FINAL REPORT

Evaluation of Perchlorate Sources in the Rialto-Colton and Chino California Subbasins using Chlorine and Oxygen Isotope Ratio Analysis

ESTCP Project ER-200942

MARCH 2015

Paul B. Hatzinger
CB&I Federal Services, LLC

J.K. Böhlke
John Izbicki
Nicholas Teague
U.S. Geological Survey

Neil C. Sturchio
University of Delaware

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. REPORT DATE *(DD-MM-YYYY)* 03-20-2015	**2. REPORT TYPE** Final	**3. DATES COVERED** *(From - To)* 10/09/2009 - 3/31/2015

4. TITLE AND SUBTITLE EVALUATION OF PERCHLORATE SOURCES IN THE RIALTO-COLTON AND CHINO CALIFORNIA SUBBASINS USING CHLORINE AND OXYGEN ISOTOPE RATIO ANALYSIS	**5a. CONTRACT NUMBER** W912-HQ-08-C-0061 **5b. GRANT NUMBER** NA **5c. PROGRAM ELEMENT NUMBER** NA
6. AUTHOR(S) Hatzinger, Paul B., Ph.D. Böhlke, J.K., Ph.D. Sturchio, Neil C., Ph.D. Izbicki, John, Ph.D. Teague, Nicholas	**5d. PROJECT NUMBER** ER-200942 **5e. TASK NUMBER** NA **5f. WORK UNIT NUMBER** NA
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) CB&I Federal Services, LLC., Lawrenceville, NJ U.S. Geological Survey, Reston VA and San Diego, CA University of Delaware, Newark, DE	**8. PERFORMING ORGANIZATION REPORT NUMBER** NA
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Environmental Security Technology Certification Program 4800 Mark Center Drive, Suite 17D08 Alexandria, VA 22350-3600	**10. SPONSOR/MONITOR'S ACRONYM(S)** ESTCP **11. SPONSOR/MONITOR'S REPORT NUMBER(S)** NA

12. DISTRIBUTION/AVAILABILITY STATEMENT

Distribution Statement A: Approved for Public Release, Distribution is Unlimited

13. SUPPLEMENTARY NOTES

None

14. ABSTRACT

Perchlorate in groundwater can be from synthetic or natural sources, the latter of which include both historical application of imported nitrate fertilizers from the Atacama Desert of Chile and atmospheric perchlorate. The objective of this study was to evaluate the use of isotopic data to distinguish sources of perchlorate in groundwater in a specific region of the Rialto-Colton and Chino, CA groundwater subbasins. Perchlorate extracted from wells in this region was analyzed for chlorine and oxygen stable isotope ratios and radioactive chlorine-36 isotopic abundance, along with other geochemical, isotopic, and hydrogeologic data. The stable isotope and chlorine-36 data provided relatively unambiguous discrimination of synthetic and Atacama perchlorate sources in most wells having relatively high concentrations, providing regional perspective on anthropogenic perchlorate contamination in the Rialto-Colton and Chino subbasins. Where indigenous natural perchlorate was indicated as a substantial component, total perchlorate concentrations were low and concentrations of anthropogenic components were near background levels.

15. SUBJECT TERMS

perchlorate, isotope ratio analysis, chlorine, oxygen, chlorine-36, groundwater, forensic, Atacama, nitrate, fertilizer, Chile, Rialto

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** Dr Paul B. Hatzinger
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(Include area code)*
U	U	U	UU		609-895-5356

Reset

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Table of Contents

List of Figures

List of Tables

List of Acronyms and Abbreviations

‰	per mil
δ, Δ	delta, relative difference of isotope ratios
Ag	silver
AgCl	silver chloride
$AgNO_3$	silver nitrate
AMS	accelerator mass spectrometry
$BaSO_4$	barium sulfate
bls	below land surface
C	carbon
^{12}C	carbon-12
^{13}C	carbon-13
°C	degrees Celsius
CB&I	CB&I Federal Services, LLC
CF	continuous-flow
CF-IRMS	continuous-flow isotope ratio mass spectrometry
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
DI	dual-inlet
DI-IRMS	dual-inlet isotope ratio mass spectrometry
DIW	deionized water
DO	dissolved oxygen
DoD	Department of Defense
EIGL	Environmental Isotope Geochemistry Laboratory
ESTCP	Environmental Security Technology Certification Program
Fe	iron
Fe^{3+}	Iron (III)
$FeCl_3$	iron (III) chloride
$FeCl_4^-$	tetrachloroferrate
GIS	geographic information system
^2H	deuterium
^3H	tritium
HCl	hydrochloric acid

HCO_3^-	bicarbonate
He	helium
HNO_3	nitric acid
H_2O	water
H_2O_2	hydrogen peroxide
hr	hours
IAEA	International Atomic Energy Agency
IC	ion chromatography
IRMS	isotope-ratio mass-spectrometry
ITRC	Interstate Technology & Regulatory Council
IX	ion exchange
k	one thousand
KCl	potassium chloride
$KClO_4$	potassium perchlorate
kg	kilogram
km^2	square kilometer
KNO_3	potassium nitrate
KOH	potassium hydroxide
L	liter
LPM	liters per minute
μg	microgram
μg/L	microgram per liter
μmol	micromole
M	molar
MΩ	megaohm
MADEP	Massachusetts Department of Environmental Protection
MCL	maximum contaminant level
mg	milligram
mL	milliliter
mm	millimeter
MRGB	Middle Rio Grande Basin
MVSL	Mid-Valley Sanitary Landfill
m/z	mass to charge ratio
N	nitrogen or normal or number of entities
N_2	nitrogen gas
NaCl	sodium chloride
NADP	National Atmospheric Deposition Program
$NaNO_3$	sodium nitrate
ng	nanogram
NH_4ClO_4	ammonium perchlorate
N_2	nitrogen gas
NO_2	nitrogen dioxide
NO_3^-	nitrate
NWIS	National Water Information System
O	oxygen
^{16}O	oxygen-16

^{17}O	oxygen-17
^{18}O	oxygen-18
O_2	oxygen gas
O_3	ozone
pCi	picoCuries
pCi/L	picoCuries per liter
per mil (‰)	part per thousand ($\times 10^{-3}$)
PRIME	Purdue Rare Isotope Measurement Laboratory
QA/QC	Quality Assurance/Quality Control
R	ratio
RFF	rockets, fireworks, and flares
rg	reference gas
S	sulfur
SARWQCB	Santa Ana Regional Water Quality Control Board
SERDP	Strategic Environmental Research and Development Program
SHP	Southern High Plains
SIMS	secondary ion mass spectrometry
SLAP	Standard Light Antarctic Precipitation
SMOC	Standard Mean Ocean Chloride
SO_4^{2-}	sulfate
TAC	Technical Advisory Committee
TPA	tetrapentylammonium
TPABr	tetrapentylammonium bromide
$TPAClO_4$	tetrapentylammonium perchlorate
UIC	University of Illinois at Chicago
U.S.	United States
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
USGS	U.S. Geological Survey
VSMOW	Vienna Standard Mean Ocean Water
wt	weight
yr	year

Abstract

Perchlorate (ClO_4^-) in groundwater can be from synthetic or natural sources, the latter of which include both historical application of imported nitrate fertilizers from the Atacama Desert of Chile and naturally deposited ClO_4^- that forms atmospherically and accumulates in arid regions such as the southwestern US. The objective of this study was to evaluate the use of isotopic data to distinguish sources of ClO_4^- in groundwater in a specific region of the Rialto-Colton and Chino, CA groundwater subbasins (Study Area). This region includes two groundwater ClO_4^- plumes emanating from known military/industrial source areas, and a larger area outside of these plumes having measurable ClO_4^-. Perchlorate extracted from wells in this region was analyzed for chlorine and oxygen stable isotope ratios ($\delta^{37}Cl$, $\delta^{18}O$, $\delta^{17}O$) and radioactive chlorine-36 (^{36}Cl) isotopic abundance, along with other geochemical, isotopic, and hydrogeologic data. Isotope data indicate synthetic, Atacama, and indigenous natural ClO_4^- were present in the Study Area. Stable isotope data from nearly all sampled wells within the contours of the two characterized plumes, including those located in a perched zone and within the regional groundwater aquifer, were consistent with a dominant synthetic ClO_4^- source. In wells downgradient from the synthetic plumes and in the Chino subbasin to the southwest, isotopic data indicate the dominant source of ClO_4^- largely was Atacama, presumably from historical application of nitrate fertilizer in this region. Past agricultural land use and historical records are consistent with this source being present in groundwater. The ^{36}Cl and $\delta^{18}O$ data indicate that wells having predominantly synthetic or Atacama ClO_4^- also commonly contained small fractions of indigenous natural ClO_4^-. The indigenous ClO_4^- was most evident isotopically in wells having the lowest overall ClO_4^- concentrations (< 1 µg/L), consistent with its occurrence as a low-level background constituent in the region. A small subset of wells outside the contours of the two synthetic plumes, including an upgradient well, had characteristics indicating small amounts of synthetic ClO_4^- mixed with one or both of the natural source types. Hydrogeologic data indicate synthetic ClO_4^- in the upgradient well may be from a source other than the identified plume sources, but it is not known whether this source might also be present in other wells at low concentrations. The stable isotope and ^{36}Cl data provided relatively unambiguous discrimination of synthetic and Atacama ClO_4^- sources

in most wells having relatively high concentrations, providing regional perspective on anthropogenic ClO_4^- contamination in the Rialto-Colton and Chino subbasins. Where indigenous natural ClO_4^- was indicated as a substantial component, total ClO_4^- concentrations were low and concentrations of anthropogenic components were near background levels.

1.0 Introduction

The contamination of groundwater in the United States by perchlorate (ClO_4^-) has become an issue of national concern. It was once assumed that ClO_4^- contamination of groundwater largely resulted from historical testing and disposal practices by the military, the aerospace and ordnance industries, and ClO_4^- manufacturers. However, during the past decade it has become apparent that widespread agricultural use of nitrate fertilizer from the Atacama Desert of Chile (Urbansky et al., 2001a,b; Böhlke et al., 2005; Böhlke et al., 2009; Sturchio et al., 2011, 2012, 2014) as well as mobilization of indigenous natural ClO_4^- (Dasgupta et al., 2005, 2006; Rao et al, 2007) may also contribute to groundwater contamination. Isotopic techniques have been developed over the past decade to characterize different sources of ClO_4^- in the environment. The objective of this study was to evaluate sources of ClO_4^- in groundwater in a specific region of the Rialto-Colton and Chino, CA subbasins (Study Area) using chlorine and oxygen stable isotope ratio analysis and chlorine-36 (^{36}Cl) radioactive isotope analysis. In conjunction with ClO_4^- isotopic analysis, additional geochemical and hydrogeological data were collected in this region and evaluated. This evaluation included (1) water level mapping to evaluate the flow of groundwater, and the potential for ClO_4^- transport in the study area; (2) water chemistry analyses, including major ion composition, ClO_4^- concentrations, stable isotope ratios of hydrogen, oxygen, nitrogen, and sulfur in water, nitrate, and sulfate, groundwater age dating parameters, and dissolved gases; and (3) coupled well-bore flow and depth-dependent water quality data for several groundwater supply wells. The geochemical and hydrogeological data, along with interpretations, were published previously (Izbicki et al., 2014). That paper provides the hydrogeologic framework to support the isotopic study described herein.

1.1 Perchlorate Sources

The following sections summarize information about the principal sources of ClO_4^- in the environment.

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 contain NH_4ClO_4 (Cunniff et al., 2006). Potassium perchlorate ($KClO_4$) is also used for many military applications. 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., 2006). 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. Many groundwater plumes, which are often extensive and have ClO_4^- concentrations up to several hundred milligrams per liter (mg/L), 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 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; Munster et al., 2008; Munster, 2008; 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 Atacama 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, with concentrations as high as 6.8 % reported (Schilt, 1979; Ericksen, 1981, 1983; Dasgupta et al., 2006). These NO_3^- deposits, sometimes referred to as “nitrate 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 imported Atacama NO_3^- was used in California as fertilizer between 1923 and 1998 (California Department of Food and Agriculture, 1999). The final ClO_4^- concentration of processed Atacama NO_3^- fertilizer prior to 2002 was variable, and likely ranged from ~1,500 to 10,000 mg/kg (i.e., 0.15 to 1.0 wt. %) based upon analysis of historical samples (Eldridge et al., 2000; Urbansky et al, 2001a,b; Dasgupta et al., 2006). 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., 2006). Thus, apart from synthetic sources, past application of Atacama NO_3^- fertilizer provides a potential source of ClO_4^- in groundwater and drinking water in the U.S.

