	−5.6	+8.8	+0.4	+49.6	+16.2[a,f]

[a] NA, not analyzed. [b] $\delta^{18}O = R_{sample}/R_{standard} - 1$, where $R = {}^{18}O/{}^{16}O$. [c] $\delta^{15}N = R_{sample}/R_{standard} - 1$, where $R = {}^{15}N/{}^{14}N$. [d] $\delta^{37}Cl = R_{sample}/R_{standard} - 1$, where $R = {}^{37}Cl/{}^{35}Cl$. [e] $\Delta^{17}O = ((1 + \delta^{17}O)/(1 + \delta^{18}O)^{0.525}) - 1$. [f] ‰ = parts per thousand; $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ values are referenced to 0 for SMOC, VSMOW, and VSMOW, respectively.

from the Atacama Desert have been interpreted as evidence that ClO_4^- were formed in part by reactions involving ozone (O_3) in the atmosphere, as atmospheric O_3 is known to be ^{17}O-enriched with measured and modeled $\Delta^{17}O$ values of ∼ +30 to 40‰ (*12, 13*). Moreover, concentrations of cosmogenic ^{36}Cl are consistent with an upper atmospheric origin for natural ClO_4^- (*14*). Reported kinetic isotope effects accompanying biological reduction of ClO_4^- alter its isotopic composition in a predictable manner (*15, 16*) that does not obscure distinctions between synthetic and Atacama ClO_4^- when all relevant isotope systems are considered (i.e., $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$).

At present, almost no information is available regarding the stable isotopic composition of natural ClO_4^- indigenous to the U.S. Two samples from groundwater wells in the SHP had reported isotopic compositions ($\delta^{37}Cl = +6.2, +5.1‰$; $\delta^{18}O = +4.7, +2.5‰$; $\Delta^{17}O = +0.4, +0.5‰$) that were different from those of both anthropogenic and Atacama ClO_4^- (*10*). These data indicated that the SHP groundwater ClO_4^- was either a mixture of biologically fractionated, electrochemically produced ClO_4^- and a much smaller amount of Atacama-like ClO_4^-, or that it represented an isotopically distinct type of natural ClO_4^-. As a result of recent studies on the distribution and potential sources of ClO_4^- in the SHP (*4*), and rapidly increasing detection of trace ClO_4^- in soils (*6*), groundwater (*5, 8*), and precipitation (*7*) throughout the U.S., the latter explanation now appears more likely, but additional ClO_4^- isotope data are required to confirm this hypothesis and expand the database to other indigenous ClO_4^- occurrences. In addition, because ClO_4^- and NO_3^- typically coexist in terrestrial environments, relations between NO_3^- and ClO_4^- isotopes can provide important constraints on their sources and transport.

The purpose of this paper is to report new data indicating substantial variation in the isotopic composition of natural ClO_4^- indigenous to the southwestern U.S. Samples were collected from natural occurrences in soils and groundwater from the SHP of Texas and New Mexico and the MRGB in New Mexico; unsaturated subsoil from the SHP of Texas; and surficial NO_3^--rich caliche deposits from the Mojave Desert near Death Valley, CA. These data were combined with other chemical and isotopic data to evaluate environmental factors responsible for ClO_4^- distribution and isotopic characteristics, including the origin and isotopic composition of co-occurring NO_3^-.

Materials and Methods

Sampling Locations. Samples for ClO_4^- stable isotope ratio analysis were obtained from groundwater, unsaturated subsoils, and caliche-type saline mineral deposits within the southwestern U.S. (Figure 1 and Supporting Information (SI) Figure S1). These sites were selected because previous studies indicate that they represent natural occurrences. Additional samples were obtained from the Atacama Desert including one groundwater sample and five soil/caliche samples (SI Table S1 and S2).

Groundwater ClO_4^- samples were obtained from the SHP (including one sample from the adjacent rolling plains) of western Texas and eastern New Mexico ($n = 8$) and from the MRGB of central New Mexico ($n = 2$) (Table 2 and SI Table S2). The SHP wells were at five distinct sites, with two wells (MW2 and MW3) installed at the same location but screened at different intervals. These wells were sampled in duplicate (MW2A,B and MW3A,B). A single sample (SHP-V) was obtained from a natural subsurface accumulation of salts within unsaturated subsoils at the Range Ecology Research Site at Texas Tech University (Figure 1 and SI Figure S1). This site is a 142 ha section of land that has been used to study numerous aspects of range ecology but has not been irrigated or subjected to other surface activity that would impact the presence of ClO_4^-. Lastly, ClO_4^- was obtained from near-surface caliche-type salt deposits on clay hills at four locations in the Death Valley region of the Mojave Desert, CA (Figure 1 and SI Figure S1). Clay-hills caliche salts in this area were studied previously because of their unusually high NO_3^-concentrations, which resemble those in the Atacama Desert (*17–21*).

Sample Collection. ClO_4^- in groundwater was collected by pumping water from each well through columns containing ClO_4^--selective anion-exchange resin (Purolite A-530E, Purolite Co., Bala Cynwyd, PA). Groundwater from wells MW3, MW2, BW2, RR8, and RR16 was pumped through resin columns in the field at flow rates ranging from ∼0.1 to 2 L min^{-1}. For the remaining wells, water was pumped into clean polyethylene drums (208-L capacity), which were then transported to Texas Tech University where the water was passed through ion-exchange columns, as described above. The total volume of water pumped through each column varied with ClO_4^- concentration, with the final objective being to extract at least 5 mg of ClO_4^- for purification and isotopic analysis. Groundwater was also collected for major anions,

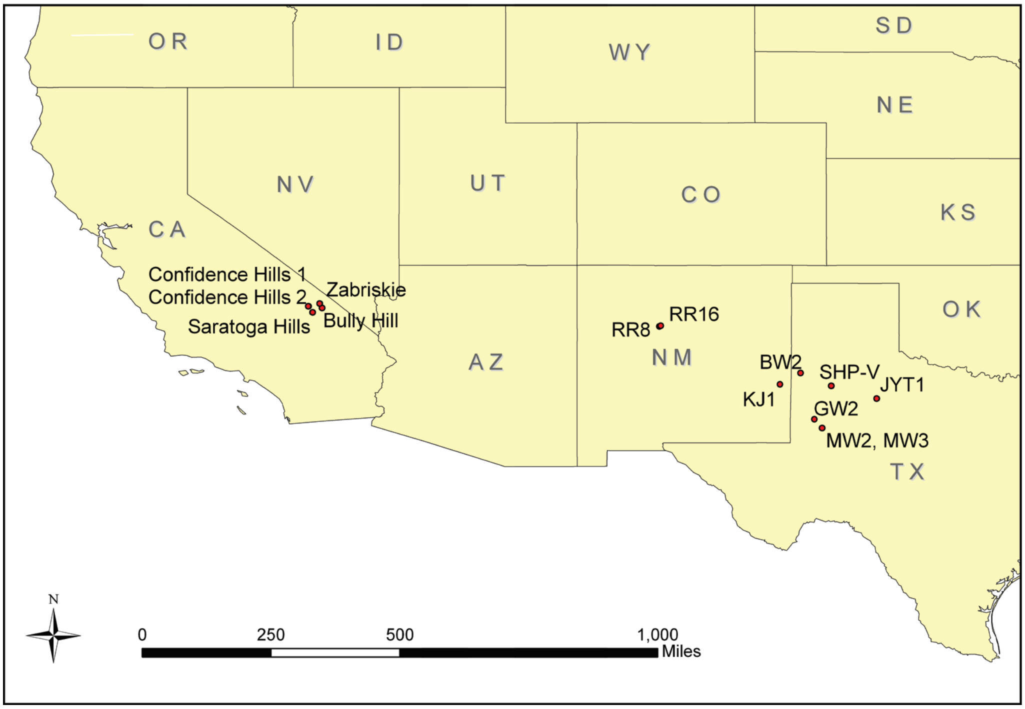

FIGURE 1. Sample locations (for a more detailed map see SI).

other isotopic analyses (NO_3^-, SO_4^{2-}, H_2O), major dissolved gases, and environmental tracers including ^3H, ^3He, SF_6, and chlorofluorocarbons (CFCs) (SI Table S2).

Perchlorate dispersed in the unsaturated zone (SHP-V) was collected by leaching soluble salts from the subsoil and then passing the leachate through a resin column as described above for groundwater. Initially, depth-dependent samples were obtained by hand auger to evaluate the vertical distribution of salts in the unsaturated zone. Based on these data, subsoil from approximately 2–4 m (depth range of maximum ClO_4^- concentration) was collected using a back hoe and placed on a tarp. Salts were extracted by mixing batches of subsoil (40–60 L) and water (80 L) in a precleaned cement mixer for ~10 min to form a slurry. Tap water from Lubbock, Texas was used for the extraction. Prior to use, the water was passed through a large column (~1000 cm^3) packed with Purolite A-530E resin to reduce ClO_4^- to <0.05 $\mu g\ L^{-1}$. After mixing, the slurry was allowed to settle for several hours, and then the water was decanted into polyethylene drums. The slurry in the drums was allowed to settle further overnight, after which the supernatant was pumped through a sediment prefilter (50 μM pore-size; General Electric Co., Trevose, PA) and then through a resin column. Influent and effluent samples were taken routinely to determine the concentration of ClO_4^- applied to the column and the efficiency of perchlorate removal by the column. A total of ~5600 kg of soil and ~3000 L of water were processed for the extraction.

The specific location and depth of the caliche-type salt accumulations collected from Death Valley were based on the NO_3^- content of the deposits, which were determined by field testing. NO_3^- was used as an indicator of ClO_4^- based on previous data. Bulk samples (20–50 kg) from each location were shipped to Texas Tech University and portions of these samples were leached using ClO_4^--free (<0.05 $\mu g\ L^{-1}$) distilled deionized water. The samples were sequentially extracted three times with a ~1:5 solid to water mass ratio each time. The ClO_4^- dissolved in the supernatant of these extracts was combined and collected on resin columns as described above. The concentrations of soluble salts in the bulk solids were estimated after drying and weighing the leached material after extraction. Aliquots of the leachate solutions were filtered and stored for chemical and isotopic analysis of solutes including ClO_4^-, NO_3^-, SO_4^{-2}, and Cl^-.

Sample Purification and Analysis. Procedures used for ClO_4^- extraction and purification from the resin columns and analysis of $\delta^{18}O$, $\Delta^{17}O$, and $\delta^{37}Cl$ are described elsewhere (see SI and refs *9–12, 16*). Perchlorate was eluted from the resin columns and purified at Oak Ridge National Laboratory. Purified ClO_4^- in the form of $CsClO_4$ was shipped to the USGS laboratory in Reston Virginia for analysis of $\delta^{18}O$ and $\Delta^{17}O$ on O_2 produced by decomposition. Chloride residue from the decomposed ClO_4^- was analyzed for $\delta^{37}Cl$ at the University of Illinois at Chicago. ClO_4^- concentrations were measured by sequential ion chromatography–mass spectroscopy-mass spectroscopy (IC-MS/MS) with a method detection limit of 0.05 $\mu g\ L^{-1}$ (*6*). Major anions (Cl^-, NO_3^-, SO_4^{2-}, and Br^-) were analyzed by ion chromatography following EPA Method 300.0. Major dissolved gases, and stable isotope ratios in NO_3^- and SO_4^{2-} ($\delta^{18}O$, $\delta^{15}N$, and $\delta^{34}S$), were analyzed at the USGS in Reston (see SI and ref). $\Delta^{17}O$ analyses of NO_3^- were also performed at the USGS in Reston on O_2 produced by thermal decomposition of purified NO_3^- (see SI). Tritium was analyzed by electrolytic enrichment and scintillation counting at the USGS in Menlo Park, CA. ^{14}C was analyzed by accelerator mass spectrometry under contract to the USGS National Water-Quality Laboratory (SI Table S2).