Based on a reasonable assumption of ~2,000 mg ClO_4^-/kg Atacama fertilizer (0.2%) (Dasgupta et al., 2006), one metric ton of processed Atacama fertilizer (prior to 2002) contained about 2 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 removal processes. Additional information on Atacama NO_3^- fertilizers as a source of ClO_4^- can be found in published papers (Ericksen, 1981, 1983; Bao and Gu, 2004; Dasgupta et al., 2006; Jackson et al., 2006; Böhlke et al., 2009; Sturchio et al., 2011, 2012, 2014). Some other fertilizer materials, including plant products such as kelp, have been reported to contain ClO_4^-, but the concentrations in these materials are generally orders of magnitude lower than those historically present in Atacama NO_3^-, and they are considered less likely to be of widespread environmental significance (Dasgupta et al., 2006; Böhlke et al., 2009).

1.1.3 Indigenous Natural Perchlorate in the US

Natural ClO_4^- that is not associated with fertilizers from the Atacama has also been detected in soils, groundwaters, and mineral deposits collected from arid regions in the western 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; Dasgupta et al., 2005; Rajagopolan et al., 2006), in the Middle Rio Grande Basin of New

Mexico (Plummer et al., 2006), and also in the northwestern U.S. (Hatzinger et al., 2013). Natural ClO_4^- also was reported in the Great Lakes (Poghosyan et al., 2014). Based on groundwater dating, some New Mexico samples (having 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). Natural ClO_4^- is hypothesized to form in the atmosphere through photochemical reactions (Murphy and Thomson, 2000; Bao and Gu, 2004; Dasgupta et al., 2005; Kang et al., 2008; Sturchio et al., 2009) and to reach Earth's surface via precipitation or dry deposition. This hypothesis was supported by ubiquitous occurrence of 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 wet and dry deposition can accumulate with time in the vadose zone, along with other deposited salts. Rao et al. (2007) detected ClO_4^- in the vadose zone at several sites in the southwestern U.S. with an average accumulated mass per unit area of 408 ± 88 g/ha. The ClO_4^- concentrations were correlated ($r = 0.59$-0.99) with those of meteoric Cl^- accumulated over the last 6 to 100 kyr, indicating that these anions accumulated together via similar processes. Indigenous natural ClO_4^- also is associated with natural surficial NO_3^- deposits in the vicinity of Death Valley, California at concentrations ranging from 0.25 to 23 mg/kg (Jackson et al., 2010; Lybrand et al., 2013). Similarly, ClO_4^- concentrations as high as 1.1 mg/kg were reported in surficial deposits in the Dry Valleys region of Antarctica (Kounaves et al., 2010; Jackson et al., 2013).

When unsaturated-zone salt accumulations in arid environments become subject to large-scale irrigation, such as in the SHP and other agricultural regions of the western U.S., accumulated ClO_4^- can be mobilized and transported to the water table. Such agricultural mobilization is hypothesized to account for high ClO_4^- concentrations 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 also may be associated with transport of ClO_4^- to groundwater from crops treated with Atacama nitrate fertilizer (Böhlke et al., 2009; Sturchio et al., 2014)

1.2 Location and Characteristics of the Study Area

Release of synthetic ClO_4^- from military and industrial sources in the northern region of the Rialto-Colton subbasin of San Bernadino County, CA has impacted a number of municipal supply wells. Previously identified sources include two sites: (1) a 160-acre industrial site formerly occupied by several different industries, and also known as the "Rockets, Fireworks, and Flares" (RFF) site (USEPA, 2014), and (2) properties adjacent to the current Mid-Valley Sanitary Landfill (MVSL) operated by San Bernardino County, including the Rialto Ammunition Backup Storage Point, a site of several World War II era bunkers that were later used for the manufacture, transport, and/or disposal of fireworks, flares, explosives and other potentially hazardous materials (SAIC, 2004). This site is known as the "Mid Valley Sanitary Landfill/Bunker Site" (Geologic Associates, 2003; SARWQCB, 2005; Woolfenden, 2007) or the "Former Bunker Area". The distribution of ClO_4^- concentrations in wells indicates two parallel plumes emanating from those sites (Figure 1.1). As defined by previous studies, the mapped plume from the 160-acre site is parallel to the Rialto-Colton fault and extends at least 6 km downgradient of the site in the southeast direction of groundwater flow (GeoLogic Associates, 2013). Recent USEPA reports suggest that this plume may reach as far as 9 km downgradient, but the distal extent is not yet known (USEPA, 2014). The mapped plume from the Bunker Site/MSVL extends ~ 3 km downgradient, parallel to the RFF site plume.

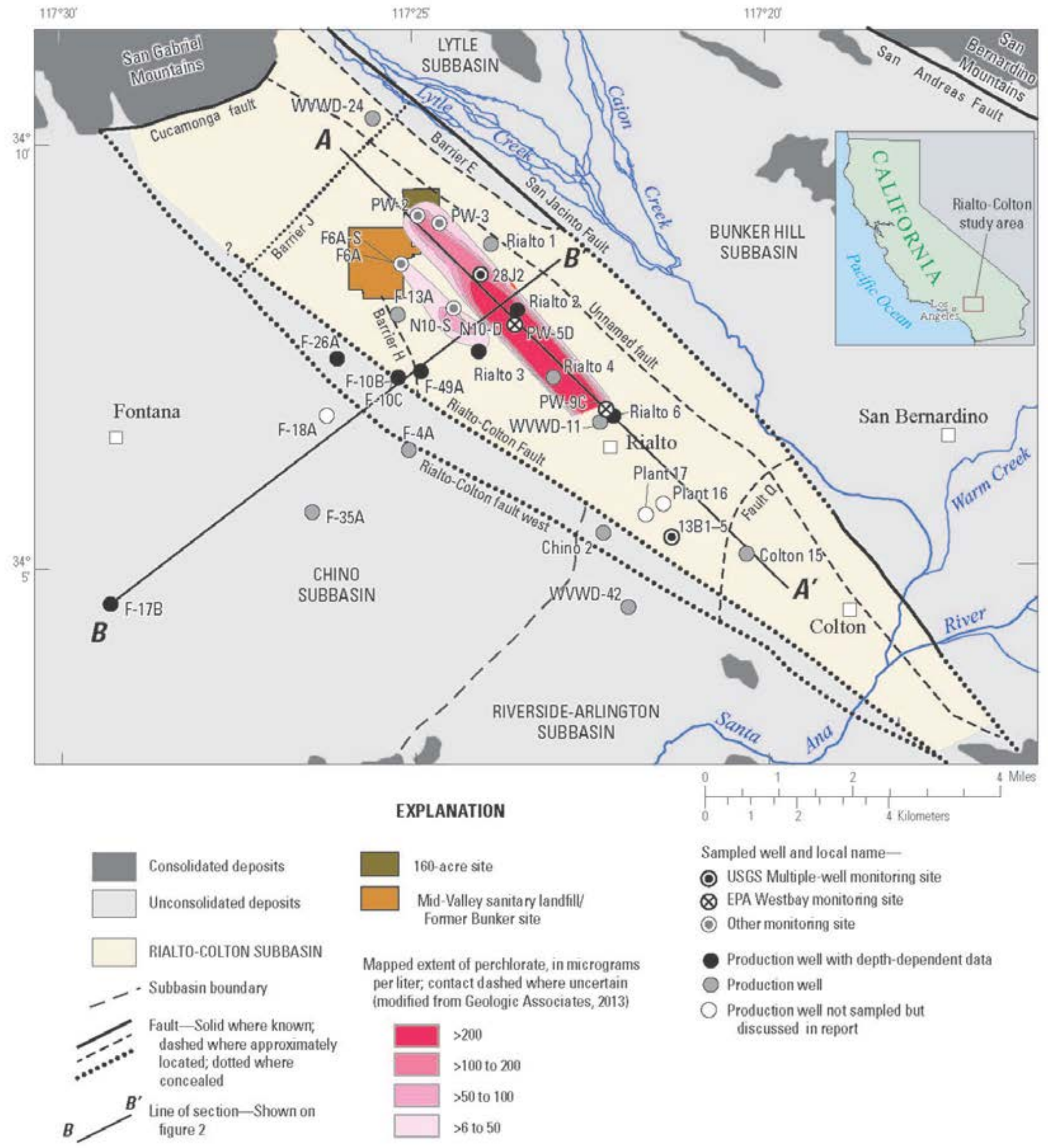


Figure 1.1. Overhead view of the Study Area with the two previously identified source areas and the associated perchlorate plumes delineated. Figure from Izbicki et al. (2014). This plume map was generated previously and modified from Geologic Associates (2013). The map does not include concentration data from this study, the most recent USEPA site sampling (USEPA, 2014) or Izbicki et al. (2014).

The extent of high-level ClO_4^- contamination (e.g., > 50 μg/L) emanating as plumes from the two military/industrial sites is reasonably well defined. However, ClO_4^- has also been detected in groundwater wells throughout the Study Area at lower concentrations (~ 1 to 20 μg/L). Perchlorate has been measured in groundwater wells to the southeast of the two known plumes in the general direction of groundwater flow, such as Colton 15 and 13B1-5 (RHSW-5), and in wells to the south of the sources but outside the hypothesized groundwater flow path, including a number of wells positioned to the south of the Rialto-Colton Fault in the Chino subbasin, such as F-35A, F-4A, F-17B and others (Figure 1.1). Several wells in the Chino subbasin positioned between the Rialto-Colton Fault and the postulated Rialto-Colton Fault West (Paulinski, 2012), such as F-26A and Chino 2 (Figure 1.1), also have measurable ClO_4^-, albeit at very low concentrations (< 2 μg/L). The general pattern of low-level ClO_4^- contamination in groundwater throughout the Study Area (apart from the plumes emanating from the two source areas) suggests the possibility of additional sources of ClO_4^- in the area, possibly including ClO_4^- derived from historical Atacama fertilizer application, natural indigenous ClO_4^-, and secondary synthetic sources from flares, fireworks, blasting, or others. The focus of this project was to use stable isotope ratio analysis and ^{36}Cl analysis to evaluate the major source(s) of ClO_4^- throughout the Study Area. A separate report provides information on groundwater flow and additional hydrogeochemical characteristics in the Study Area (Izbicki et al., 2014).

1.3 Isotopic Analyses of ClO_4^-

The two elements comprising the ClO_4^- molecule (i.e., Cl and O) each have multiple stable isotopes. Oxygen has three stable isotopes (^{16}O, ^{17}O, and ^{18}O), which have molar abundances (mole fractions) of approximately 99.8 %, 0.04 %, and 0.20 %, respectively (Coplen et al., 2002). Chlorine has two stable isotopes (^{35}Cl and ^{37}Cl), with molar abundances of approximately 75.8 % and 24.2 %, respectively (Coplen et al., 2002).

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 is generally an international measurement standard. For oxygen:

$$[\text{Eq. 1.1}] \qquad \delta^{18}\text{O} = R(^{18}\text{O}/^{16}\text{O})_{\text{sample}}/R(^{18}\text{O}/^{16}\text{O})_{\text{standard}} - 1$$

[Eq. 1.2] $$\delta^{17}O = R(^{17}O/^{16}O)_{sample}/R(^{17}O/^{16}O)_{standard} - 1,$$

where the standard in both equations is Vienna Standard Mean Ocean Water (VSMOW). R = molar ratio. Values of $\delta^{18}O$ and $\delta^{17}O$ are reported in parts per thousand (per mil, or ‰). By international convention, the $\delta^{18}O$ scale is defined by two reference materials, with VSMOW at 0.0 ‰ 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:

[Eq. 1.3] $$(1 + \delta^{17}O) = (1 + \delta^{18}O)^{\lambda},$$

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 1.3:

[Eq. 1.4] $$\varDelta^{17}O = [(1 + \delta^{17}O) / (1 + \delta^{18}O)^{0.525}] - 1.$$

Values of $\varDelta^{17}O$ are reported in parts per thousand (per mil, or ‰). Alternative definitions of $\varDelta^{17}O$ used to describe ClO_4^- isotope data can yield slightly different $\varDelta^{17}O$ values for the same measured $\delta^{18}O$ and $\delta^{17}O$ values; those differences range from about 0.0 to 0.2 ‰ for groundwater data summarized in this report.

For reporting chlorine stable isotope ratios:

[Eq. 1.5] $$\delta^{37}Cl = R(^{37}Cl/^{35}Cl)_{sample} / R(^{37}Cl/^{35}Cl)_{standard} - 1$$

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 ‰).

Chlorine also has a long-lived radioactive isotope (^{36}Cl) with a half-life of ~ 301,000 yr. The relative abundance of ^{36}Cl is small (typically $<10^{-15}$ to 10^{-12} relative to the stable Cl isotopes) but it can be useful for studying origins of chloride and Cl-bearing compounds (Phillips, 2000). Techniques to analyze the stable isotopes of both chlorine and oxygen in the ClO_4^- molecule, as well as its ^{36}Cl isotopic abundance, have been developed and used to characterize a variety of natural and man-made ClO_4^- samples, including Atacama nitrate fertilizers and caliche deposits, a wide array of synthetic ClO_4^- types and ClO_4^--containing products (e.g., laboratory reagents, fireworks, flares, gunpowder, military sources), and samples from the southwest US that contain natural indigenous ClO_4^- (Bao and Gu, 2004; Böhlke et al., 2005, 2009; Jackson et al., 2010; Gu et al., 2011; Sturchio et al., 2006, 2009, 2012; Hatzinger et al., 2011, 2013). A summary of these techniques as applied to ClO_4^- isotopic analysis of Study Area groundwater samples is provided in Section 2.

1.3.1 Stable Isotope Ratios of Cl and O in Synthetic ClO_4^-

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), Sturchio et al. (2006, 2011), and Hatzinger et al. (2011, 2013). The δ^{37}Cl values of all synthetic ClO_4^- samples published to date group within a range from -3 ‰ to + 2 ‰. These values are similar to those reported for common industrial sources of NaCl, such as halite from Phanerozoic bedded marine evaporites, which has a mean δ^{37}Cl value 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 the Cl isotope ratio in the ClO_4^- product is similar to that in the starting NaCl. The published δ^{18}O values of synthetic ClO_4^- vary over a wider range than those for δ^{37}Cl, from -25 ‰

to -13 ‰ (Figure 1.2). It has been hypothesized that the $\delta^{18}O$ values of the synthetic ClO_4^- samples generally reflect the $\delta^{18}O$ in the H_2O used for production modified by O isotopic fractionation during ClO_4^- synthesis (Sturchio et al., 2006). In contrast to $\delta^{18}O$, $\Delta^{17}O$ values of all synthetic ClO_4^- samples analyzed to date are indistinguishable (0.0 ± 0.1 ‰), indicating that there is negligible mass-independent isotopic fractionation of O during ClO_4^- synthesis (Sturchio et al., 2006).

1.3.2 Stable Isotope Ratios of Cl and O in Atacama ClO_4^-

Current data from isotopic analyses reveal that the $^{37}Cl/^{35}Cl$ isotope ratio ($\delta^{37}Cl$ value) of naturally-occurring ClO_4^- from Chile is consistently and significantly lower than that of synthetic ClO_4^- from all other sources tested (Figure 1.2). In fact, the reported $\delta^{37}Cl$ values for Atacama ClO_4^- are the lowest for any common substance on Earth (Coplen et al., 2002). Based on samples analyzed to date, which include soils, caliche deposits and a groundwater sample from the Atacama Desert (blue diamonds in Figure 1.2), and samples of commercial Atacama nitrate fertilizer (green diamonds in Figure 1.2), the $\delta^{37}Cl$ values range from -19 to -9 ‰ (Bao and Gu, 2004; Böhlke et al., 2005; Sturchio et al., 2006, 2012; Böhlke et al., 2009; Jackson et al., 2010; Hatzinger et al., 2011, 2013; unpublished results from SERDP Project ER-1435 for a subset of the Atacama soil samples). The $^{18}O/^{16}O$ isotope ratio ($\delta^{18}O$ value) of Atacama natural ClO_4^- spans a wide range, from -25 to -2 ‰, which overlaps that of synthetic ClO_4^- (Figure 1.2).

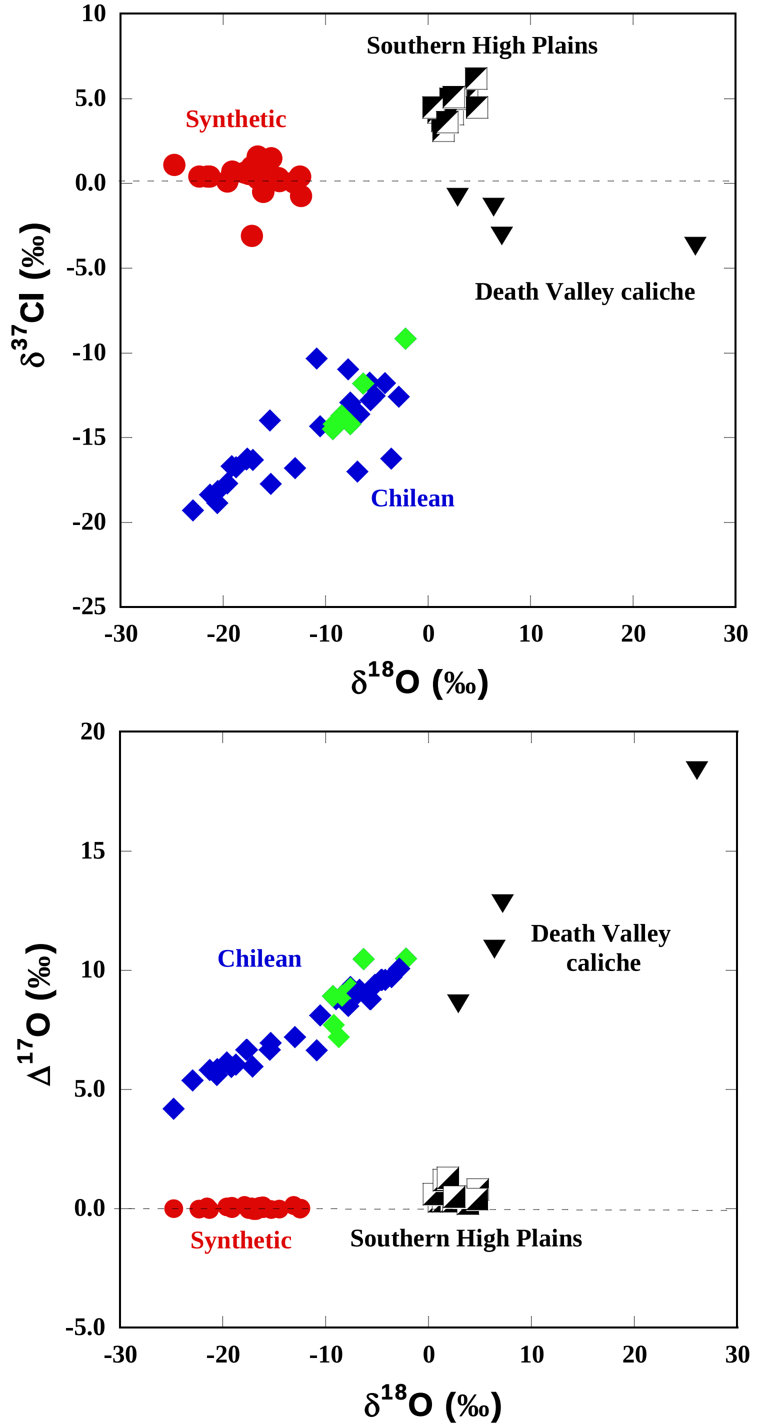


Figure 1.2. Comparison of δ^{37}Cl versus δ^{18}O (top panel) and Δ^{17}O versus δ^{18}O (bottom panel) in natural indigenous ClO_4^- of the US Southern High Plains (black and white squares) and Death Valley caliche (black triangles), natural Atacama ClO_4^-, (blue diamonds for caliche and groundwater and green diamonds for nitrate fertilizer samples) and synthetic ClO_4^- (red circles). Sources of data are provided in the accompanying text.

One important isotopic difference between synthetic ClO_4^- and natural ClO_4^- from the Atacama Desert is revealed by analysis of ^{17}O abundances. Synthetic ClO_4^- samples have $\Delta^{17}O$ values near 0, consistent with ClO_4^- production from brine by electrolysis. In contrast, $\Delta^{17}O$ values of Atacama ClO_4^- samples analyzed to date range from + 4 to +11 ‰, with commercial nitrate fertilizer ClO_4^- samples being in the upper end of this range (Figure 1.2). Elevated $\Delta^{17}O$ values in Atacama ClO_4^- were first measured by Bao and Gu (2004), who noted that the ^{17}O enrichment is consistent with an atmospheric formation mechanism. The data indicate that oxidation of volatile Cl species by ozone (O_3) (which is known to have elevated $\Delta^{17}O$ values; Johnson et al., 2000) in the upper atmosphere may be responsible for the initial production of this ClO_4^- (Bao and Gu, 2004; Rao et al., 2010).

1.3.3 Stable Isotope Ratios of Cl and O in Indigenous Natural ClO_4^-

As previously discussed, research conducted during the past decade has revealed that natural ClO_4^- occurs in 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 dry valley soils and lakes, and also on the surface of Mars, have caused additional interest in natural ClO_4^- (Hecht et al. 2009; Ming et al. 2010; Catling et al. 2010; Kounaves et al. 2010; Jackson et al., 2013).

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. has recently been reported (Jackson et al., 2010; Hatzinger et al., 2013). 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 and from the Middle Rio Grande Basin (MRGB) of central New Mexico. A single sample was obtained from a natural subsurface accumulation of salts within unsaturated sub-soils at the Range Ecology Research Site at Texas Tech University. Lastly, ClO_4^- was collected from near-surface caliche-type salt deposits on clay hills at four locations in the Death Valley region of the Mojave Desert, CA. 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 (Ericksen et al., 1983; Böhlke et al., 1997; Lybrand et al., 2013).

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 δ^{37}Cl values ranging from +3 to +5 ‰, δ^{18}O values ranging from 0 to +4 ‰, and Δ^{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 Atacama 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 1.2). Similar isotopic characteristics to those of the SHP and MRGB samples were also recently observed for presumably indigenous ClO_4^- from the U.S. Great Lakes (lake water) and from the Umatilla Basin, Oregon (groundwater), although the Δ^{17}O values were slightly higher for some of these samples, ranging to +2.9 ‰ in Umatilla and +2.7 ‰ in the Great Lakes (Hatzinger et al., 2013; Poghosyan et al., 2014). The smaller, but significantly positive, Δ^{17}O values of indigenous groundwater ClO_4^- in comparison to Atacama $ClO_4^{-,}$ could indicate either (1) indigenous groundwater ClO_4^- is formed predominantly by a different mechanism than Atacama $ClO_4^{-,}$ or (2) the indigenous ClO_4^- initially had higher Δ^{17}O but was affected by post depositional O exchange with groundwater.

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), have isotopic characteristics that differ from those of Atacama and synthetic ClO_4^-, and from those of SHP and MRGB samples. In comparison to the SHP samples, the Death Valley samples have lower δ^{37}Cl values (from -0.8 to -3.7 ‰) and much higher Δ^{17}O values (+8.6 to +18.4 ‰). As is apparent from Figure 1.2, Δ^{17}O values of Death Valley samples are similar to or, in some instances, higher than those of the Atacama samples, consistent with an important component of atmospheric origin and relative lack of post depositional exchange of O with groundwater. The SHP/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 values, this indigenous grouping remains isotopically distinct from synthetic and Atacama ClO_4^-.

Given present data, it is not yet possible to fully explain the origin of the observed variations in the stable isotopic composition of natural ClO_4^- sources. 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, it appears 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 affected water supplies, such as those in the Study Area.