Results and Discussion

Death Valley Caliche Salts. In the U.S., surficial NO_3^--rich caliche deposits exist in the clay hills around the southern end of Death Valley within the Mojave Desert. These NO_3^- deposits were first described in the early 1920s and are much smaller in both aerial extent and total mass than the Atacama deposits, although the NO_3^- concentrations and NO_3^-/Cl^- ratios locally are similar to those of the Atacama NO_3^- ores (*17–20*). Isotopic analyses of the Death Valley NO_3^- deposits indicate a large fraction of the NO_3^- may be atmospheric in origin, whereas the remainder is presumed to have formed via microbial nitrification (*17, 21*). Similar processes were hypothesized to account for NO_3^- in the Atacama NO_3^- deposits based on isotopic analyses with a larger fraction

TABLE 2. Selected Chemical and Isotopic Data for Groundwater Samples from the Southwestern United States and Chile

well	location	ClO_4^-	NO_3^--N	Cl^-	O_2	^3H	dissolved inorganic carbon ^{14}C	ClO_4^- $\delta^{37}Cl$[d]	ClO_4^- $\delta^{18}O$[b]	ClO_4^- $\Delta^{17}O$[g]	NO_3^- $\delta^{15}N$[c]	NO_3^- $\delta^{18}O$[b]	NO_3^- $\Delta^{17}O$[g]
		$\mu g\ L^{-1}$	mg L^{-1}			TU[e] (±)	pmc[f] (±)		‰			‰	
MW2A	SHP, Texas and New Mexico, USA	24	2.9	1,300	6.8	2.5 (0.2)	38.4(0.3)	+4.2	+1.0	+0.3	+5.5	+2.0	+0.3
MW2B								+3.7	+1.4	+0.3	NA	NA	NA
MW3A		19	8.1	930	5.6	0.3 (0.2)	33.6(0.3)	+5.0	+2.2	+0.3	+6.6	+2.0	NA
MW3B								+4.1	+2.4	+0.3	NA	NA	NA
GW2		200	1.8	1,000	2.9	1.2 (0.2)	98.1(0.4)	+5.0	+3.8	+0.2	+19.5	+16.0	NA
BW2		1.8	1.7	61	7.6	0.1 (0.2)	83.5(0.5)	+4.5	+0.55	+0.6	+9.1	+3.7	NA
JYT1		3.8	6.1	190	6.1	3.7 (0.2)	99.7(0.4)	+5.1	+2.7	+0.5	+9.9	+5.2	NA
KJ1		15	5.2	430	7.4	0.2 (0.2)	91.5(0.4)	+4.5	+4.8	+0.8	+6.3	+0.3	+0.1
RR-8	MRGB, New Mexico,USA	0.67	2.6	9.0	NA	−0.2 (0.3)	11.6(0.2)	+3.1	+1.5	+1.2	+4.8	−1.2	NA
RR 16		0.85	1.9	21	NA	0.3 (0.2)	5.9 (0.1)	+3.6	+1.9	+1.3	+4.9	−1.0	NA
UIC-25	Chile	21,600	2,900	7,840	NA	NA[a]	NA	−12.9	−7.6	+9.3	+0.4	+49.9	+16.5[h]

[a] NA, not analyzed. [b] $\delta^{18}O = R_{sample}/R_{standard} - 1$, where $R = {}^{18}O/{}^{16}O$. [c] $\delta^{15}N = R_{sample}/R_{standard} - 1$, where $R = {}^{15}N/{}^{14}N$. [d] $\delta^{37}Cl = R_{sample}/R_{standard} - 1$, where $R = {}^{37}Cl/{}^{35}Cl$. [e] TU = Tritium Units $=10^{18} \times {}^3H$ atoms/H atoms. [f] pmc = percent modern carbon (not normalized for $\delta^{13}C$). [g] $\Delta^{17}O = ((1 + \delta^{17}O)/(1 + \delta^{18}O)^{0.525}) - 1$. [h] ‰ = parts per thousand; $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ values are referenced to 0 for SMOC, VSMOW, and VSMOW, respectively.

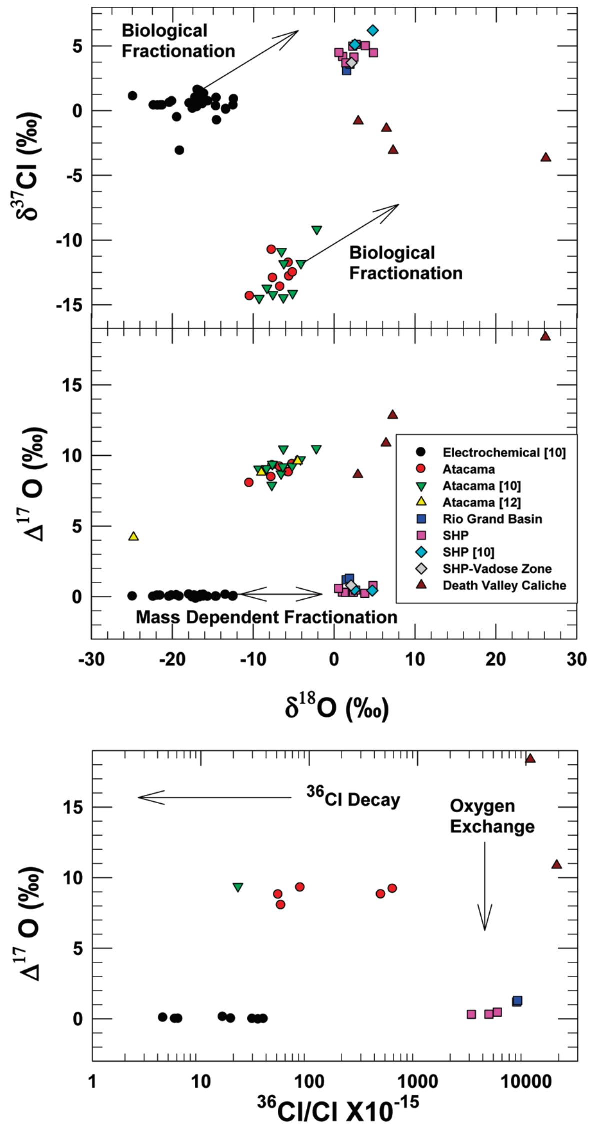

FIGURE 2. Summary of new isotope data for ClO_4^- from Southern High Plains (SHP) and Middle Rio Grande Basin (MRGB) groundwater, SHP unsaturated subsoil, Death Valley, and Atacama caliches displayed with previously published ClO_4^- isotope data (*10–12*). Arrows represent microbial fractionation slopes (*15, 16*), direction of mass dependent fractionation, direction of ^{36}Cl decay, and direction due to oxygen exchange. $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ values are referenced to 0 for SMOC, VSMOW, and VSMOW, respectively. ^{36}Cl values are from ref *14* with the exception of the Zabriskie sample (Death Valley caliche with the highest $\Delta^{17}O$) (Table 1). $\delta^{18}O = R_{sample}/R_{standard} - 1$, where $R = {}^{18}O/{}^{16}O$; $\delta^{37}Cl = R_{sample}/R_{standard} - 1$, where $R = {}^{37}Cl/{}^{35}Cl$ and $\Delta^{17}O = ((1 + \delta^{17}O)/(1 + \delta^{18}O)^{0.525}) - 1$.

due to atmospheric origin (*17, 21*). As part of the current study, new samples of NO_3^- and ClO_4^- from caliche salts and groundwater in the Atacama Desert were analyzed isotopically, confirming previous results (Figure 2; Table 1). Unlike the Atacama deposits, where the presence of ClO_4^- is well established, ClO_4^- has not previously been documented as a common constituent of the Death Valley deposits (*19, 23*).

In the collected Death Valley caliche samples, ClO_4^- concentrations ranged from 0.25 to 1.7 mg kg^{-1}, which are the highest reported ClO_4^- concentrations in any natural material in North America, but still approximately 1–3 orders of magnitude lower than in the Atacama NO_3^--rich caliches (*23*). Interestingly, the NO_3^- content of the Death Valley caliche is similar to that of the Atacama caliche, or at most an order of magnitude lower (SI Figure S2; Table 1). Nitrate

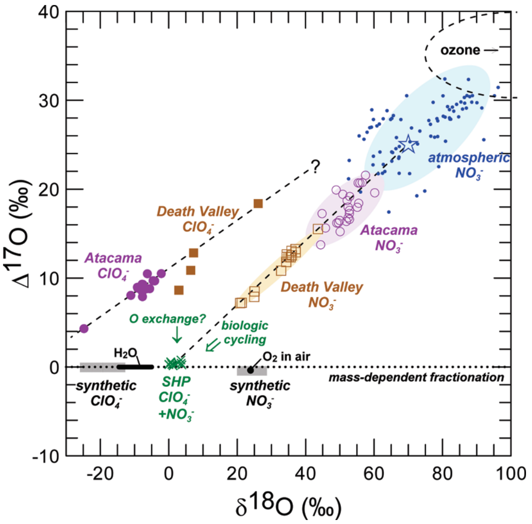

FIGURE 3. Relations between $\Delta^{17}O$ and $\delta^{18}O$ in ClO_4^- and NO_3^- (data from this study and from refs *10–12, 22, 29*). $\delta^{18}O$ and $\Delta^{17}O$ values are referenced to 0 for VSMOW (*10*). A hypothetical trend line is shown for NO_3^- mixtures consisting of biogenic and atmospheric (O_3-generated) end-members. A hypothetical trend line through Atacama and Death Valley ClO_4^- could indicate varying expression of O_3-generated components.

stable isotope ratios ($\delta^{18}O$, $\Delta^{17}O$, and $\delta^{15}N$) of the Death Valley caliche samples collected for this study overlap previously reported values for these deposits (*17, 21*), confirming a substantial atmospheric component of the NO_3^- (Table 1).

Perchlorate stable isotopic compositions of the Death Valley caliches are distinct from those of previously reported sources (Figure 2; Table 1). The $\delta^{37}Cl$ values are higher than those of Atacama ClO_4^- (including new data reported here) and generally lower than those of synthetic ClO_4^-. The $\delta^{18}O$ values are higher than those of both Atacama and synthetic ClO_4^-. However, the $\Delta^{17}O$ values of Death Valley caliche ClO_4^- generally are similar to those of Atacama ClO_4^- with the exception of the Zabriskie sample ($\Delta^{17}O = +18.4‰$), which has the highest $\Delta^{17}O$ value reported to date for ClO_4^- (Figure 2) Combined data from Death Valley and Atacama indicate a positive correlation between $\Delta^{17}O$ and $\delta^{18}O$ in caliche ClO_4^-, with one end of the correlation line pointing toward the isotopic composition of atmospheric O_3 and the other end approaching the terrestrial mass-dependent fractionation line at a negative $\delta^{18}O$ value (Figure 3) (see also ref *12*12). This pattern is similar to the one defined by NO_3^- isotopic data, for which atmospheric and biogenic end-members have been proposed (Figure 3).

Middle Rio Grande Basin Groundwater. ClO_4^- is present in Pleistocene and Holocene groundwater (0 to 28 000 years old) with minimal anthropogenic influence in the MRGB, New Mexico, at concentrations ranging from 0.12 to 1.8 $\mu g\ L^{-1}$ and with no systematic relation between groundwater age and ClO_4^- concentration (*5*). Wells sampled for the current study (RR8 and RR16; Table 2) are within the area of Pleistocene groundwater mapped previously as "northwestern recharge zone" and attributed to mountain-front recharge from low elevations around the southern part of the Jemez Mountains (*24*). This water is relatively dilute, with high dissolved O_2, and major anion concentrations (Cl^-, Br^-, SO_4^{-2}) that may largely represent atmospheric fluxes with varying amounts of evapotranspiration (*24*). The $\delta^{18}O$ values of the NO_3^- in these wells are much lower than those of atmospheric NO_3^- and are consistent with values produced by nitrification in soils. The $\delta^{15}N$ values of the NO_3^- are higher than those of atmospheric N species, possible indicating partial loss and isotope fractionation of N in soils prior to nitrification (*5, 25*) (see SI Figure S4). Dissolved gas concentrations and NO_3^- isotopes do not indicate denitrification in the saturated zone, hence it is also unlikely that ClO_4^- was reduced in the saturated zone given the residual NO_3^- in solution.

The sampled wells in this previously documented aquifer location had similar ClO_4^- concentrations and ClO_4^- isotopic compositions (Figure 2; Table 2). Estimated groundwater ages for both samples are greater than 10 000 yrs ($^3H \leq 0.3$ TU and DIC $^{14}C < 12$ pmc) (SI Table S2). Multiple lines of chemical, isotopic, and chronologic evidence indicate that this groundwater ClO_4^- is natural in origin (*5, 24*), SI Table S2, yet the ClO_4^- isotopic composition is distinct from those of the natural caliche-type occurrences, particularly with respect to the much lower MRGB $\Delta^{17}O$ values (Figure 2). Instead, the MRGB ClO_4^- is similar isotopically to ClO_4^- from SHP groundwater (see next section and ref *10*).

Southern High Plains Groundwater. ClO_4^- is present in groundwater (~0.1 to 200 $\mu g\ L^{-1}$) in at least 54 counties covering 155 000 km^2 in the SHP of Texas and New Mexico (*4*). The distribution and total mass of ClO_4^- in SHP groundwater appear to preclude anthropogenic sources (e.g., Atacama nitrate fertilizer, chlorate defoliants, fireworks, explosives, or flares) (*4*). Rather, the SHP ClO_4^- was interpreted to be natural and may represent wet and/or dry atmospheric deposition that accumulated in the unsaturated zone over millennial time scales and then was flushed to groundwater as widespread irrigation became common starting in the 1930s (*4*). Groundwater from wells evaluated in this study have apparent groundwater ages that range from modern (e.g., JYT-1 with 100% modern C and postbomb ^3H) to more than 10 000 years (e.g., MW3 with 34% modern C and ^3H near the detection limit); however, there is evidence for mixing of old and young water in some cases (MW2 with low ^{14}C and postbomb ^3H) (Table 2).

Samples for ClO_4^- isotopic analysis were collected from groundwater at five sites in the SHP, including two previously sampled sites, spread across an area of ~40 000 km^2 (Figure 1). ClO_4^- concentrations in these samples ranged from 1.8 to 200 $\mu g\ L^{-1}$ (Table 2). The new SHP ClO_4^- samples all have similar isotopic compositions that are indistinguishable from those of the two SHP ClO_4^- samples analyzed previously (*10*) (Figure 2; Table 2). Two hypotheses were advanced previously as possible explanations of ClO_4^- isotope data in SHP groundwater: (1) it is a mixture of biologically degraded synthetic ClO_4^- plus a small (~5%) amount of Atacama ClO_4^-; or (2) it is an isotopically distinct form of natural ClO_4^- (*10*). Given the reported ubiquity of ClO_4^- in the SHP groundwater and soils, its relatively homogeneous isotopic composition in samples with a wide range of concentrations, and its similarity to ClO_4^- in old groundwater in the MRGB, it appears likely these data represent a major natural ClO_4^- province that is isotopically different from the Atacama and Death Valley caliche ClO_4^- occurrences (Figure 2). The alternative hypothesis (mixing of biodegraded synthetic perchlorate plus Atacama ClO_4^-) would require the unlikely circumstance of a consistent mixing proportion of synthetic and Atacama ClO_4^-, along with a constant isotopic shift due to biodegradation, over a wide geographical region.

NO_3^- in the SHP groundwater generally had $\delta^{18}O$ values consistent with biogenic sources. Two SHP NO_3^- samples had low $\Delta^{17}O$ values (+0.3 and +0.1 ‰ for MW2 and KJ1, respectively), also consistent with a predominantly biogenic source of the NO_3^-. Sample GW2 had relatively low O_2 concentration, high $\delta^{15}N$, and high $\delta^{18}O$, possibly indicating partial denitrification.

Southern High Plains Unsaturated Zone. To further test the hypothesis that ClO_4^- in SHP groundwater was remobilized after having accumulated naturally in the unsaturated (vadose) zone, a sample of ClO_4^- for isotopic analysis (SHP-V) was extracted from unsaturated subsoil (2–4 m) beneath undisturbed rangeland (SI Figure S1). High concentrations of disseminated salts peaking at depth in the unsaturated zone are common in the southwestern U.S. and have been interpreted as atmospheric salts accumulated largely during Holocene time since the last major wet climate period in this region (*6, 26, 27*). The ClO_4^- and Cl^- concentrations in these accumulations are correlated (r = 0.59−0.99) and the estimated mass of ClO_4^- in the unsaturated zone (408 ± 88 g ha^{-1}) is more than sufficient to account for the estimated mass of ClO_4^- in SHP groundwater (*6*). The depth profiles of ClO_4^- and Cl^- at our sample site are similar to previously reported profiles in the SHP and elsewhere in the southwestern U.S., with an apparent concentration maximum at ∼3−4 m depth and maximum Cl^- and ClO_4^- concentrations of 370 mg kg^{-1} and 3.3 μg kg^{-1}, respectively (SI Figure S3). Our profile data are incomplete, as we did not sample below 4 m, yet the mass of Cl^- above 4 m represents > 5000 years of accumulation based on a Cl^- deposition rate of 157 mg/ha-year (*6*). The ClO_4^- isotopic composition of this sample (δ^{37}Cl = +3.7‰; δ^{18}O = +2.1‰; and Δ^{17}O = +0.8 ‰) falls within the range of the SHP and MRGB groundwater samples (Figure 2). This sample therefore supports the interpretation that widespread ClO_4^- in groundwater throughout the SHP is of natural origin and has a characteristic isotopic composition distinct from those of Atacama and Death Valley caliches.

Isotopic Constraints on Origins of Natural Perchlorate. The data presented in this paper expand the range of known isotopic variation in natural ClO_4^-, based on a combination of δ^{37}Cl, δ^{18}O, and Δ^{17}O data. Three major sample groups compared in this study have distinctive isotopic characteristics: Atacama caliche-type ClO_4^-, Death Valley caliche-type ClO_4^-, and SHP unsaturated-zone and groundwater ClO_4^- (Figure 2). The most variable of these individual groups is the Death Valley samples, which exhibit a wide range and positive correlation of δ^{18}O and Δ^{17}O values, including the highest values reported to date for ClO_4^- (Figure 3). Isotopic differences within and among these groups could be variably related to (1) isotopic compositions of precursor compounds prior to ClO_4^- formation, (2) isotopic fractionations accompanying ClO_4^- formation, (3) isotopic exchange between ClO_4^- and associated chemical species such as H_2O in the environment, and (4) kinetic isotopic fractionation caused by ClO_4^--consuming reactions such as microbial reduction. The importance of these different effects and their relation to regional variation in terrestrial ClO_4^- isotopic composition are not completely resolved. Additional constraints are provided by laboratory experiments, ^{36}Cl concentrations in ClO_4^-, and O isotopes in NO_3^-.

One possible explanation for isotopic differences between different natural ClO_4^- occurrences is different mechanisms and (or) locations of ClO_4^- formation. High Δ^{17}O values presumably indicate O transfer from O_3 during photochemical Cl oxidation in the atmosphere, whereas low Δ^{17}O values could indicate photochemical processes involving oxidants other than O_3, possibly occurring in the atmosphere or at the Earth's surface. Experiments indicate that ClO_4^- can be produced from reactions of oxy-chlorine intermediates (HOCl, ClO_2^-) by irradiation with UV or sunlight (*28, 29*). Chlorine dioxide (ClO_2) exists in the stratosphere and may be a precursor compound for a non-O_3-mediated process of ClO_4^- generation (*30*). The apparent correlation between Δ^{17}O and δ^{18}O values in both Atacama and Death Valley ClO_4^- could be interpreted as a mixing line between O_3 mediated and non-O_3-mediated production mechanisms similar to atmospheric NO_3^- (*12, 32*) (Figure 3). However, this hypothesis may be difficult to reconcile with the geographic distributions of ^{36}Cl/Cl ratios and Δ^{17}O values in ClO_4^-. Published data for a subset of our samples indicate relatively high concentrations of cosmogenic ^{36}Cl in natural ClO_4^- from both the Death Valley and SHP occurrences, and lower concentrations in Atacama ClO_4^- (Figure 2) (*14*). High ^{36}Cl/Cl ratios in the U.S. samples (8000−28 000 × 10^{-15}) seem to preclude formation of ClO_4^- from common Cl precursors in the troposphere or near the land surface. The ^{36}Cl data could be consistent with ClO_4^- having formed in the upper atmosphere and deposited onto the land surface, followed by varying amounts of radioactive decay depending on the accumulation times of the different deposits (of the order of 10^6−10^7 years in the Atacama and 10^4 years in Death Valley and the SHP) (*14*). If the bulk of the ClO_4^- in all of these occurrences formed in the stratosphere and was unreactive after deposition, then differences in the measured stable Cl and O isotopes would seem to require spatial variations in either the formation mechanisms or the isotopic compositions of precursor compounds in the atmosphere. However, the large range of Δ^{17}O values locally among the Death Valley samples, and the near absence of elevated Δ^{17}O values in the other southwestern U.S. ClO_4^- samples compared to the Death Valley samples, would be difficult to rationalize on the basis of high-altitude source variations.

Alternatively, postdeposition alteration of ClO_4^- isotopic composition could account for local variations in the stable isotopic composition of atmospherically produced ClO_4^-, and it could be related to similar processes affecting the isotopic composition of atmospheric NO_3^-. Microbial reduction of ClO_4^- is known to occur in soils and groundwaters under suboxic conditions, and it is known to cause large fractionation effects in Cl and O isotopes (*15, 16*). However, available data indicate these isotope fractionation effects would not be consistent with many of the differences observed among the natural ClO_4^- sample groups in Figure 2 (e.g., microbial reduction follows a specific trajectory in δ^{37}Cl and δ^{18}O and would not alter Δ^{17}O substantially because it is mass-dependent), so biodegradation is not considered to be the major cause of the observed differences.