1.4 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 as ^{36}Cl/Cl) has proven to be another important tool for distinguishing ClO_4^- sources. 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). Isotopic abundances of ^{36}Cl measured in 35 different ClO_4^- samples from synthetic, Atacama, and southwestern U.S. sources ranged over more than four orders of magnitude (Figure 1.3 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 evaporite 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 southwestern U.S. that were tested (including some of the SHP and MRGB groundwater samples and Death Valley deposits described in the previous section and shown in Figure 1.2 with differing δ^{37}Cl and Δ^{17}O values) had unusually high ^{36}Cl/Cl values, ranging from $3{,}130 \times 10^{-15}$ to $28{,}800 \times 10^{-15}$. Groundwater samples with indigenous ClO_4^- (and some with mixed indigenous/synthetic ClO_4^-) from eastern Oregon similarly had elevated ^{36}Cl/Cl values ($4{,}530$ – $15{,}900\times 10^{-15}$; Hatzinger et al., 2011) as did samples collected from the U.S. Great Lakes, where the isotopic characteristics of ClO_4^- (which were similar to the southwestern U.S.) suggested a dominantly indigenous source ($7{,}400$ – $71{,}200\times 10^{-15}$). 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 samples from southwestern U.S. groundwater having detectable tritium, and apparently it is present in indigenous ClO_4^- in the upper Great Lakes, which still contain much of the water that was present in the 1950s and 1960s (Poghosyan et al., 2014). However, ^{36}Cl/Cl values as high as $8{,}400 \times 10^{-15}$ were measured in ClO_4^- from old groundwater in New Mexico with estimated recharge ages of > 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 Atacama deposits had $^{36}Cl/Cl$ ratios from 22 × 10^{-15} to 590 × 10^{-15}, much lower than any of the natural samples from the southwestern U.S., Great Lakes, or Umatilla area. The Atacama samples may have had higher initial $^{36}Cl/Cl$ ratios that decreased via radioactive decay. This could be consistent with a relatively long history of Atacama ClO_4^- accumulation, as hyper-arid conditions in this region have persisted for at least 3 to 8 million years (Alpers and Brimhall, 1988; Hartley and Chong, 2002), which is 10 or more times the 301,000-yr half-life of ^{36}Cl. The $^{36}Cl/Cl$ ratios in Cl^- from the Atacama Desert are similar to those of the coexisting ClO_4^- as shown in Figure 1.3, which indicates that ^{36}Cl in these samples may be near radioactive equilibrium with its environment. The accumulation time of ClO_4^- in the arid southwestern U.S. appears to have been much shorter (of the order of 10^4 yr) than that in the Atacama Desert, and natural ClO_4^- accumulated from the atmosphere during the past 10^4 years would still possess most of its initial ^{36}Cl activity (Jackson et al., 2010). More importantly for forensic studies of ClO_4^-, ^{36}Cl abundances in combination with stable isotope ratios of O and Cl help differentiate synthetic, Atacama, and indigenous U.S. ClO_4^- sources (Sturchio et al., 2009; Hatzinger et al., 2011).

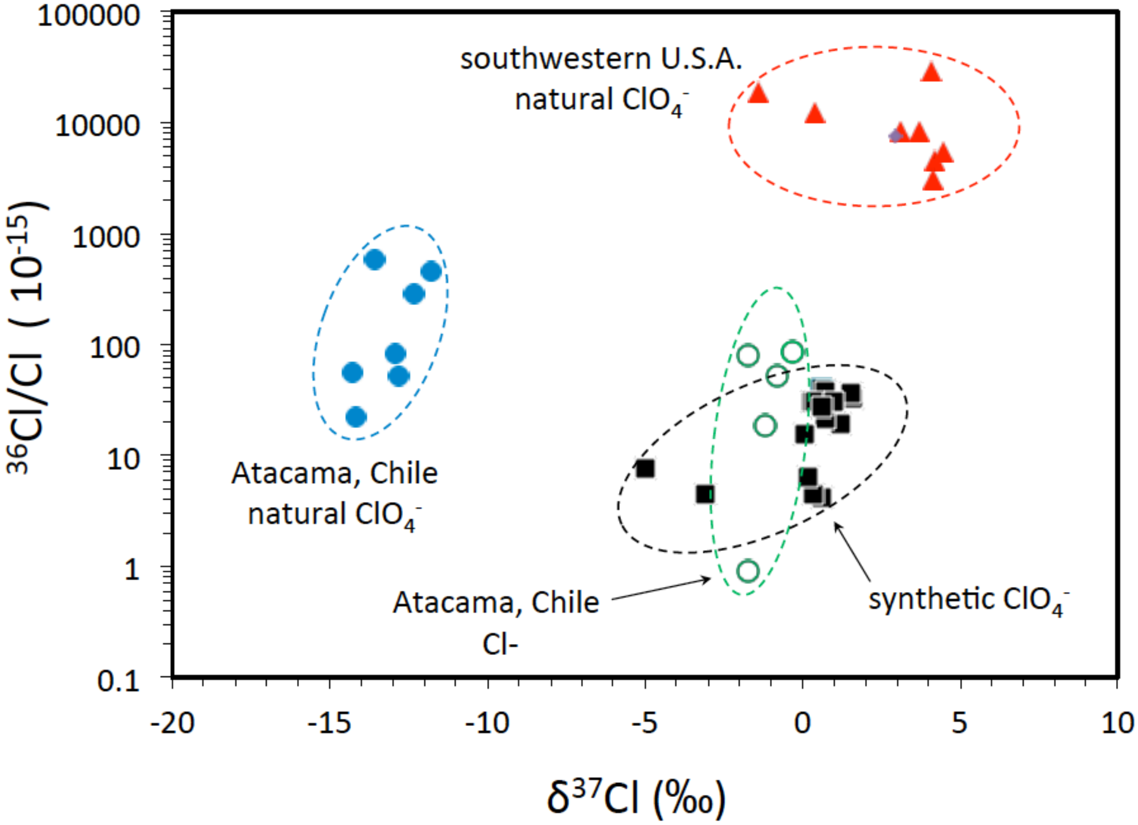


Figure 1.3. **Values of ^{36}Cl/Cl (mole fraction) versus δ^{37}Cl (‰) in representative samples of synthetic ClO_4^- reagents and products, natural ClO_4^- extracted from soil and groundwater from the Atacama Desert, Chile, and natural ClO_4^- extracted from groundwater and soil from the southwestern U.S. (modified from Sturchio et al., 2009).**

2.0 Materials and Methods

2.1 Selection of Wells for Groundwater Sample Collection

In the early phase of this project, U.S. Geological Survey (USGS) personnel in San Diego, CA compiled a GIS database of groundwater wells in the Study Area using information from numerous sources, including the California Department of Public Health, USGS National Water Information System, U.S. Environmental Protection Agency (EPA), County of San Bernardino, and various local water agencies and consultants. From this database, a preliminary group of 27 groundwater wells in the Rialto-Colton and Chino subbasins was selected by the project team for isotopic sampling, and 16 wells were selected as possible alternates. North-south and east-west transects across the two synthetic plumes were used as a basis for well selection. These transects included wells within each of the two defined plume areas, and wells that were upgradient (northwest), downgradient (southeast), and crossgradient (northeast and southwest) of the mapped plume areas. Wells were also selected on each side of, and in close proximity to, the Rialto-Colton Fault, and between the Rialto-Colton Fault and the Rialto-Colton Fault-West. Wells selected for sample collection were reviewed by a Technical Advisory Committee (TAC) established for the project which included local water purveyors, regulatory agencies, and other stakeholders. Substitutions of wells were made at the suggestion of the TAC and in the field, where necessary to meet the objectives of this study, when initial well selections were precluded based on well conditions and/or well accessibility, low ClO_4^- concentrations, or other issues observed in the field.

A total of 27 wells (17 production wells, 8 monitoring wells, and 2 Westbay wells) were selected and sampled for ClO_4^- isotopes (Figure 2.1). In addition, in conjunction with coupled well bore-flow and depth-dependent water quality sampling (Izbicki et al., 2014), depth-dependent ClO_4^- stable isotope samples were collected from five of the production wells (Rialto 2, Rialto 3, Rialto 6, F-17B, F-26A). Additional details on the study area hydrogeology and well characteristics are provided in a previously published paper (Izbicki et al., 2014).

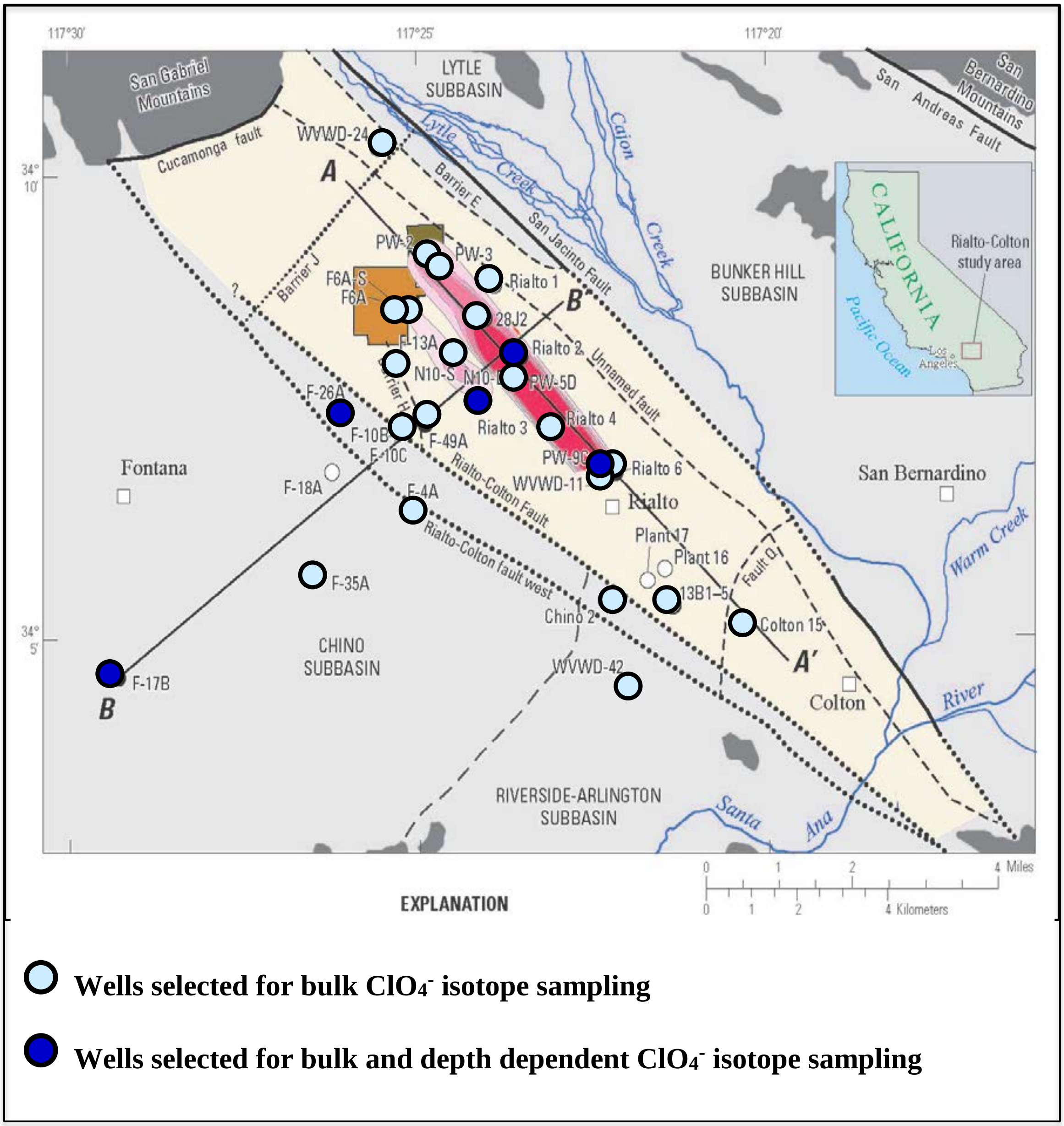


Figure 2.1. Wells selected for bulk discharge ClO_4^- isotope sampling (light blue symbols) and depth-dependent ClO_4^- isotope sampling (dark blue symbols). Depth-dependent well bore flow and water quality analysis was also performed on wells F-10C and F-49A (see Izbicki et al., 2014). The map does not include concentration data from this study, the most recent USEPA site sampling (USEPA, 2014) or Izbicki et al. (2014).
See Figure 1.1 for explanation of map.