Our data indicate strong positive correlations between Δ^{17}O and δ^{18}O values in ClO_4^- and NO_3^- from Death Valley and the Atacama Desert (Figure 3). Both compounds had relatively high Δ^{17}O in hyper-arid and barren settings (Atacama and Death Valley clay hills), although the relative positions of Atacama and Death Valley samples were reversed for the two compounds. Both compounds had relatively low Δ^{17}O values in less arid settings. For NO_3^-, although atmospheric production mechanisms have been proposed to vary both spatially and temporally, published analyses indicate consistently high mean annual Δ^{17}O values in atmospheric NO_3^- from many regions of the world, and it is considered likely that the full range of Δ^{17}O in terrestrial NO_3^- is largely a reflection of varying proportions of atmospheric NO_3^- (with high Δ^{17}O) and biogenic NO_3^- (with Δ^{17}O at or near 0) (*21, 31, 32*). In the current study, the highest Δ^{17}O values in NO_3^- (+17 to +21 ‰) were from the Atacama Desert and could indicate 60−80% of the NO_3^- was unaltered atmospheric NO_3^-, assuming a long-term average atmospheric NO_3^- Δ^{17}O value of +25 ‰ (*21*). Somewhat lower Δ^{17}O values in NO_3^- from the Death Valley region (+7 to +15 ‰) could indicate somewhat lower fractions of atmospheric NO_3^- (30−60%), based on the same assumption. Much lower NO_3^- Δ^{17}O values were obtained from two of the SHP samples (+0.1 and +0.3 ‰), indicating almost no unaltered atmospheric NO_3^-. From the strong correlation between values of Δ^{17}O and δ^{18}O for NO_3^- (Figure 3), we infer that the generally low δ^{18}O values of the other groundwater samples from SHP and MRGB also indicate little or no unaltered atmospheric NO_3^- in those samples. The presence or absence of atmospheric isotopic characteristics in NO_3^- in these environments is qualitatively consistent with the potential for biological N cycling in local soils (assimilation, N_2 fixation, mineralization, and nitrification) (see also SI Figure S4). These processes are expected to be more active in the SHP than in the Atacama Desert or the clay hills of Death Valley because of the low precipitation and general absence of plant life and organic soils in the latter environments. However, whereas nitrification of reduced N (including atmospheric NO_3^- formerly assimilated into biota and remineralized) is a well-documented mechanism for diluting or replacing the atmospheric $\Delta^{17}O$ signature of deposited NO_3^-, a comparable mechanism for similarly altering the isotopic composition of ClO_4^- has not been shown. Therefore, although terrestrial biologic processes can account for O isotopic variations in NO_3^-, and although the distribution of $\Delta^{17}O$ variations in both NO_3^- and ClO_4^- appear to be related spatially to local biologic activity, it is not yet possible to attribute ClO_4^- isotopic variation to the same processes that generally are thought to affect NO_3^- isotopes in these environments.

Another possible explanation for local variations in natural terrestrial ClO_4^- derived from the atmosphere is postdeposition isotope exchange (partial equilibration). Isotope exchange between ClO_4^- and H_2O would be expected to cause a decrease in $\Delta^{17}O$ and could be consistent with the ClO_4^- isotope data if exchange was more advanced in wetter or more biologically active environments. Equilibrium O isotope fractionation factors between ClO_4^- and H_2O are not known, but we expect $\delta^{18}O$ of ClO_4^- could be higher than $\delta^{18}O$ of coexisting H_2O by analogy with reported fractionation effects ranging from about +14 to +30 ‰ for SO_4^{2-}, HSO_4^-, NO_3^-, and NO_2^- at room temperature (*33*−*36*). Therefore, both the $\Delta^{17}O$ and $\delta^{18}O$ values of SHP and MRGB ClO_4^- could be qualitatively consistent with partial O isotopic exchange of Death Valley-type ClO_4^- with local H_2O ($\delta^{18}O = -13$ to -5 ‰) (Figure 3). Theoretical calculations indicate that $\delta^{37}Cl$ of ClO_4^- could be 73‰ higher than that of coexisting Cl^- at equilibrium (*37*). Thus, the relatively high $\delta^{37}Cl$ values of SHP and MRGB ClO_4^- might indicate partial exchange of Cl isotopes between ClO_4^- and Cl^- (or another Cl species) with increasing moisture and(or) biologic activity if the ClO_4^- source(s) had relatively low $\delta^{37}Cl$, as in Atacama or Death Valley ClO_4^-. However, it is difficult to envision a mechanism that could accomplish Cl isotope exchange, especially in the absence of O isotope exchange (e.g., to explain differences between Atacama and Death Valley $\delta^{37}Cl$ and $\Delta^{17}O$). Limited data indicate abiotic exchange of O isotopes between ClO_4^- and H_2O is slow, if it occurs at all, in simple laboratory experiments (time constant >100 years (*38*); > 4000 years (J.K. Böhlke and S.J. Mroczkowski, unpublished data)), but exchange might be catalyzed by other solid or aqueous species in soils and groundwaters, perhaps including organic compounds, as demonstrated for NO_3^- and PO_4^{3-} (*35, 39, 40*). Field data indicate that Atacama ClO_4^- introduced into humid soils and groundwaters in the eastern U.S., and synthetic ClO_4^- contamination in groundwater in southern Nevada, did not exchange Cl or O isotopes substantially, despite groundwater residence times of the order of 30−40 years (*9, 10*), although potential catalyzed exchange in unsaturated soils may have been precluded in those particular settings by rapid infiltration and recharge. Thus, although postdepositional isotope exchange could provide an explanation for some of the local natural ClO_4^- isotopic variations, it is not possible to predict rates of exchange with certainty, and it is not clear if any simple exchange model would produce the range of natural ClO_4^- isotopic compositions observed.

Implications for Perchlorate Isotope Forensics. Given present information, it is not yet possible to fully explain the observed variations in the isotopic composition of natural ClO_4^- sources, other than to say that some of the Atacama and Death Valley ClO_4^- probably formed as a result of reactions with O_3. The data permit the interpretation that natural ClO_4^- may have more than one formation mechanism, there may be global variations in the isotopic compositions of precursor compounds, and it may be subject to isotopic modification in the terrestrial environment. Resolving these issues would contribute to understanding atmospheric Cl chemistry, as well as the veracity of the isotopic approach for quantifying ClO_4^- sources in the environment. Nevertheless, despite uncertainty about processes responsible for some of the isotopic variations, this study indicates that natural ClO_4^- indigenous to the southwestern U.S. is distinguishable from synthetic ClO_4^- and from imported Atacama ClO_4^- on the basis of isotopic composition. These differences in isotopic composition may find important applications in resolving questions of ClO_4^- source apportionment for contaminated water supplies.

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Supporting Information Available

Additional notes on analytical methods and samples, a table of chemical and isotopic data for groundwater samples, a figure showing the SHP-V subsoil salt profile, and a figure comparing molar ratios of Cl^-/ClO_4^- and NO_3^-/ClO_4^- in various settings, are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information- Isotopic composition and origin of indigenous natural perchlorate and co-occurring nitrate in the southwestern United States

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10 Pages, Including 2 tables and 4 figures.

Methods for nitrate stable isotope analysis

$\delta^{15}N$ and $\delta\ ^{18}O$ in NO_3^- were measured by continuous-flow isotope-ratio mass spectrometry on N_2O produced from NO_3^- by bacterial reduction [1, 2, 3]. The data were calibrated by analyzing NO_3^- isotope reference materials using calibration data in Böhlke et al. [4]: For USGS34, $\delta^{15}N$ = -1.8 ‰ and $\delta^{18}O$ = -27.9 ‰; for USGS32, $\delta^{15}N$ = 180.0 ‰; for USGS35, $\delta^{18}O$ = +57.5 ‰. For samples with elevated $\Delta^{17}O$ of NO_3^-, $\delta^{15}N$ values measured by the bacterial method using conventional normalization equations were adjusted downward to account for non-mass-dependent $\Delta^{17}O$ effects on the N_2O ion ratios, based on the measured $\Delta^{17}O$ values of the NO_3^- [1, 4, 3]. This adjustment to $\delta^{15}N$ was equal to 0 when $\Delta^{17}O$ = 0 and -1.1 ‰ when $\Delta^{17}O$ = +21 ‰.

$\Delta^{17}O$ in NO_3^- was measured by dual-inlet isotope-ratio analysis of O_2 produced by off-line partial decomposition of $AgNO_3$ [5]. NO_3^- was isolated from mixed salt solutions by trapping on large-volume AG1X8 ion-exchange resin columns, followed by gradual elution with 0.5 M KCl to separate anions [6]. The KCl-KNO_3 eluent was passed through AG-MP50 cation-exchange resin columns in the Ag form to remove Cl and exchange K for Ag, then freeze dried to produce $AgNO_3$ salt. The $AgNO_3$ was heated under vacuum at 520°C while connected to a 5A° mol-sieve trap cooled with liquid N_2 to collect O_2, which was then isolated and transferred to the mass spectrometer and analyzed against tank O_2. No adjustments were made to the $\Delta\ ^{17}O$ data, as the measured $\Delta^{17}O$ values of NO_3^- isotopic reference materials RSIL-N11 and USGS35 were indistinguishable from reported values of -0.2 and +21.1 ‰, respectively [4,5].

Reporting of perchlorate isotope data

Tabulated and plotted values of $\delta^{18}O$ and $\Delta^{17}O$ for ClO_4^- were determined by off-line sealed-tube decomposition and dual-inlet isotope-ratio mass spectrometry on O_2 (designated O2-DIIRMS), and CH_3C, land the data were calibrated by analyzing ClO_4^- reference materials with the samples as described elsewhere [7,8]: For USGS37, $\delta^{37}Cl$ = +0.6 ‰, $\delta^{18}O$ = -17.0 ‰, and $\Delta^{17}O$ = 0.0 ‰; for USGS38, $\delta^{37}Cl$ = -87.2 ‰, $\delta^{18}O$ = +52.4 ‰, and $\Delta^{17}O$ = +73.3 ‰. A subset of the samples were also analyzed for $\delta^{18}O$ by an alternative method involving high-temperature reaction with C to produce CO, with continuous-flow isotope-ratio mass spectrometry on the CO (designated CO-CFIRMS), calibrated using the same reference materials as above [4]. For reagents and samples with relatively high original ClO_4^- concentrations, $\delta^{18}O$ values determined by O2-DIIRMS and CO-CFIRMS methods generally were indistinguishable. For some samples purified from low ClO_4^- soils and groundwaters, however, the O2-DIIRMS values tend to be slightly lower (commonly of the order of 0.5 to 1.0 ‰). These differences are not completely understood and may be due to trace contaminants in samples that are most difficult to purify. Nevertheless, the analytical differences are small compared to the range of isotopic compositions reported for the different ClO_4^- sources. Detailed descriptions of analytical interferences and calibrations will be reported elsewhere (Böhlke and others, in preparation).

Methods for separating and purifying perchlorate for isotopic analysis

Isotopic analysis of ClO_4^- isotope ratios requires mg amounts of pure alkali-ClO_4^- salts, but most environmental materials generally contain ClO_4^- at only ng kg^{-1} (ppt) to µg kg^{-1} (ppb)concentrations. For example, it may be necessary to process of thousands of liters of groundwater, or thousands of kg of soil, to extract a sufficient quantity of ClO_4^- for isotopic analysis. Groundwater and soil samples contain much higher concentrations of other anions, dissolved and suspended solids, and organic impurities, which complicate the extraction and purification of ClO_4^-.

Perchlorate from groundwater is concentrated onto packed PVC columns containing a ClO_4^--specific bifunctional anion-exchange resin (Purolite A-530E). Water is pumped through the resin column to trap ClO_4^-. For a typical 100-mL column, a flow rate of 1-2 L/min is used for processing water containing µg L^{-1} concentrations of ClO_4^-. At this flow rate, and assuming a groundwater concentration of 2 µg L^{-1}, ~ 3 – 6 mg of ClO_4^- could be concentrated on the resin column in 24 h. A pre-filter may be used before the column to remove any suspended solids from the water. To concentrate ClO_4^-

from soils or other solids, the samples are generally homogenized and then leached with ClO_4^--free water. The leachate is filtered to remove particulates and pumped through the anion-exchange resin column as described above. After sampling is completed, the resin column is stored at 4°C until ClO_4^- extraction and analysis.