2.2 Groundwater Sampling Procedure

Approximately 20 µmol of pure ClO_4^- salt (as $KClO_4$, prepared as described in Section 2.3) is normally sufficient to obtain duplicate stable isotope ratio measurements by IRMS for both O and Cl in the ClO_4^- ion, as well as a measurement of ^{36}Cl isotopic abundance. However, because of potential losses during sample collection and purification (Section 2.3), and allowing sufficient sample for additional replicate analyses, it is generally desirable to collect samples containing at least 100 µmol (i.e. 10 mg) of ClO_4^- from each source. For groundwaters having low ClO_4^- concentrations (i.e., < 5 µg/L), shipping enough water to obtain 10 mg of ClO_4^- is impractical. Instead, small columns containing about 100 mL (~ 60 g dry wt) of Purolite A-530E ClO_4^--specific anion exchange resin (IX resin) have been developed to preconcentrate ClO_4^- from large volumes of water in the field. 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, the columns are capable of trapping 10 mg of ClO_4^- on a small volume of resin. The ClO_4^- is then extracted from the resin and purified prior to IRMS analyses, as described in Section 2.3.

For this project, the USGS performed all groundwater sampling, as described elsewhere (Izbicki et al., 2014). Resin columns were used for sample collection from all wells, except the Westbay wells for which aqueous ClO_4^- concentrations were high enough for water to be collected and shipped directly to the laboratory without using the IX column collection technique. All IX columns for sampling were prepared at the Environmental Isotope Geochemistry Laboratory (EIGL) of the University of Illinois at Chicago (UIC) and sent directly to the USGS with unique identification numbers. In many instances, two or more (up to 8) columns were set up at a single well to collect enough ClO_4^- for stable isotope analysis from low-concentration waters, and in some cases to provide independent replicate samples for isotopic analysis so that method reproducibility could be evaluated. In some cases, groundwater was passed through columns for as long as two weeks to accumulate sufficient ClO_4^- for analysis. The original goal of this project was to conduct duplicate analyses (i.e, process and analyze independent sample columns) on 25% of the wells sampled. This goal was exceeded, as replicate samples were obtained for 10 of the 33 well locations (wells plus depth-dependent samples).

Most production wells were sampled from the surface discharge of the existing well pump. Depth-dependent samples were collected from selected depths within five production wells under pumping conditions (see Izbicki et al., 2014). Sample depths were identified on the basis of available geologic and geophysical logs and unpumped and pumped well-bore flow logs collected as part of the study. Samples from those wells also were collected from the surface discharge of a temporary pump installed within the well after the production pump was removed. Monitoring wells were sampled using a positive displacement gas-reciprocating pump (Bennett pump) capable of lifting water from depths greater than 200 m below land surface (bls). Production and monitoring wells were purged to remove at least three casing volumes prior to sample collection. Field parameters (pH, temperature, and specific conductance) were monitored during purging using a thermometer and portable meters. After field parameters stabilized, groundwater samples were collected for measurement of major ion concentrations (including ClO_4^- and NO_3^-), groundwater dating parameters, dissolved gases, and $\delta^{18}O$ and δ^2H in water, as described in Izbicki et al. (2014). Samples were collected from Westbay installations using equipment designed by the manufacturer for this purpose.

At the conclusion of all required water quality sampling, one (or more) ion exchange column(s) was connected to the groundwater discharge from each well pump. The flow to the columns was generally set at 1 to 2.5 liters per minute (LPM). Periodically, samples were collected from the influent and effluent of the columns to evaluate stability of influent concentration with time, to detect column breakthrough of ClO_4^-, and to estimate the total amount of ClO_4^- trapped on each column. After a pre-determined time, ranging from a few hours to as long as two weeks (based on flow rate and starting ClO_4^- concentration in each well), the IX columns were removed from the each well, sealed in Zip-Loc type bags, placed at 4°C (or on ice), and shipped to the UIC EIGL for ClO_4^- extraction and purification.

2.3 Sample Purification and Isotopic Analysis

2.3.1 Sample purification

The preparation of ClO_4^- present on the IX resin for chlorine and oxygen isotope ratio analysis involved two main procedures prior to IRMS: (1) elution and recovery of ClO_4^- from the resin and (2) separation of ClO_4^- from other materials trapped on the IX resin, including a variety of anions and organics. The sample elution and purification procedures were conducted by laboratory technicians under the supervision of Dr. Neil Sturchio at UIC EIGL. Briefly, the key steps in the extraction and purification method were as follows: (1) the resin was washed ultrasonically with deionized water (DIW) and flushed with several pore volumes of 4M HCl to remove adsorbed SO_4^{2-}, NO_3^-, HCO_3^-, and some of the humics, but not ClO_4^- which is more strongly held by the bifunctional resin than most other anions or organics; (2) ClO_4^- was eluted from the resin bed using 1 M $FeCl_3$-4M HCl solution (Gu et al., 2001, 2011); (3) eluted ClO_4^- was purified by a series of cation exchange, oxidation, and evaporation steps; (4) KOH was added to precipitate $KClO_4$ for isotopic analysis; and (5) $KClO_4$ crystals were washed with methanol and their purity was measured by ion chromatography (IC).

Tetrachloroferrate ($FeCl_4^-$) ions are present in the 1 M $FeCl_3$ and 4 M HCl eluant solution and these ions remove ClO_4^- from the Purolite A530E resin (Gu et al., 2001). The $FeCl_3$-HCl eluent containing dissolved ClO_4^- was diluted to convert $FeCl_4^-$ to cationic Fe^{3+} species, then it was passed through a large glass chromatography column packed with AG-50W-X12 resin to remove Fe. The eluent from this column was collected and evaporated on a hot plate, with addition of several mL concentrated H_2O_2 to oxidize organic compounds, until the remaining solution volume was reduced to about 50 mL. The evaporation produces an azeotropic mixture (~6 M HCl) so that most of the excess HCl was removed by evaporation. To separate residual NO_3^- from ClO_4^-, the concentrated sample was reloaded onto 1 mL of A530E resin, flushed with 4 M HCl, re-eluted with $FeCl_3$-HCl, and the resulting eluent evaporated to <5 mL. The remaining excess dissolved Cl^- (HCl) was then removed by passing the sample through an OnGuard II Ag Sample Pretreatment Cartridge (Dionex, Sunnyvale, California). OnGuard II H (cation-exchange hydronium form resin) cartridges were then used to remove any dissolved Ag. Residual organics were removed by oxidation with H_2O_2 or by Strata

SDB-L (Phenomenex, Torrance, California) solid phase extractant.

The ClO_4^- in solution was then precipitated with an excess of KOH to produce $KClO_4$. Residual KOH was removed from $KClO_4$ by rinsing the residue with methanol. The $KClO_4$ crystals were then collected by filtration and rinsed with a few drops of 90 % methanol (by volume, in water). The purified $KClO_4$ was then dissolved in DIW and a small aliquot was analyzed by IC to assess purity, with a target of <1% anionic impurities. If necessary to achieve target purity, samples were further treated by addition of tetrapentylammonium bromide (TPABr) to precipitate ClO_4^- as $TPAClO_4$, followed by ethanol washing to remove excess TPABr, followed by reaction of $TPAClO_4$ with KOH-methanol solution to reprecipitate $KClO_4$ (Poghosyan et al., 2014). The final $KClO_4$ product was rinsed with ethanol and redissolved in DIW for IC analysis of purity. Mass balance of O during sample decomposition for O isotope analysis was evaluated subsequently to further assess sample purity (i.e., to determine if the sample yielded more or less O than expected from pure $KClO_4$). In some samples, presence of C or N was also evaluated as part of the IRMS analysis (See Section 2.3.2).

2.3.2 Analysis of Oxygen Isotope Ratios in Perchlorate by IRMS

After the $KClO_4$ 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 2.3.3 for Cl. Analysis of O isotopes in ClO_4^- was conducted by three different methods when sufficient sample was available. These methods were (1) Off-line conversion to O_2 with dual-inlet isotope-ratio mass spectrometry using a liquid nitrogen trap (O_2-DI-IRMS(+N_2)); (2) Off-line conversion to O_2 with dual-inlet isotope-ratio mass spectrometry without a liquid nitrogen trap (O_2-DI-IRMS((-N_2)); and (3) On-line conversion to CO, with continuous-flow isotope-ratio mass spectrometry (CO-CF-IRMS). The O_2-DI-IRMS method yielded values of $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$ in O_2 gas. A liquid N_2 trap (+N_2) minimized potential interferences caused by condensable gases (e.g., CO_2 and H_2O) entering the IRMS with the O_2 sample; thus O_2-DI-IRMS(+N_2) was the primary method applied to all samples. Performed without a liquid N_2 trap (-N_2), this method permitted condensable gases to enter the IRMS where they could be ionized and measured. The O_2-DI-IRMS(-N_2)

method was used to evaluate contaminants and co-products of ClO_4^- decomposition. The CO-CF-IRMS method yielded values of δ^{18}O, but not δ^{17}O or Δ^{17}O. This method included measurement of the relative amount of N_2 as an indication of potential contamination by air or N-O salts such as NO_3^- and it was used selectively as an independent test for major problems with the O_2 methods. The methods are described in more detail in sections 2.3.2.1 and 2.3.2.2.

All samples were analyzed at least once by O_2-DI-IRMS(+N_2), and many samples were analyzed multiple times. The data from this technique were used for comparisons provided in the *Results and Discussion* section, and generally for the stable isotope data published previously by this group (e.g., Böhlke et al., 2009; Jackson et al., 2010). Most samples were also analyzed by O_2-DI-IRMS(-N_2) to determine approximate relative susceptibility of O isotopes to C contamination effects. Relatively few samples were analyzed by CO-CFIRMS, as this method was not compatible with Cl isotopic analysis. Data from all three techniques are summarized in Section 3.4 (Table 3.7; Figure 3.10).

2.3.2.1 Analysis of δ^{18}O and δ^{17}O by Off-Line Conversion to O_2, with Dual-Inlet IRMS (O2-DI-IRMS)

To perform DI-IRMS on O_2 derived from ClO_4^-, aliquots of pure $KClO_4$ were weighed into quartz glass tubes (mass equivalent to 2.5 µmol of ClO_4^- per tube). The tubes were evacuated and sealed with a torch and then baked at 650 °C for 20 min to produce O_2 gas from the ClO_4^-. The tubes were broken manually in an evacuated tube cracker, and the O_2 expanded into a liquid N_2 cold trap for 1 min to remove traces of condensable gases (O_2-DI-IRMS (+N_2)) or no N_2 trap was used (O_2-DI-IRMS (-N_2)) if the effects of condensable gases were under study. The O_2 was 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 δ^{18}O measurements by O_2-DI-IRMS on multiple aliquots of $KClO_4$ (typically three to four) in a given batch is generally around ±0.2‰ or better for the reference material USGS37 and ±0.5‰ or better for the reference material USGS38 (Hatzinger et al., 2011).

2.3.2.2 Analysis of δ^{18}O by On-Line Conversion to CO, with Continuous-Flow IRMS (CO-CF-IRMS)

To perform CF-IRMS on CO derived from ClO_4^-, aliquots of pure $KClO_4$ were weighed into silver foil cups (mass equivalent to 2 µmol of ClO_4^- per cup). The loaded cups were 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 was 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 δ^{18}O measurements by CO-CF-IRMS on multiple aliquots (typically four to eight) in a given batch is generally around ±0.2‰ or better for USGS37 and ±0.2‰ or better for USGS38 (Hatzinger et al., 2011).

2.3.3 Analysis of Chlorine Isotope Ratios in Perchlorate by IRMS

The analysis of Cl stable isotope ratios was conducted on the KCl produced by thermal decomposition of $KClO_4$ as described in Section 2.3.2.2 for production of O_2. The Cl^- derived from ClO_4^- was converted to methyl chloride (CH_3Cl) gas (Eggenkamp, 1994; Holt et al., 1997), which was 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 in several papers and book chapters as described previously, and additional details on method procedures and QA/QC are given in Hatzinger et al. (2011).