In the laboratory, the resin is dispersed in deionized water or 4M HCl, ultrasonically cleaned, and then repacked into a column for elution. Prior to elution, the resin is flushed with three to five bed volumes (BV) of 4M HCl to remove anions (NO_3^-, SO_4^{2-}, HCO_3^-, organic anions, etc.) and other impurities. Then ClO_4^- is eluted with 3-5 BV of a mixed solution of 1M $FeCl_3$ and 4M HCl, and is usually concentrated in <0.5 BV of the eluent solution. To remove Fe^{+3} from the eluent solution, two approaches may be used: (1) neutralization with NaOH solution to pH 9-10, followed by settling and centrifugation to remove Fe^{+3} precipitates, or (2) cation exchange separation of Fe using a cation resin such as BioRad AG50WX12. In both methods, the resulting clear solution is then reduced by evaporation to a smaller volume (0.5-10 mL) for analysis of ClO_4^- concentration and other anionic impurities by ion chromatography (IC). Hydrogen peroxide may be added during evaporation to oxidize organics. If necessary, a second stage of purification using a smaller A-530E column or solid-phase extractant may be used to remove residual ions and impurities to achieve desired purity of ClO_4^-. Finally, the purified and concentrated ClO_4^- in solution is crystallized by the addition of CsCl or CsOH to cause supersaturation and precipitation of $CsClO_4$. The $CsClO_4$ precipitate is then washed with 90% MeOH and air dried prior to isotopic analysis by isotope-ratio mass spectrometry. Purity of final $CsClO_4$ crystals is verified by micro-Raman spectroscopy. Additional details pertaining to the use of A-530E resin for ClO_4^- extraction and purification are given in [9-12].

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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Table S1. Additional information about soil and caliche samples.

Sample ID	Location	Land Use	Latitude	Longitude	Date Sampled	Sample Depth	Sample Description	Elevation (m)
Confidence Hills 1	Death Valley, California, USA (Clay Hills)	National Park	N 35 50.350	W 116 35.256	2/16/2006	<1 m	Salt-cemented salt and clay	4
Confidence Hills 2			N 35 50.372	W 116 35.47	1/25/2008	~10-30cm	Salt-cemented green and red clay with chunks of mixed salts	40
Saratoga Hills			N 35 40.050	W 116 28.197		~5-30cm	Salt-cemented red clay streaked with white veins	130
Bully Hill			N 35 47.647	W 116 12.346		~5-30cm	Salt-cemented green and red clay with chunks of mixed salts	390
Zabriskie		Bureau of Land Management	N 35 55.103	W 116 16.234		~5-30cm	Salt-cemented green and red clay with chunks of mixed salts	420
P1	Baquedano District, Chile	Surface NO_3^- mines	S23 11.863	W69 40.635	10/12/2007	>6m	Salts in fractured andesite	1279
P2			S23 11.863	W69 40.635		>6m	Salts in fractured andesite	1279
P3			S23 12.059	W69 40.205		25cm	Unconsolidated sediments	1304
P4			S23 12.059	W69 40.205		50cm	$NaNO_3$ caliche	1304
GJ01	Chile	Unknown	Unknown		Unknown	Unknown	caliche	Unknown
UIC 24	Chile	Railway Cut	S23.16.53	W 69.46.14	11/03/2007	5m	NO_3^- vertical vein in regolith	1137

Table S2.Well information with chemical and isotopic data for groundwater sample

	Middle Rio Grande Basin		Southern High Plains					
Well Name	RR8	RR16	MW2	MW3	BW2	JYT1	GW2	KJ1
Well Type	PSW[1]	PSW	Monitor	Monitor	Monitor	Irrigation	Monitor	PSW
County, State	Sandoval, NM	Sandoval, NM	Martin, TX	Martin, TX	Bailey, TX	Kent, TX	Gaines, TX	Roosevelt NM
Latitude (N)	35.274	35.292	32.417	32.416	33.966	33.246	32.667	33.643
Longitude (W)	-106.732	-106.693	-102.155	-102.155	-102.765	-100.622	-102.376	-103.34
Land Surface Elevation (m)	1776	1686	881	881	1170	612	954	1285
Mid-Screen Elevation (m)	1383	1257	843	830	1147	594	943	
Screen Elevation ± (m)	94	178	1.2	3	3	1.2	3	
Water-Table Elevation (m)	1468	1488	846	846	1150	604	945	1250
Unsaturated-Zone Thickness (m)	308	198	35	35	21	8	9.0	35
Sample Date	9/12/2007	9/13/2007	11/8/2005	11/7/2005	11/9/2005	1/10/2006	6/1/2006	3/1/2007
Field parameters								
T (°C)			22.6	21.5	20.4	25.9	20.1	16.1
Specific Conductivity (µs/cm)			4709	4508	731	1818	6935	2411
Field O_2 (µmol/L)			213	174	236	190	91	230
Field pH			6.95	8.25	7.47		6.45	6.64
Water Chemistry								
TDS (g/l)			3.06	2.97	0.52	1.8	4.96	1.89
F (µmol/L)	38	58	215	192	128		190	66
Cl (µmol/L)	255	598	25000	37000	1600	5300	29000	12000
Br (µmol/L)	2	2	68	111	5	8	98	27
NO_3 (µmol/L)	187	137	577	209	120	437	129	370
SO_4 (µmol/L)	669	1039	13000	9500	1100	8100	26000	7400
ClO_4 (µmol/L)	0.0067	0.0085	0.20	0.11	0.02	0.04	2.05	0.15
Alkalinity (µmol/L as HCO_3)			4200	4000	4500	3200	6600	2800
Isotopes								
H_2O δ^2H (‰)	-85.4	-96.8	-42.6	-46.6	-39.0	-32.1	-39.0	-42.8
H_2O δ^{18}O (‰)	-11.66	-12.90	-5.75	-6.54	-5.71	-5.22	-5.43	-5.96
H_2O ^{3}H (TU) (±)	-0.22 (0.27)	0.32(0.22)	2.54(0.2)	0.34(0.17)	0.14(0.16)	3.68(0.22)	1.15(0.19)	0.15(0.23)
DIC δ^{13}C (‰)	-7.7	-6.4	-6.4	-6.4	-3.9	-11.2	-9.9	-7.7
DIC ^{14}C (pmc[2])(±)	11.6(0.2)	5.9(0.1)	38.4(0.3)	33.6(0.3)	83.5(0.5)	99.7(0.4)	98.1(0.4)	91.5(0.4)
DIC pmc Age (years)[3]	17300	22700	7700	8700	1450	25	151	710
SO_4^{2-} δ^{34}S(‰)	1.1(0.2)	4.8(0.2)	7.3(0.2)	7.7(0.2)	7.4(0.2)	10.2(0.2)	8.7(0.2)	10.1(0.2)
SO_4^{2-} δ^{18}O (‰)	3.0(0.2)	4.5(0.1)	7.7(0.1)	8.4(0.1)	4.6(0.2)	8.8(0.2)	3.7(0.1)	2.9(0.1)
Dissolved Gases								
CH_4 (µmol/L) (±)	0.000	0.000	0.000	0.000	0.000	0.055 (0.007)	0.000	0.000
Ar (µmol/L) (±)	12.35 (0.02)	13. (0.03)	13.91 (0.03)	13.9 (0.08)	13.91 (0.09)	13.52 (0.08)	15.22	13.21 (0.01)
N_2 (µmol/L) (±)	497(2)	534(1)	606(2)	581(4)	557(2)	589(8)	615	547(2)
Ar-N_2 equilibration T (°C)	19.2	16.3	20.5	18.6	15.2	23.2	12.8	18.3
Ar-N_2 excess air (ccSTP/L)	1.4	1.7	3.7	2.5	1.4	3.4	2.0	2.2

[1]PSW=public supply well; [2]pmc not normalized for δ^{13}C; [3]Conventional age from Libby half-life (8033 yr), not normalized for δ^{13}C