2.3.3.1 Analysis of δ^{37}Cl by Off-Line Conversion to Methyl Chloride, with Dual-Inlet IRMS (CH_3Cl-DI-IRMS)

Chlorine isotopic analyses were performed on samples of KCl from decomposition of ClO_4^- salts as described above for preparation of O_2 for isotopic analysis (Section 2.3.2). KCl residue in a decomposition tube was dissolved using 10 mL of warm 18.2 MΩ deionized water. The dissolved alkali halide residue was transferred into a 50-mL polypropylene conical tube and acidified with 100 µL concentrated nitric acid (HNO_3). This solution was then heated to 80 °C and an excess of silver nitrate

($AgNO_3$) was added as described in Eggenkamp (1994). Silver chloride (AgCl) precipitates were then allowed to ripen in a dark cabinet for ~ 24 hr. The AgCl solids were then centrifuged, the supernatant was removed, and 0.03 M HNO_3 was used to rinse the solids three times. Solids were 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 was dry, the combustion tube was evacuated and CH_3I was cryogenically transferred into the tube which was then sealed and baked for 2 h at 300 °C as described in Holt et al. (1997). The resulting CH_3Cl was purified using gas chromatography, cryo-concentrated, and then admitted to the IRMS and analyzed in dual-inlet mode by monitoring peaks at *m/z* 52 ($^{12}C^1H_3{}^{37}Cl$) and 50 ($^{12}C^1H_3{}^{35}Cl$). Typical reproducibility of $\delta^{37}Cl$ measurements on multiple aliquots in a given batch are generally ±0.2‰ or better for USGS37 and ±0.3‰ or better for USGS38 (Hatzinger et al., 2011).

2.3.4 Standards for Oxygen and Chlorine Stable Isotopic Analysis

Equations 1.1 and 1.2 are expanded to permit routine calibration of ClO_4^- analyses using a pair of ClO_4^- isotopic reference materials (USGS37 and USGS38) (see description in Hatzinger et al., 2011) with contrasting isotopic compositions on the VSMOW-SLAP scale, a process commonly referred to as “normalization”:

[Eq. 2.1]
$$\delta^{18}O_{i/VSMOW} = \delta^{18}O_{37/VSMOW} + [\delta^{18}O_{i/rg} - \delta^{18}O_{37/rg}]_{meas.} \cdot [\delta^{18}O_{38/VSMOW} - \delta^{18}O_{37/VSMOW}] / [\delta^{18}O_{38/rg} - \delta^{18}O_{37/rg}]_{meas.}$$

[Eq. 2.2]
$$\delta^{17}O_{i/VSMOW} = \delta^{17}O_{37/VSMOW} + [\delta^{17}O_{i/rg} - \delta^{17}O_{37/rg}]_{meas.} \cdot [\delta^{17}O_{38/VSMOW} - \delta^{17}O_{37/VSMOW}] / [\delta^{17}O_{38/rg} - \delta^{17}O_{37/rg}]_{meas.},$$

where 37 and 38 refer to the ClO_4^- isotopic reference materials USGS37 and USGS38, and rg is an internal laboratory reference gas (either CO or O_2) 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. The $\delta^{18}O$ scale is based on CO-CF-IRMS analyses 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 1.4; Böhlke et al., 2005). Perchlorate calibration values used for data normalization in this study are consistent with those reported previously (Böhlke et al., 2009): for USGS37, $\delta^{18}O = -17.00$ ‰ and $\delta^{17}O = -8.96$ ‰; for USGS38, $\delta^{18}O = +52.5$ ‰ and $\delta^{17}O = +102.5$ ‰. For USGS37, our $\Delta^{17}O$ value of 0.0 ‰ defined by Equation 1.4 is in agreement with a mean value of -0.11 ± 0.06 ‰ reported for synthetic ClO_4^- using an alternative $\Delta^{17}O$ definition (Bao and Gu, 2004).

The most widely-used Cl isotope reference material is chloride prepared from seawater which has uniform $\delta^{37}Cl$ to within ± 0.08 ‰ (Godon et al., 2004). Routine calibration of ClO_4^- isotopic analyses was also conducted by using the pair of ClO_4^- isotopic reference materials (USGS37 and USGS38) as follows:

[Eq. 2.3]
$$\delta^{37}Cl_{i/SMOC} = \delta^{37}Cl_{37/SMOC} + [\delta^{37}Cl_{i/rg} - \delta^{37}Cl_{37/rg}]_{meas.} \cdot [\delta^{37}Cl_{38/SMOC} - \delta^{37}Cl_{37/SMOC}] / [\delta^{37}Cl_{38/rg} - \delta^{37}Cl_{37/rg}]_{meas.}$$

where, as with O isotope analysis, 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. Perchlorate calibration values used in this study are (Böhlke et al., 2009): for USGS37, $\delta^{37}Cl = +0.6$ ‰; for USGS38, $\delta^{37}Cl = -87.2$ ‰.

2.3.5 Analysis of ^{36}Cl in ClO_4^-

Analysis of ^{36}Cl in ClO_4^- was performed by accelerator mass spectrometry (AMS) using Cl^- derived from ClO_4^-. The ^{36}Cl analyses on ClO_4^- collected during this project were performed at the Purdue Rare Isotope Measurement Laboratory (PRIME) at Purdue University (www.physics.purdue.edu/ primelab). The procedure used to produce Cl^- for AMS is as described in Section 2.3.3 of this document to the point of AgCl precipitation, washing, and drying of crystals (i.e., prior to the reaction with CH_3I). A portion of the sample prepared to this step for Cl stable isotopic analysis was saved for ^{36}Cl analysis. The AgCl was subsequently re-dissolved and the Cl^- 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 with a value of 0.5×10^{-15} (Argento et al., 2010).

3.0 Results and Discussion

3.1 ClO_4^- Concentrations in Groundwater Wells

Measured concentrations of ClO_4^- in Study Area groundwater ranged from 0.3 µg/L to 1,150 µg/L in wells that were sampled for ClO_4^- isotopes (Figure 3.1; Table 3.1). With the exception of Well F-17B in the Chino subbasin, all of the wells with concentrations above the California MCL of 6 µg/L were located within the two mapped ClO_4^- plumes (Figure 3.1). In general, the average influent concentrations from the IX columns used to collect ClO_4^- for isotopic analysis were similar to the individual samples taken for ClO_4^- analysis (Table 3.1). A statistical analysis of the variation of ClO_4^- concentration entering the columns with time is provided in Izbicki et al., (2014). There was no apparent correlation between the average ClO_4^- concentration and the variability in that concentration.

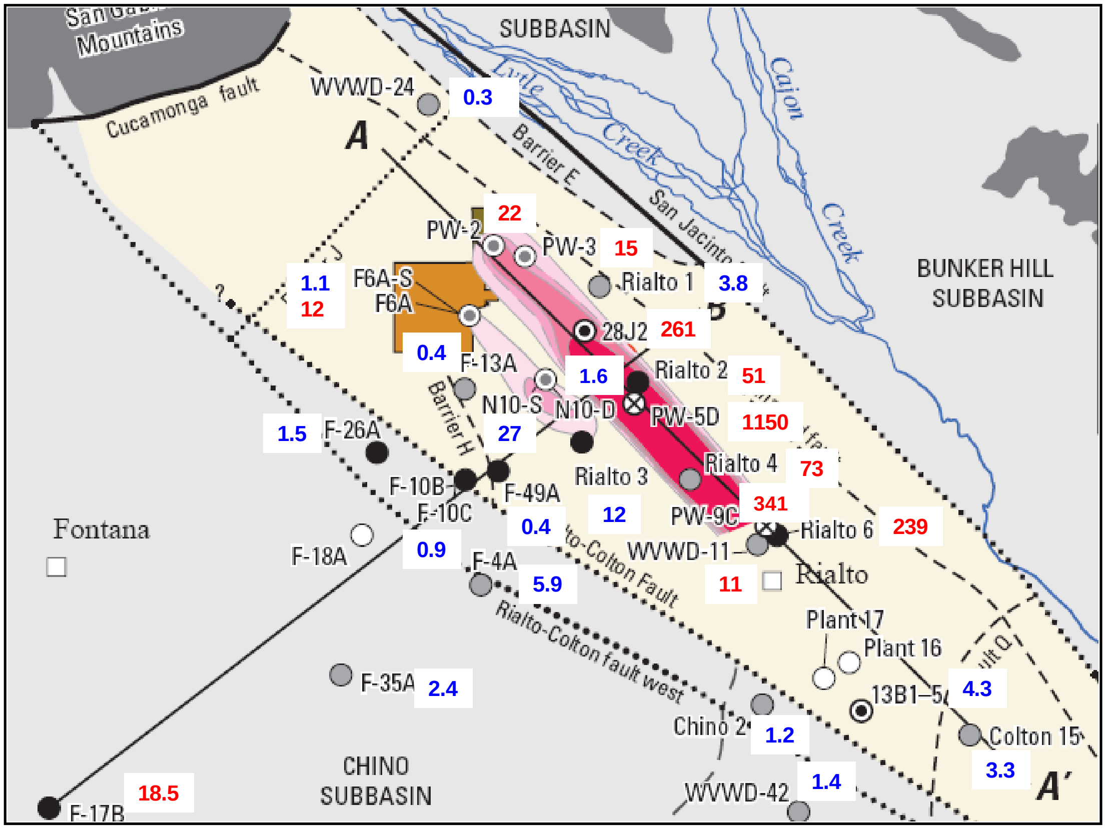


Figure 3.1. Concentration of ClO_4^- in groundwater wells during stable isotope sampling. Values provided are the average influent concentration to IX columns used for groundwater sampling except for F-10C, F-49A, PW-5D and PW-9C, where individual analyses are provided. Concentrations above 6 µg/L are shown in red, and those below 6 µg/L are shown in blue. See Figure 1.1 for explanation of the map.

3.2 Isotope Results for ClO_4^-

The Cl and O stable isotope results for ClO_4^- in Study Area well samples are provided in dual isotope plots in comparison to previous source data for synthetic, Atacama, and selected indigenous natural ClO_4^- samples (SHP, MRGB, and Death Valley caliche) in Figures 3.2 and 3.3. The isotopic values ($\delta^{37}Cl$, $\delta^{18}O$ $\Delta^{17}Cl$, and $^{36}Cl/Cl$) are plotted with respect to the inverse of the measured ClO_4^- concentrations in Figure 3.4 to illustrate potential mixing and dilution trends. Average isotope values and ClO_4^- concentrations in the column influent are provided in Table 3.1.

In general, it appears that ClO_4^- from all three proposed sources was present in varying proportions in Study Area groundwater (Figures 3.2-3.4). Samples having relatively high ClO_4^- concentrations (values of inverse ClO_4^- concentration < 1, i.e. ClO_4^- concentrations > 1 μg/L) generally plot near a single dominant ClO_4^- source, either synthetic or Atacama (Figure 3.4), whereas samples having lower concentrations commonly indicate mixtures with varying fractions of indigenous natural ClO_4^-. These relations are consistent with the presence of a low background concentration of indigenous ClO_4^-, toward which the isotopic composition of ClO_4^- converges as fractions of the other two ClO_4^- sources approach zero (Figure 3.4).

To facilitate discussion of results, hypothetical mixing zones among three potential ClO_4^- endmembers (synthetic, Atacama, indigenous) are plotted with the Study Area stable isotope data ($\delta^{37}Cl$ vs $\delta^{18}O$ and $\Delta^{17}Cl$ vs $\delta^{18}O$) and with ^{36}Cl data ($^{36}Cl/Cl$ vs $\delta^{37}Cl$) in Figure 3.5. A similar three-endmember mixing approach was also recently used to determine the dominant source of ClO_4^- in groundwater of the nearby location of Pomona, CA, using $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ data (^{36}Cl values were not reported) (Sturchio et al., 2014). Characteristics of three ClO_4^- endmembers for the Study Area groundwaters were determined as follows: (1) The Atacama and synthetic endmembers were obtained by separate linear least-squares regressions of $\delta^{37}Cl$, $\delta^{18}O$, and $\Delta^{17}O$ values vs. inverse ClO_4^- concentrations. This procedure is based on the assumption that all samples may have varying amounts of background ClO_4^-, and the Atacama and synthetic endmembers are most likely to dominate at high concentrations (Sturchio et al., 2014). The best-fit regression parameters (slope and intercept, with 2-sigma errors) for samples having ClO_4^- concentrations exceeding 1 μg/L were determined using the regression function of Microsoft Excel. This concentration cutoff was based on the fact that samples in this concentration range could clearly be seen as having either a dominantly Atacama or dominantly synthetic source, based on all three stable isotope values (see Figure 3.4). (2) For the indigenous endmember, no sample of ClO_4^- was obtained from the Study Area that was clearly of "pure" indigenous origin, so published data for the SHP and MRGB groundwater ClO_4^- samples from Sturchio et al. (2006) and Jackson et al. (2010) were used to define its stable isotopic composition (Sturchio et al., 2014). This represents one possible endmember choice, and other alternatives are also discussed below. (3) Because of relatively large variability in measured $^{36}Cl/Cl$ ratios (particularly for samples relatively enriched in the indigenous endmember), in contrast with the stable isotope ratios, regression analysis did not yield precise estimates of $^{36}Cl/Cl$ ratios in the dominant endmembers from the Study Area. Therefore, medians and ranges of published values were used to represent $^{36}Cl/Cl$ ratios of all three endmembers in mixing calculations (Sturchio et al., 2009; Jackson et al., 2010; Poghosyan et al., 2014). The endmember values used for the analysis are provided in Table 3.2 (mean and 2-sigma errors).

The $\delta^{37}Cl$ vs. $\delta^{18}O$, $\Delta^{17}O$ vs. $\delta^{18}O$, and $^{36}Cl/Cl$ vs. $\delta^{37}Cl$ plots of Study Area sample data, in comparison with the three ClO_4^- source endmembers defined above, indicate that the proposed three-component mixing is capable of accounting for the observed variations in isotopic composition in nearly all samples, given uncertainties and potential variability of endmember characteristics (Figure 3.5). The mixing regions between the end members (shown as boxes with each side being the limit of 2-sigma error) are indicated by the gray lines in Figure 3.5. The mixing results in Figure 3.5, as well as the $\Delta^{17}O$ vs 1/concentration plot in Figure 3.4, indicate that the $\Delta^{17}O$ range of the proposed indigenous Study Area endmember is similar to that in the SHP, MRGB, eastern Oregon and Great Lakes samples (i.e., +0.3 to +2.9 ‰) rather than the much higher range observed for Death Valley caliche samples (i.e., + 8.6 to +18.4 ‰) (Jackson et al., 2010; Hatzinger et al., 2013; Poghosyan et al., 2014).

To estimate mixing fractions of each of the three endmembers in the Study Area samples, the average values of all stable isotope ratio analyses for each well (from Table 3.1) along with endmember mean values and standard deviations (from Table 3.2) were used as input for the spreadsheet program *IsoError1_04.xls* [described in Phillips and Gregg (2001) and in the instructions accompanying the spreadsheet]. These spreadsheet calculations yielded quantitative endmember fractions for each sample, based on assumptions given above, accounting for sample measurement uncertainties and population sizes of endmembers. Mixing fractions were calculated with 2-sigma error estimates from three pairs of isotope values, δ^{37}Cl vs. δ^{18}O, Δ^{17}O vs. δ^{18}O, and ^{36}Cl/Cl vs. δ^{37}Cl. The 95 % confidence limits (maximum and minimum mixing fractions) from these calculations are provided in Table 3.3 to Table 3.5. Mixing fractions calculated from δ^{37}Cl vs. δ^{18}O generally agree with those calculated from Δ^{17}O vs. δ^{18}O; there is a cluster of samples near the Atacama endmember, a cluster of samples near the synthetic endmember, and a few intermediate mixed samples (that are also the samples with the lowest total ClO_4^- concentrations). Some calculated maximum values of mixing fractions at a 95 % confidence interval exceeded 1 (with a maximum value of 1.1) and a few of the minimum values were negative at a 95 % confidence limit (with a minimum value of -0.2), reflecting uncertainties in the assumed endmember characteristics. The dominant sources indicated by the ^{36}Cl/Cl vs δ^{37}Cl mixing analysis were generally consistent with those determined using the stable isotope values (Table 3.5). The data also indicated minor fractions of indigenous ClO_4^- in many of the samples as is apparent in Figure 3.5 and discussed in more detail later in this section.

Measured values of δ^{18}O, Δ^{17}O, and δ^{37}Cl were consistent with those of synthetic ClO_4^- sources for all sampled wells located in the perched aquifer within the two mapped ClO_4^- plumes (28J-2, F-6, F6A-S, N-10S) (Figures 3.3-3.5; Tables 3.1, 3.3, 3.4). Similarly, isotopic data from wells in the regional aquifer within the mapped plumes also were consistent with a dominantly synthetic source (with minimum mixing fractions generally ranging from 60 – 90% and maximum fractions at 100 to 110 % using a 95 % confidence interval), including PW-2, PW-3, Rialto 2, Rialto 2 (880’), PW-5D, Rialto 3, Rialto 3 (670’), PW-9C, Rialto 6, Rialto 6 (480’), Rialto 6 (560’), and Rialto 4) (Table 3.3, 3.4). All of these samples had mean δ^{37}Cl values between -1.0 and +1.5 ‰ and Δ^{17}O values between -0.1 and + 0.2 ‰, consistent with dominantly synthetic ClO_4^-. The δ^{18}O values varied from -12.5 to -20.3 ‰, also within the range previously reported for synthetic ClO_4^- sources. However, the relatively wide range in δ^{18}O for these samples also appears to reflect mixing with small fractions of natural indigenous ClO_4^- (see next paragraph) in addition to possible variation in synthetic source isotopic ratios.

Table 3.1. Perchlorate concentrations and Cl and O isotope data for samples collected from wells in the Study Area, June 2010 to February 2012.

State well number	Local well name	Date	δ^{37}Cl (‰)	δ^{18}O (‰)	Δ^{17}O (‰)	^{36}Cl ^{36}Cl/Cl x 10^{-15}	Perchlorate (μg/L) single	Perchlorate (μg/L) column influent
Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume								
1N/5W-28J2	28J-2	07/01/10	0.8 ± 0.1	-18.3 ± 0.1	-0.1 ± 0.0	102 ± 1	285	261 ± 5
1N/5W-29H1	F6	07/20/10	-0.5	-13.5	0.1	1040 (20)	8.8	12 ± 2
1N/5W-29H3	F6A-S	07/22/10	-0.9	-15.5 ± 0.3	0.2 ± 0.1	NA	0.7	1.1 ± 0.4
1N/5W-33B2	N-10S	07/21/10	1.0 ± 0.0	-12.5 ± 1.7	0.0 ± 0.1	504 (12)	33	27 ± 5
Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume								
1N/5W-21N2	PW-2	08/11/10	1.4 ± 0.1	-16.9 ± 0.4	0.0 ± 0.1	118 (4)	22	21 ± 0
1N/5W-21P2	PW-3	08/10/10	1.1 ± 0.2	-18.0 ± 0.2	0.1 ± 0.1	192 (17)	15	15 ± 0
1N/5W-33B1	N-10D	05/19/11	0.5	-14.1 ± 0.5	0.2 ± 0.0	3640 (200)	1.9	1.6 ± 0.2
1N/5W-34B2	Rialto 02	02/25/12	0.2	-20.3 ± 0.2	0.0 ± 0.0	NA	51	51 ± 1
1N/5W-34B2	Rialto 02 (800')	02/25/12	0.3	-20.1 ± 0.1	0.0 ± 0.0	NA	35	35 ± 1
1N/5W-34G4	PW-5D	08/04/10	0.7 ± 0.4	-17.6 ± 0.6	0.0 ± 0.1	82 (9)	1150	NA
1N/5W-34M1	Rialto 03	03/15/11	0.6 ± 0.3	-15.2 ± 0.1	0.0 ± 0.2	687 (14)	11	12 ± 0
1N/5W-34M1	Rialto 03 (670')	03/15/11	0.6	-14.4 ± 0.1	0.0 ± 0.0	502 (23)	11	11 ± 0
1S/5W-02B3	PW-9C	08/05/10	1.3	-16.1 ± 0.3	0.0 ± 0.1	127 (18)	341	NA
1S/5W-02G1	Rialto 06	03/11/11	1.3 ± 0.3	-16.9 ± 0.2	0.1 ± 0.1	86 (4)	226	239 ± 13
1S/5W-02G1	Rialto 06 (480')	03/11/11	1.0	-17.1 ± 0.0	-0.1 ± 0.1	194 (30)	198	206 ± 13
1S/5W-02G1	Rialto 06 (560')	03/11/11	1.1	-15.7 ± 0.2	0.0 ± 0.1	310 (70)	109	115 ± 13
1S/5W-03A1	Rialto 04	10/20/10	1.1 ± 0.1	-17.6 ± 0.2	0.0 ± 0.2	131 (3)	72	73 ± 2
Wells outside the mapped plume								
1N/5W-17K2	WVWD 24	06/29/10	1.5 ± 0.4	-8.4 ± 0.3	1.2 ± 0.1	6021 (110)	0.3*	0.3 ± 0.0j
1N/5W-27D1	Rialto 01	05/18/11	-0.2 ± 0.1	-15.9 ± 0.2	0.2 ± 0.0	2660 ± 127	3.7	3.8 ± 0.5
1N/5W-33N1	F-49A	04/23/11	-2.4 ± 0.0	-8.5 ± 1.0	2.8 ± 0.2	28,900 (1600)	0.4*	NA
1S/4W-18G1	Colton 15	07/08/10	-12.3 ± 0.7	-4.6 ± 0.1	8.6 ± 0.1	1590 (40)	3.2	3.3 ± 0.1
1S/5W-02K1	WVWD 11	06/30/10	-0.5 ± 0.4	-15.3 ± 0.6	1.0 ± 0.2	66 (3)	9.7	11 ± 1
1S/5W-05A5	F-10C	04/18/11	-4.3 ± 0.2	-9.8 ± 0.5	3.4 ± 0.1	10,200 (400)	0.9*	NA
1S/5W-13B5	13B1-5 (RHSW 5)	08/12/10	-9.8	-7.1 ± 0.1	6.9 ± 0.0	2210 (160)	4.4	4.2 ± 0.1
1N/5W-32A1	F-13A	05/11/11	-5.5 ± 0.2	-4.8 ± 0.0	4.7 ± 0.2	24,200 (1200)	0.4*	0.4 ± 0.0j
Wells in the Chino (or Arlington) subbasins								
1S/5W-23A1	WVWD 42	07/08/10	-10.3 ± 0.1	-7.0 ± 0.0	7.1 ± 0.1	1785 ± 134	1.4	1.4 ± 0.0
1N/5W-32N1	F-26A	12/12/10	-9.7	-8.3 ± 0.0	6.1 ± 0.0	5450 (130)	2.0	1.5 ± 0.2
1N/5W-32N1	F-26A (800')	12/12/10	-9.9	-8.4 ± 0.1	6.2 ± 0.0	5140 (90)	1.6	1.5 ± 0.1
1S/5W-04N1	F-4A	07/28/10	-11.8 ± 0.3	-7.9 ± 0.2	7.6 ± 0.1	1380 (30)	5.8	5.9 ± 1.7
1S/5W-04N1	F-4A (J613; 2007 sample)	03/09/07	-11.9	-8.0	7.6	NA	12	NA
1S/5W-07R1	F-35A	07/27/10	-11.1	-9.4 ± 0.1	6.4 ± 0.1	415 (15)	0.6	2.4 ± 0.4
1S/5W-14B1	Chino 02	07/22/10	-11.1	-6.8 ± 0.2	7.4 ± 0.0	780 (40)	2.1	1.2 ± 0.8
1S/6W-23D2	F-17B	06/17/10	-13.5 ± 0.0	-6.6 ± 0.3	8.2 ± 0.1	91 ± 4	22	19 ± 0.7
1S/6W-23D2	F-17B (580')	06/17/10	-13.0 ± 0.2	-8.0 ± 0.2	8.1 ± 0.1	100 (4)	20	18 ± 1

NA - data not available

Means and standard deviations are provided for all individual analyses per well . When individual values are provided samples were analyzed once.

δ^{18}O and Δ^{17}O were analyzed by O_2-DI-IRMS(+N_2). See Equation 1.4 for definition of Δ^{17}O.

j - estmated value between the MDL and PQL by IC

* Analysis by IC-MS at Texas Tech University

" Column influent" samples were collected intermittently over a period of hours to days while isotope samples were being loaded onto columns.

"Single" samples were collected once when samples for other chemical and isotopic analyses were collected (Izbicki et al.,2014).

For ^{36}Cl, values in parentheses are laboratoy reported uncertainty for individual samples while +/- values are standard deviations for multiple analyses.