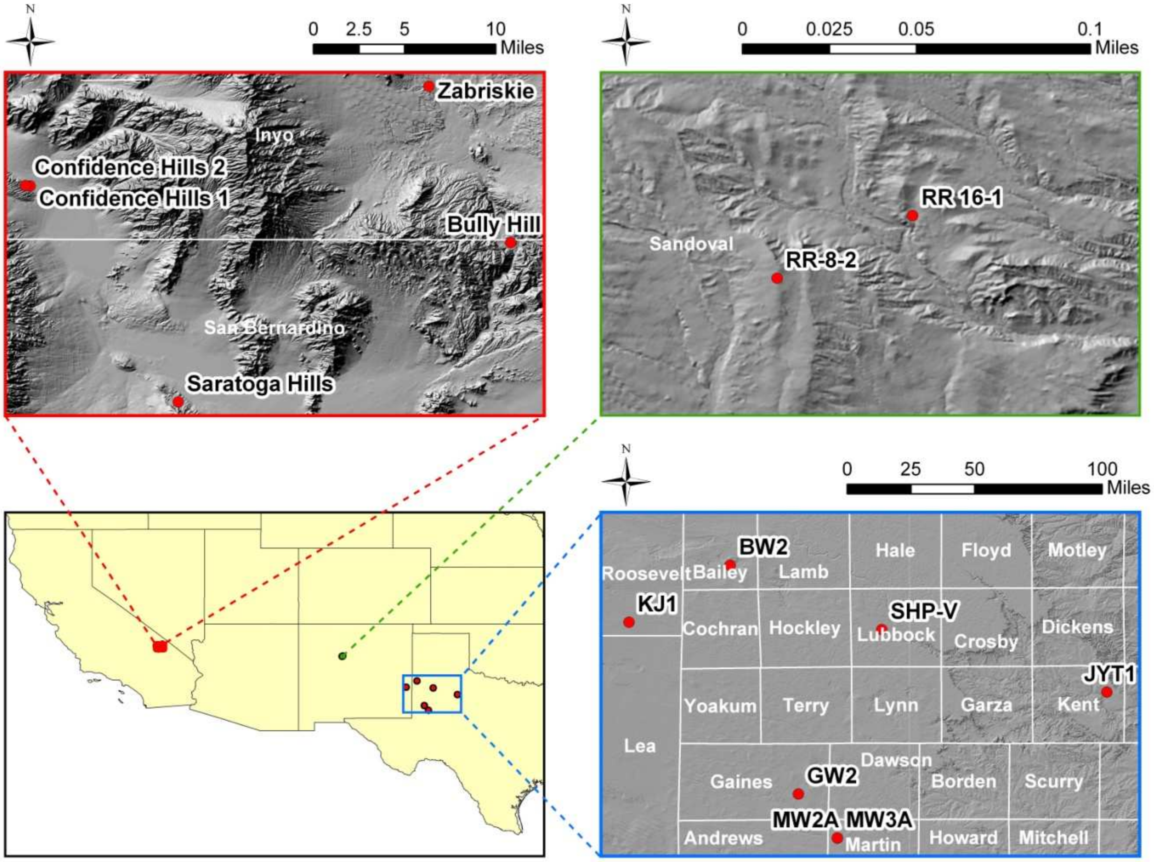

Figure S1. Sample Locations

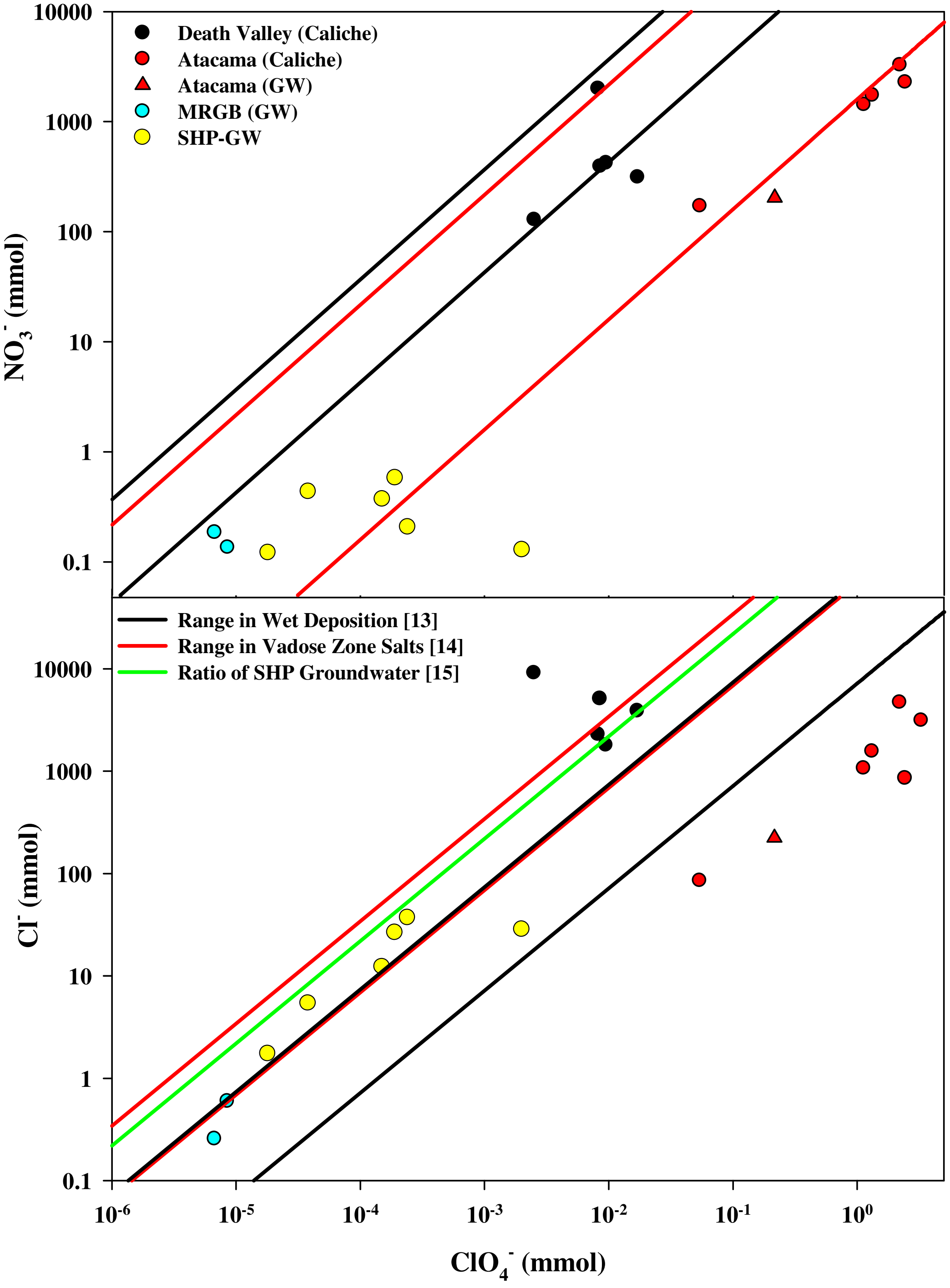

Figure S2. Comparison of NO_3^-/ClO_4^- and Cl^-/ClO_4^- molar ratios in new samples with previously published values for wet deposition across the contiguous United States (excluding coastal sites)[13] and vadose-zone salt accumulations in the southwestern United States[14]. The reported average Cl^-/ClO_4^- ratio is shown for groundwater (GW) in the SHP [15].

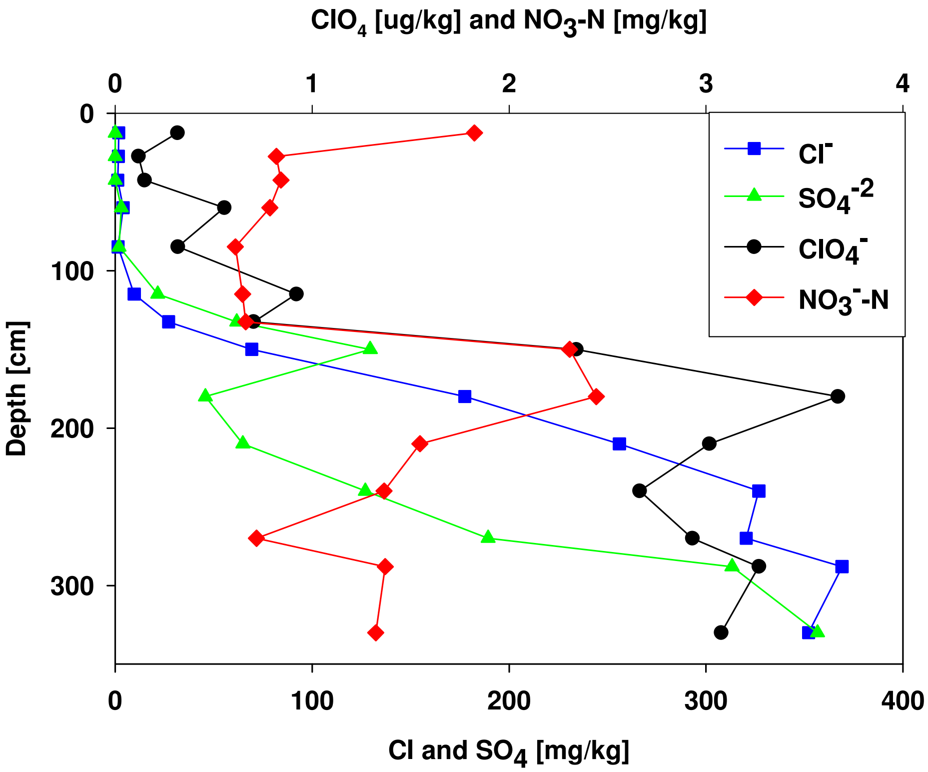

Figure S3. Distribution of ClO_4^- and other anions with depth below land surface at a rangeland site in the southern High Plains, western Texas. The water table was more than 15 m below land surface. Concentrations are given as mass of leachable anions per mass of solid material that was leached. Sample SHP-V was taken from 200-400 cm below land surface at this site.

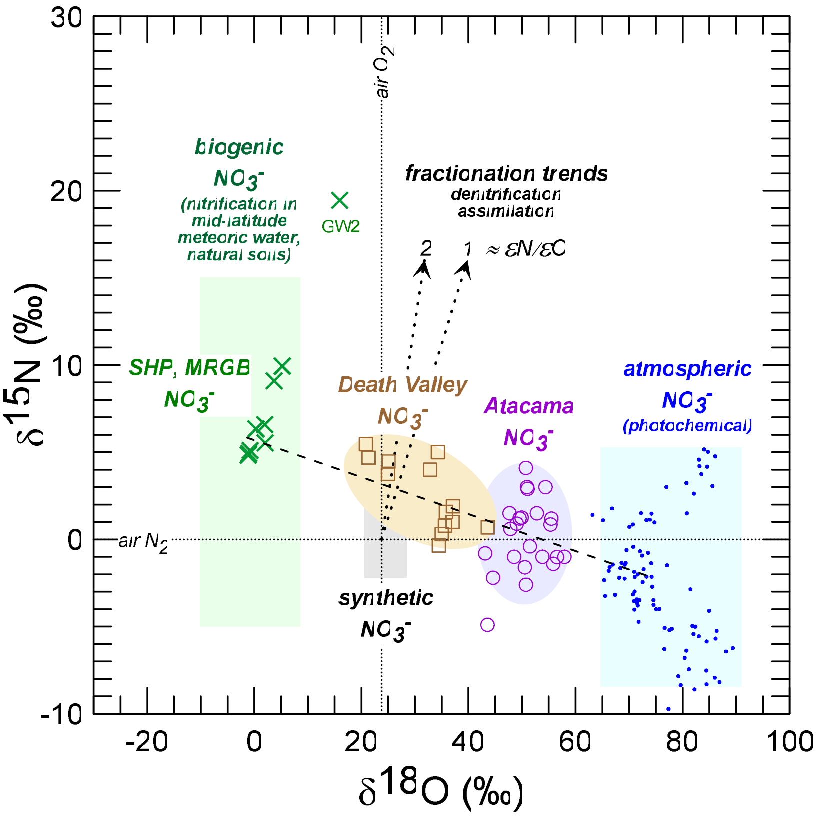

Figure S4. Relation between $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- in groundwater and leachate samples. A rough inverse correlation between $\delta^{15}N$ and $\delta^{18}O$ shown here is consistent with varying mixtures of natural biogenic NO_3^- and atmospheric NO_3^- indicated by a positive correlation between $\delta^{17}O$ and $\delta^{18}O$ in the paper (Figure 3).

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Chlorine-36 as a Tracer of Perchlorate Origin

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Perchlorate (ClO_4^-) is ubiquitous in the environment. It is produced naturally by atmospheric photochemical reactions, and also is synthesized in large quantities for military, aerospace, and industrial applications. Nitrate-enriched salt deposits of the Atacama Desert (Chile) contain high concentrations of natural ClO_4^-, and have been exported worldwide since the mid-1800s for use in agriculture. The widespread introduction of synthetic and agricultural ClO_4^- into the environment has contaminated numerous municipal water supplies. Stable isotope ratio measurements of Cl and O have been applied for discrimination of different ClO_4^- sources in the environment. This study explores the potential of ^{36}Cl measurements for further improving the discrimination of ClO_4^- sources. Groundwater and desert soil samples from the southwestern United States (U.S.) contain ClO_4^- having high ^{36}Cl abundances ($^{36}Cl/Cl = 3100 \times 10^{-15}$ to $28{,}800 \times 10^{-15}$), compared with those from the Atacama Desert ($^{36}Cl/Cl = 0.9 \times 10^{-15}$ to 590×10^{-15}) and synthetic ClO_4^- reagents and products ($^{36}Cl/Cl = 0.0 \times 10^{-15}$ to 40×10^{-15}). In conjunction with stable Cl and O isotope ratios, ^{36}Cl data provide a clear distinction among three principal ClO_4^- source types in the environment of the southwestern U.S.

Introduction

Perchlorate (ClO_4^-) is ubiquitous in trace amounts in precipitation, fresh surface water, groundwater, and soils (*1*). Synthetic ClO_4^- salts are widely used as oxidants in energetic materials such as propellants and explosives. Natural ClO_4^- is present in relatively high concentrations (~0.2 wt %) in natural nitrate-rich salt deposits from the Atacama Desert (Chile) that have been used worldwide in fertilizer production for well over a century (*2*). As a consequence of the widespread use of ClO_4^- in military, aerospace, and other industrial applications, the common application of large amounts of Chilean nitrate fertilizers in agricultural areas, and accumulation of indigenous natural ClO_4^- in arid regions (*3*–*5*), many groundwater supplies in the southwestern U.S. now have elevated concentrations of ClO_4^- in the ppb to ppm range. Perchlorate has been found in a variety of food products (*6*–*9*) and is ubiquitous in human urine and milk (*10*–*13*). The primary risk to human health from ClO_4^- ingestion comes from its inhibitory effect on iodine uptake and interference with thyroidal hormone production. A daily reference dose of 0.0007 mg/kg/day has been established (*14, 15*), and some states have set regulatory limits or action levels for drinking-water supplies ranging from 1 to 18 μg/L. Although no federal regulation for ClO_4^- in drinking water currently exists, the U.S. Environmental Protection Agency recently issued an interim health advisory level of 15 μg/L (*16*). Considerable uncertainty remains, however, about the sources, exposure pathways, and toxicity of ClO_4^- in humans (*11, 17*).

The recent development of methods for analyzing stable isotope ratios of Cl and O in ClO_4^- led to their application for distinguishing sources of ClO_4^- in the environment and for quantifying isotope effects caused by microbial reduction of ClO_4^- to Cl^- and H_2O (*18*–*22*). Natural ClO_4^- from the Atacama Desert has excess ^{17}O, indicating an atmospheric origin by photochemical reactions involving ozone (*19*); this finding is consistent with O isotope studies of NO_3^- and SO_4^{2-} from the Atacama Desert indicating atmospheric sources for those compounds as well (*23, 24*). Synthetic ClO_4^- has a Cl isotope ratio similar to that of its Cl source, and an O isotope ratio related to that of the water used for its production (*20, 25*). Although synthetic and Atacama ClO_4^- are isotopically distinct in terms of both Cl and O stable isotope ratios, some apparently indigenous natural ClO_4^-, such as that found in the High Plains region in western Texas and eastern New Mexico (*3*), has a distinct isotopic composition that cannot be unequivocally distinguished from a biodegraded mixture of synthetic ClO_4^- and Atacama ClO_4^- (*20, 25*). The differences in the isotopic composition of these two well-documented types of natural ClO_4^- (Atacama and High Plains) are not yet explained; they may represent different production mechanisms and/or different Cl reactants. To better understand the origins of different types of natural ClO_4^-, and thus to enable more diagnostic source apportionment in forensic studies, we measured the radioactive isotope ^{36}Cl in a set of representative samples.

Several atmospheric production mechanisms for natural ClO_4^- have been proposed and tested with laboratory experiments and balloon-borne measurements (*26*–*29*). The presence of ClO_4^- associated with stratospheric sulfate aerosols observed by single-particle mass spectrometry (*28*) supports a stratospheric production mechanism. Other mechanisms proposed for production of natural ClO_4^- in the troposphere or at the soil surface include ozone- and UV-catalyzed oxidation of Cl^- and OCl^-, which have been simulated in laboratory experiments (*29, 30*), and biogenic production analogous to nitrification. Stratospheric ClO_4^-, with its signature ^{17}O-enrichment inherited from stratospheric ozone, should also have a high initial abundance of cosmogenic ^{36}Cl because most ^{36}Cl production occurs in the

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TABLE 1. Chlorine Isotope Data for Synthetic Perchlorate Reagents and Products[a]

	δ^{37}Cl (‰)[b]	^{36}Cl/Cl (10^{-15})	*n*[c]
synthetic perchlorate reagents			
$KClO_4$, Aldrich (lot 11921HO)	+1.0	31 ± 4	1
$CsClO_4$, Aldrich (lot LI09119JI)	+1.6	34 ± 2	2
$HClO_4$, Baker (9656−1, lot 146358)	+0.6	28 ± 4	1
$KClO_4$, Baker (lot 45155)	+1.1	0.0 ± 2.5	1
$KClO_4$, General Chem. Co. (lot 13)	+0.6	6.2 ± 1.6	2
$NaClO_4$, Mallinckrodt (lot 1190 KHJJ)	+1.2	19 ± 4	1
NH_4ClO_4, Kerr-McGee (lot 7974F)	+0.7	22 ± 3	1
NH_4ClO_4, Kerr-McGee (lot 5094)	+1.5	37 ± 4	1
NH_4ClO_4, Kerr-McGee (lot 7914NN)	+0.3	30 ± 3	1
NH_4ClO_4, PEPCON (lot 87010)	+0.6	40 ± 3	1
NH_4ClO_4, PEPCON (lot 87015)	+0.7	38 ± 4	1
$NaClO_4$ solution, AMPAC, 2007	+0.4	30 ± 3	1
$KClO_4$, Hummel Croton	+0.2	6.4 ± 1.4	1
$KClO_4$, Taiwan	+0.3	5.8 ± 1.4	2
$NaClO_4 \cdot H_2O$, EM, Germany (lot SX0693−2)	−3.1	4.5 ± 1.3	1
$NaClO_4 \cdot H_2O$, EM, Germany (1992)	−5.0	7.7 ± 2.8	1
$NaClO_4 \cdot H_2O$, EM, Germany (1995)	n.a.	3.2 ± 1.0	1
synthetic perchlorate products			
ClO_4^- in highway safety flare	+0.1	16 ± 5	1
ClO_4^- in commercial bleach	+14.0	9.6 ± 1.6	1

[a] n.a. = not analyzed. [b] $\delta^{37}Cl = [R_{sample} - R_{standard}] - 1$, where $R = {}^{37}Cl/{}^{35}Cl$; std. dev. ± 0.2 ‰. [c] *n* = number of ^{36}Cl analyses per sample.

stratosphere (*31*). In contrast, ClO_4^- produced in the troposphere or at Earth's surface is more likely to have ^{36}Cl abundances typical of Cl^- in meteoric deposition, in which cosmogenic ^{36}Cl-enriched stratospheric Cl is diluted by marine Cl^- having negligible ^{36}Cl abundance (*32*).

The principal atmospheric production mechanism for ^{36}Cl is from galactic cosmic-ray spallation of ^{40}Ar (*31, 33*). The range of measured ^{36}Cl/Cl ratios of Cl^- in preanthropogenic groundwater across the continental U.S. is from $\sim 10 \times 10^{-15}$ near the coasts to as high as 1670×10^{-15} in the central Rocky Mountains (*34*). The lower ratios near the coasts reflect dilution by marine sea-salt aerosols in which $^{36}Cl/Cl = 0.0 \times 10^{-15}$. Evidence from fossil rat urine in packrat middens dating back to about 40 ka indicates that ^{36}Cl production rates (and therefore ^{36}Cl/Cl ratios in meteoric deposition) during the interval 35 to 10 ka may have been up to twice as high as modern values, because of fluctuations in geomagnetic intensity (*35*). No sample of soil or groundwater Cl^- having ^{36}Cl/Cl ratios as high as $2{,}000 \times 10^{-15}$ has ever been reported, except where bomb-produced ^{36}Cl is present (*32, 34*). Testing of thermonuclear bombs in the Pacific Ocean during 1952−1958 injected a large amount of ^{36}Cl, produced by neutron irradiation of seawater chloride, into the stratosphere, and produced worldwide ^{36}Cl fallout (*32*). The presence of bomb-pulse Cl^- may be identified from its anomalously high ^{36}Cl/Cl ratio relative to natural background values and from its association with high tritium activity. The highest measured ^{36}Cl/Cl ratio for bomb-affected groundwater Cl^- is $12{,}800 \times 10^{-15}$ (*34*). The ^{36}Cl/Cl ratio of Cl^- in Long Island (NY) rainwater, sampled in 1957 (during the peak of the nuclear bomb testing era in the Pacific) was as high as $127{,}000 \times 10^{-15}$ (*36*), and Arctic deposition in 1957 also had high ^{36}Cl/Cl [$28{,}600 \times 10^{-15}$] as observed in the Dye-3 ice core (*37*).

Samples and Methods

A set of 35 samples was chosen to represent the three known principal sources of ClO_4^- in the environment of the southwestern U.S., i.e., synthetic ClO_4^-, natural ClO_4^- from soils and groundwater of the Atacama Desert, and natural ClO_4^- from the southwestern U.S. They were analyzed for ^{36}Cl abundance by accelerator mass spectrometry at the Purdue Rare Isotope MEasurement (PRIME) Lab, and for stable Cl isotope ratio (^{37}Cl/^{35}Cl) at the Environmental Isotope Geochemistry Laboratory (University of Illinois at Chicago). Methods used for preparation and isotopic analyses of ClO_4^- and Cl^- are described elsewhere (*21, 22, 38*). The synthetic ClO_4^- samples were mostly laboratory reagents, but also included one sample derived from a highway safety flare and one extracted from a bottle of commercial bleach solution (6.5% NaOCl). The Atacama ClO_4^- samples were mostly extracted from bulk soils, with the exception of one sample collected from Atacama groundwater, one from industrial grade $NaNO_3$ produced in Chile from the Atacama nitrate deposits, and one from a New Jersey groundwater believed to have been contaminated with Atacama nitrate fertilizer-derived ClO_4^-. In addition to the Cl isotopic analyses of ClO_4^-, five samples of Atacama Cl^- extracts also were analyzed. The natural ClO_4^- samples from the southwestern U.S. were mostly extracted from groundwater having ClO_4^- concentrations ranging from 0.24 to 90 $\mu g\ L^{-1}$, with tritium and/or radiocarbon data indicating recharge times from pre-1945 to older than 10 ka (*3, 39*). However, two ClO_4^- samples (NM Water Canyon Gallery and TX Martin - shallow) were from groundwater having relatively high tritium activity, and one ClO_4^- sample was extracted from the leachate of a nitrate-rich caliche-type soil sample from the Mojave Desert at Saratoga Hills, near Death Valley, CA (*23, 40*).

Stable isotope ratios for Cl are given as δ^{37}Cl values relative to the Standard Mean Ocean Chloride standard, where $\delta^{37}Cl = ({}^{37}Cl/{}^{35}Cl)_{sample}/({}^{37}Cl/{}^{35}Cl)_{SMOC} - 1$, reported in parts per thousand (‰). The reproducibility of δ^{37}Cl values for ClO_4^- is given by the reported standard deviation (±0.2 ‰).

Results and Discussion

The results of Cl isotopic analyses for all samples are given in Tables 1−3. The Cl isotopic compositions of the ClO_4^- samples define three distinct, nonoverlapping clusters in a diagram of $^{36}Cl/Cl \times 10^{-15}$ vs δ^{37}Cl (Figure 1). The highest values of ^{36}Cl/Cl are those of the natural ClO_4^- samples from the southwestern U.S. (3100×10^{-15} to $28{,}800 \times 10^{-15}$); these samples have a range of δ^{37}Cl values from −1.3 to +4.5 ‰. Natural ClO_4^- samples collected from the Atacama Desert nitrate deposits have much lower values of ^{36}Cl/Cl and δ^{37}Cl

TABLE 2. Chlorine Isotope Data for ClO_4^- and Cl^- from Atacama Desert Nitrate Deposits and Products[a]

	$\delta^{37}Cl$ (‰)[b]	$^{36}Cl/Cl$ (10^{-15})	n[c]
Atacama Desert (Chile) nitrate deposits			
ClO_4^-, Baquedano District, shallow groundwater	−12.9	83 ± 10	1
Cl^-, Baquedano District, shallow groundwater	−0.3	87 ± 6	1
ClO_4^-, Baquedano District, vertical vein fill	−12.8	52 ± 16	1
Cl^-, Baquedano District, vertical vein fill	−0.8	53 ± 4	1
Cl^-, N. Tarapaca District, caliche soil	−1.7	0.9 ± 1.0	1
Cl^-, S. Tarapaca District, caliche soil	−1.2	18 ± 3	1
Cl^-, Tocopilla District, caliche soil	−1.7	79 ± 4	1
ClO_4^-, Estanque Oasis, fracture fill at −6 m (TTU-P1)	−14.3	55 ± 8	2
ClO_4^-, Estanque Oasis, fracture fill at −6 m (TTU-P2)	−13.6	590 ± 20	1
ClO_4^-, Estanque Oasis, surface pit mine (TTU-P4)	−11.8	460 ± 23	1
Atacama Desert (Chile) nitrate products			
ClO_4^-, SQM industrial grade $NaNO_3$ (purchased 2003)	−14.2	22 ± 3	1
Cl^-, SQM industrial grade $NaNO_3$ (purchased 2003)	n.a.	46 ± 7	1

[a] n.a. = not analyzed. [b] $\delta^{37}Cl = [R_{sample} - R_{standard}] - 1$, where $R = {}^{37}Cl/{}^{35}Cl$; std. dev. ± 0.2 ‰. [c] n = number of ^{36}Cl analyses per sample.

TABLE 3. Perchlorate Concentrations, Chlorine Isotope Data, and Tritium Activities of Groundwaters and Soil Leachate from the Southwestern United States[a]

	$[ClO_4^-]$, $\mu g\ L^{-1}$	^3H, TU	$\delta^{37}Cl$ (‰)[b]	$^{36}Cl/Cl$ (10^{-15})	n[c]
Southwest United States natural perchlorate					
Texas: Martin County, well water - shallow (36 to 39 m)	24	2.5 ± 0.2	+2.4	4550 ± 120	1
Texas: Martin County, well water - deep (48 to 54 m)	19	0.3 ± 0.2	+4.1	3130 ± 100	1
New Mexico: Roosevelt County, Kountry Jct., well water	15	0.2 ± 0.2	+4.5	5440 ± 170	1
New Mexico: Water Canyon Gallery Spring water	0.32	2.2 to 8.0	+4.1	28800 ± 920	1
New Mexico: Valle Grande Spring water	0.24	0.03 ± 0.09	+0.4	12300 ± 360	1
New Mexico: Albuquerque, RR 8−2 well water	0.67	−0.2 ± 0.3	+3.1	8240 ± 240	2
New Mexico: Albuquerque, RR 16−1 well water	0.85	0.3 ± 0.3	+3.7	8370 ± 270	2
California: Mojave Desert soil leachate[d]	n.a.	n.a.	−1.4	19200 ± 890	1
contaminated groundwater					
New Jersey: Bergen County, Park Ridge, well water	90	n.a.	−12.3	290 ± 12	1

[a] TU = tritium unit = ^3H atoms/10^{18} H atoms. n.a. = not analyzed. [b] $\delta^{37}Cl = [R_{sample} - R_{standard}] - 1$, where $R = {}^{37}Cl/{}^{35}Cl$; std. dev. ± 0.2 ‰. [c] n = number of ^{36}Cl analyses per sample. [d] Mojave Desert soil sample from Saratoga Hills, near Death Valley; bulk $[ClO_4^-]$ = 0.85 mg/kg.

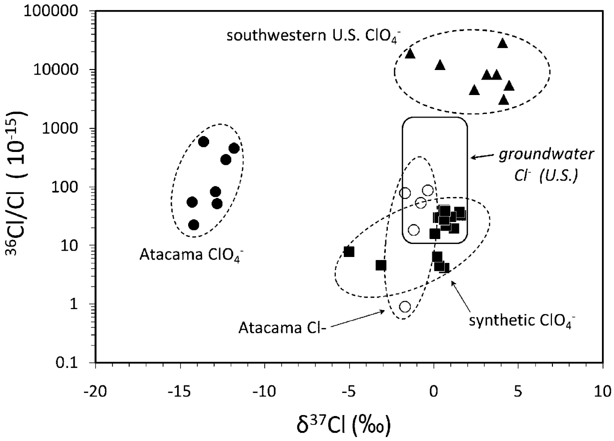

FIGURE 1. $^{36}Cl/Cl$ (atom ratio) vs $\delta^{37}Cl$ (‰) in representative samples of synthetic ClO_4^- reagents and products; natural ClO_4^- and Cl^- extracted from soil and groundwater from the Atacama Desert, Chile; and natural ClO_4^- extracted from groundwater and soil from the southwestern United States. Sizes of symbols exceed analytical errors. Delineated square area shows ranges of $^{36}Cl/Cl$ ratios and $\delta^{37}Cl$ values for Cl^- in U.S. groundwater (*46, 47*).

than those from the southwestern U.S. If the ClO_4^- in these two different regions formed by similar mechanisms and had similar initial ^{36}Cl abundances, then the contrast in measured ^{36}Cl abundance could be interpreted chronometrically if the southwestern U.S. ClO_4^- is assumed to have formed in Holocene or Pleistocene time (*2, 39*) and the mean age of the Atacama ClO_4^- is assumed to be 3−8 million years (*41, 42*), which is 10 or more half-lives of ^{36}Cl ($t_{1/2} = 301{,}000$ a). In a landscape as old as the Atacama Desert, with continuous deposition of atmospheric ClO_4^- since Miocene time, most of the ^{36}Cl would approach secular equilibrium with its environment. For the two Atacama samples in which $^{36}Cl/Cl$ was determined for coexisting ClO_4^- and Cl^-, the ratios are identical (within analytical uncertainty) and are within the range of typical subsurface equilibrium nucleogenic $^{36}Cl/Cl$ ratios in silicate rocks (*33*). The Atacama ClO_4^- sample having the highest $^{36}Cl/Cl$ ratio (590×10^{-15}), even if it had an initial $^{36}Cl/Cl$ ratio equal to the lowest of any natural ClO_4^- sample from the southwestern U.S. (3100×10^{-15}), would imply an apparent age of ∼750,000 a, which can be estimated from (*43*)

$$t = -1/\lambda_{36}\ln[(R_m - R_{se})/(R_i - R_{se})] \quad (1)$$

where t = time (a), λ_{36} = decay constant of ^{36}Cl (= $2.303 \times 10^{-6}\ a^{-1}$), R_m = measured $^{36}Cl/Cl$, R_i = initial $^{36}Cl/Cl$, and R_{se} = secular equilibrium $^{36}Cl/Cl$ ratio (assuming a typical value of 50×10^{-15}). This assumes the sample behaved as a closed system following its formation at time = t.

The reason for the difference in $\delta^{37}Cl$ values between the natural ClO_4^- samples from the Atacama Desert ($\delta^{37}Cl$ = −14.3 to −12.8 ‰) and the southwestern U.S. ($\delta^{37}Cl$ = −1.3 to +4.5 ‰) is not known because of the scarcity of available data on the isotopic composition of stratospheric Cl species and their global variations. Our data may imply a significant difference in the Cl isotopic compositions of the reactants that produce ClO_4^- at the two localities. Resolution of this issue could benefit from isotopic analyses of stratospheric Cl species and terrestrial ClO_4^- from other regions of the world, along with experimental studies of kinetic isotope effects accompanying potential stratospheric reactions that produce ClO_4^-.

Synthetic ClO_4^- typically is produced by electrochemical oxidation of NaCl brine (*44*). The Cl isotopic characteristics are therefore inherited from the source of NaCl used in the brine. Most of the synthetic ClO_4^- samples have $\delta^{37}Cl$ values in the range +0.2 to +1.6 ‰, which is consistent with a predominantly marine halite source having $\delta^{37}Cl = 0.0 \pm 0.9$ ‰ (*45*). The synthetic ClO_4^- reagent samples obtained from EM Co. (Germany) have anomalous $\delta^{37}Cl$ values of −3.1 and −5.0 ‰ that may reflect a Cl source other than typical marine halite (*46*), or fractionation during synthesis. The range in $^{36}Cl/Cl$ ratios of synthetic ClO_4^- samples (0.0×10^{-15} to 40×10^{-15}) is consistent with marine halite Cl sources, provided some nucleogenic ^{36}Cl contribution (e.g., from mudstone layers in bedded halites) to the higher values. The ClO_4^- samples known to have been produced in the southern Nevada area (Kerr-McGee and PEPCON samples, Table 1) all have similar $^{36}Cl/Cl$ ratios around 22×10^{-15} to 40×10^{-15}, whereas those produced in Germany, Taiwan, and by General Chem. Co. (production location unknown) and Hummel-Croton Co. (imported from China) appear to have a distinctly lower range in $^{36}Cl/Cl$ (3.2×10^{-15} to 7.7×10^{-15}). Only one synthetic ClO_4^- sample (from a jar of Baker $KClO_4$ dated 1963) has a $^{36}Cl/Cl$ ratio ($0.0 \pm 2.5 \times 10^{-15}$) consistent with pure marine Cl.

The high $^{36}Cl/Cl$ ratios in ClO_4^- from groundwater and soil samples from the southwestern U.S. (3100×10^{-15} to $28{,}800 \times 10^{-15}$), relative to the range of $^{36}Cl/Cl$ ratios in prebomb meteoric chloride deposition over the same geographic area (300×10^{-15} to 1110×10^{-15}) (*34*), appear to preclude a significant amount of ClO_4^- formation from Cl^- at or near the Earth's surface (e.g., by tropospheric ozone/UV irradiation, lightning strikes, or biogenic mechanisms). Such near-surface production mechanisms could not account for the elevated ^{36}Cl abundances observed in our samples of preanthropogenic ClO_4^- because the only apparent location of sufficiently ^{36}Cl-enriched Cl is the stratosphere, where cosmogenic ^{36}Cl production is highest (*31*). Although we are not aware of any evidence indicating in situ production of $^{36}ClO_4^-$ during the Pacific nuclear bomb tests, ^{36}Cl-enriched ClO_4^- would have been generated by normal production mechanisms from bomb-pulse ^{36}Cl injected into the stratosphere (i.e., bomb-pulse $^{36}ClO_4^-$). This phenomenon would have been transient, as the stratospheric residence time of bomb-pulse ^{36}Cl was around 2 yr (*37*), and any ClO_4^- produced in the stratosphere at this time would have had an anomalously high $^{36}Cl/Cl$ ratio and would have been deposited ultimately at the ocean or land surface within weeks of entering the troposphere.

Several of our samples (Water Canyon Gallery spring water, Martin shallow well water, and Mojave Desert soil leachate), on the basis of their appreciable ^3H abundances (in water samples) or exposure at the land surface (Mojave soil), could contain bomb-pulse $^{36}ClO_4^-$. The Water Canyon Gallery spring water and Mojave soil leachate ClO_4^- samples have the highest $^{36}Cl/Cl$ ratios of all we measured, and that of the Martin well shallow water sample ($^3H = 2.5$ TU) is 45% larger than that of the Martin well deep water sample ($^3H = 0.3 \pm 0.2$ TU), which also could indicate bomb-pulse $^{36}ClO_4^-$ in the younger, shallower Martin well water. For most of the southwest U.S. groundwater samples, however, low ^3H concentrations provide evidence that the high $^{36}Cl/Cl$ ratios predate thermonuclear bomb tests and are natural features of the ClO_4^-. New Mexico samples RR8 and RR16, with $^{36}Cl/Cl$ ratios exceeding 8000×10^{-15}, were obtained from groundwater with ^{14}C ages >10 ka ((*39*), Jackson and others, in preparation). The Atacama soil samples are mostly from pits or trenches and their exposure histories to atmospheric deposition during the past 50 years are less well documented; the presence of a small amount of bomb-pulse $^{36}ClO_4^-$ in some of these samples cannot be ruled out, but it would presumably have relatively minor impact because of the large reservoir of much older ClO_4^- in these deposits.

In summary, characteristic ^{36}Cl and ^{37}Cl isotopic abundances found in the three principal sources of ClO_4^- present in the environment of the southwestern U.S. allow these sources to be distinguished from each other. These results may have immediate forensic applications in delineating the sources of ClO_4^- in water supplies and foodstuffs, and they may provide important constraints for determining the natural production mechanism of ClO_4^-.

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