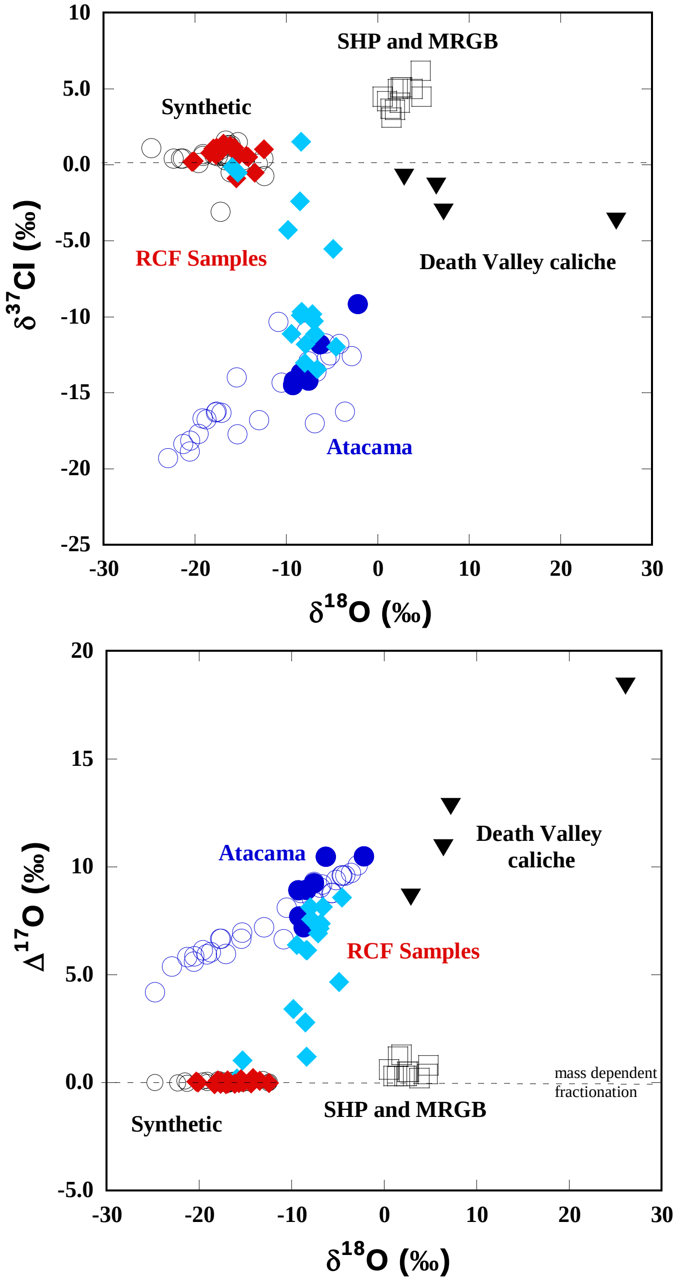


Figure 3.2. Comparison of δ^{37}Cl versus δ^{18}O (top panel) and Δ^{17}O versus δ^{18}O (bottom panel) in ClO_4^- from Study Area groundwater samples (red closed diamonds indicate wells located within the mapped ClO_4^- plume areas and light blue closed diamonds indicate wells located outside the mapped plume areas; Figure 1.1; Table 3.1; Izbicki et al., 2014) with data for synthetic ClO_4^- (open black circles), natural Atacama ClO_4^- (open blue circles for field samples and closed blue circles for Atacama nitrate fertilizer samples), and indigenous natural ClO_4^- of the southwestern U.S. including Southern High Plains (SHP) and Middle Rio Grande Basin (MRGB) groundwater (black open squares) and Death Valley caliche (black triangles). ClO_4^- isotope data from Bao and Gu., 2004; Böhlke et al., 2005; Sturchio et al., 2006, 2012; Böhlke et al., 2009; Jackson et al., 2010; Hatzinger et al., 2011, 2013; unpublished results from SERDP Project ER-1435 for a subset of Atacama field samples. See Section 1.3 for source details.

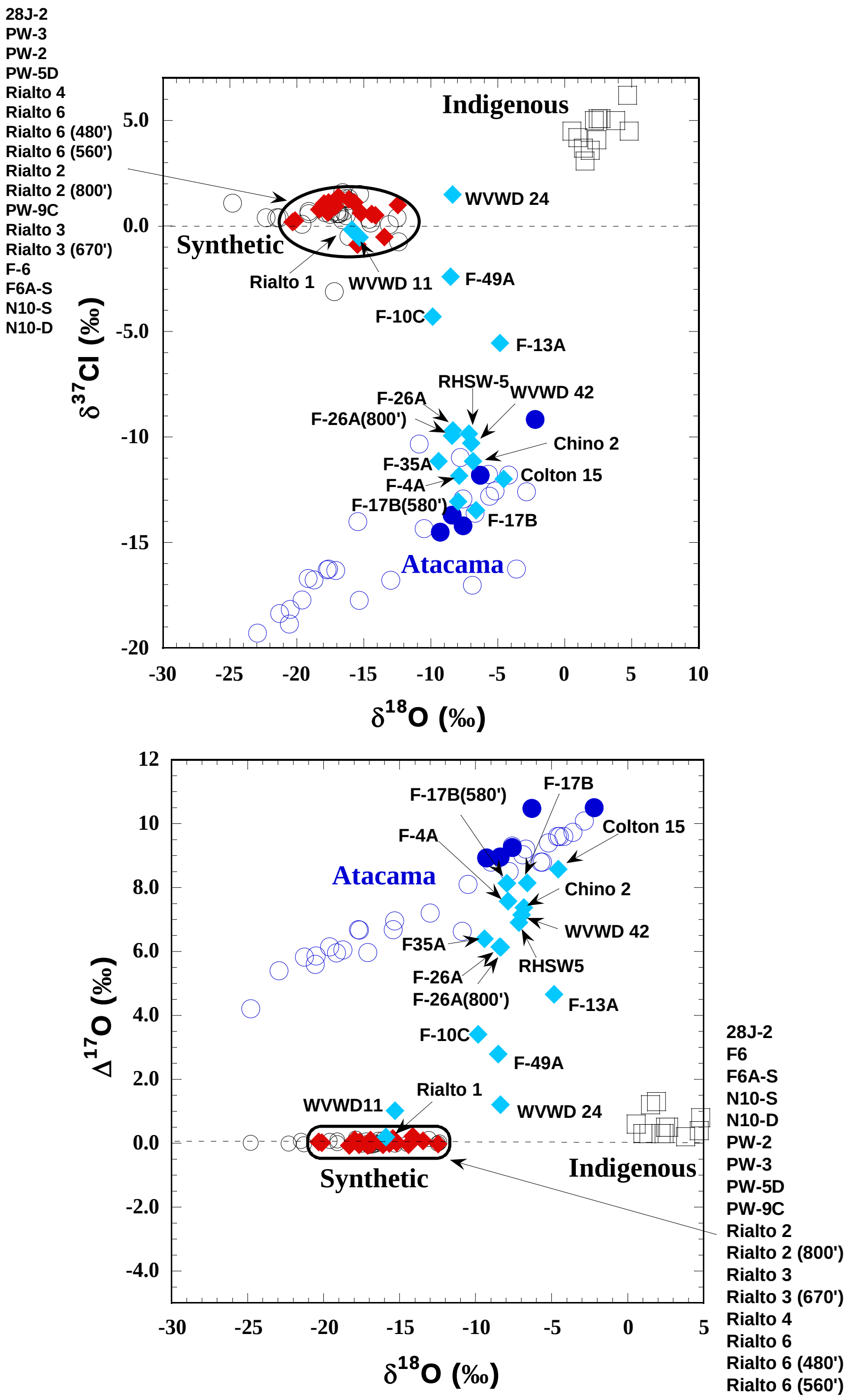


Figure 3.3. Comparison of δ^{37}Cl versus δ^{18}O (top panel) and Δ^{17}O versus δ^{18}O (bottom panel) in ClO_4^- from Study Area groundwater samples within the mapped plume areas (red closed diamonds with well designations) and outside the mapped plume areas (light blue closed diamonds) with source data (symbols as described in the caption to Figure 3.2). Sources of ClO_4^- isotope data for Atacama, Synthetic and Indigenous as described in Figure 3.2.

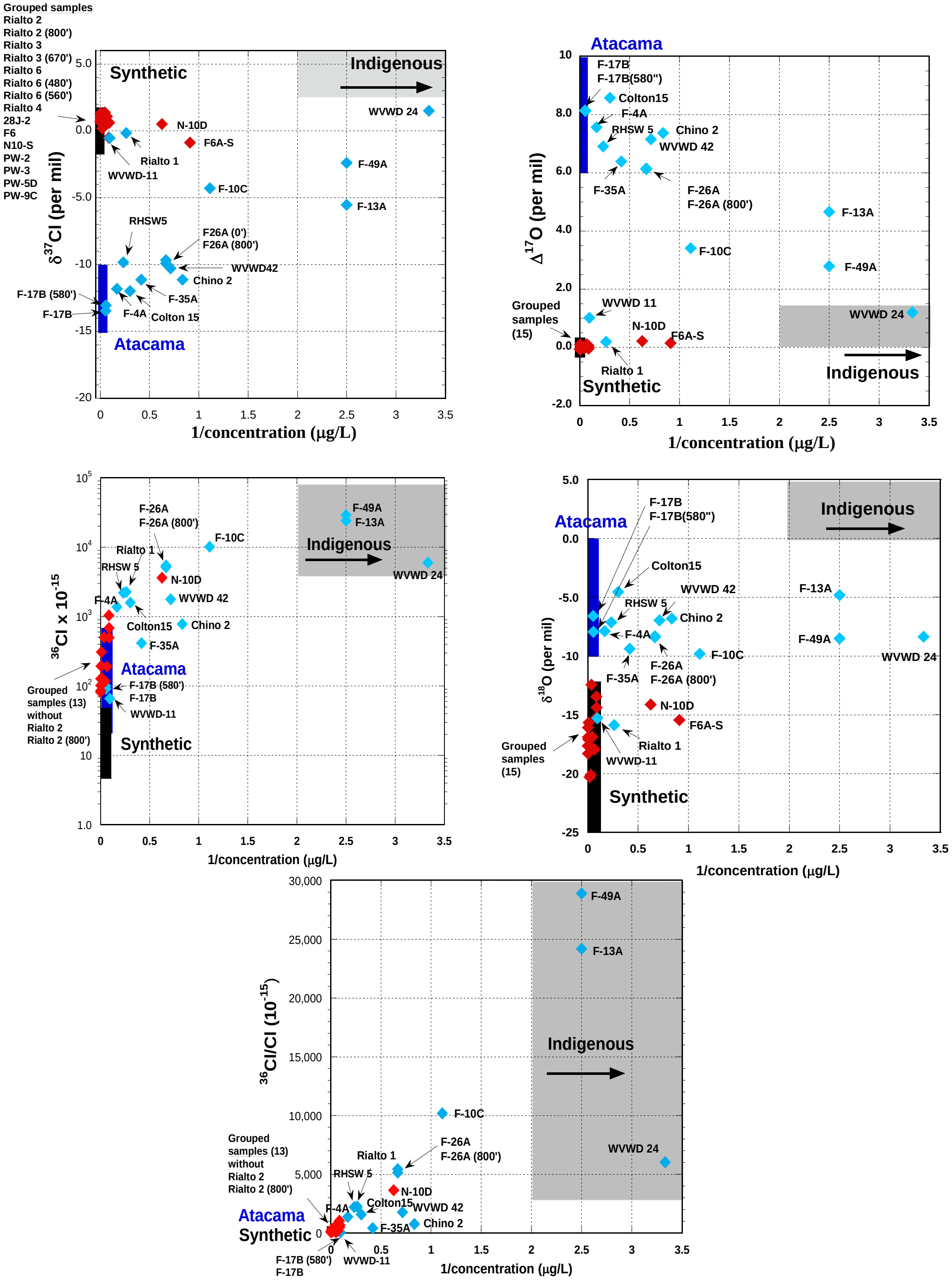


Figure 3.4. Comparison of δ^{37}Cl versus 1/ClO$_4^-$ concentration (top left panel), Δ^{17}O versus 1/ClO$_4^-$ concentration (top right panel), ^{36}Cl/Cl (x 10^{-15}) on log scale versus 1/ClO$_4^-$ concentration (middle left panel), δ^{18}O versus 1/ClO$_4^-$ concentration (middle right panel) and ^{36}Cl/Cl (x 10^{-15}) on linear scale versus 1/ClO$_4^-$ concentration (bottom middle panel), with symbols as described in the caption to Figure 3.2. The solid bars (including the wide gray bar for indigenous ClO$_4^-$) represent typical values for the different sources (see text for explanation). The concentration of indigenous ClO$_4^-$ may be lower than indicated on each panel as represented by the arrow. Grouped samples include the list in the upper left unless otherwise noted.

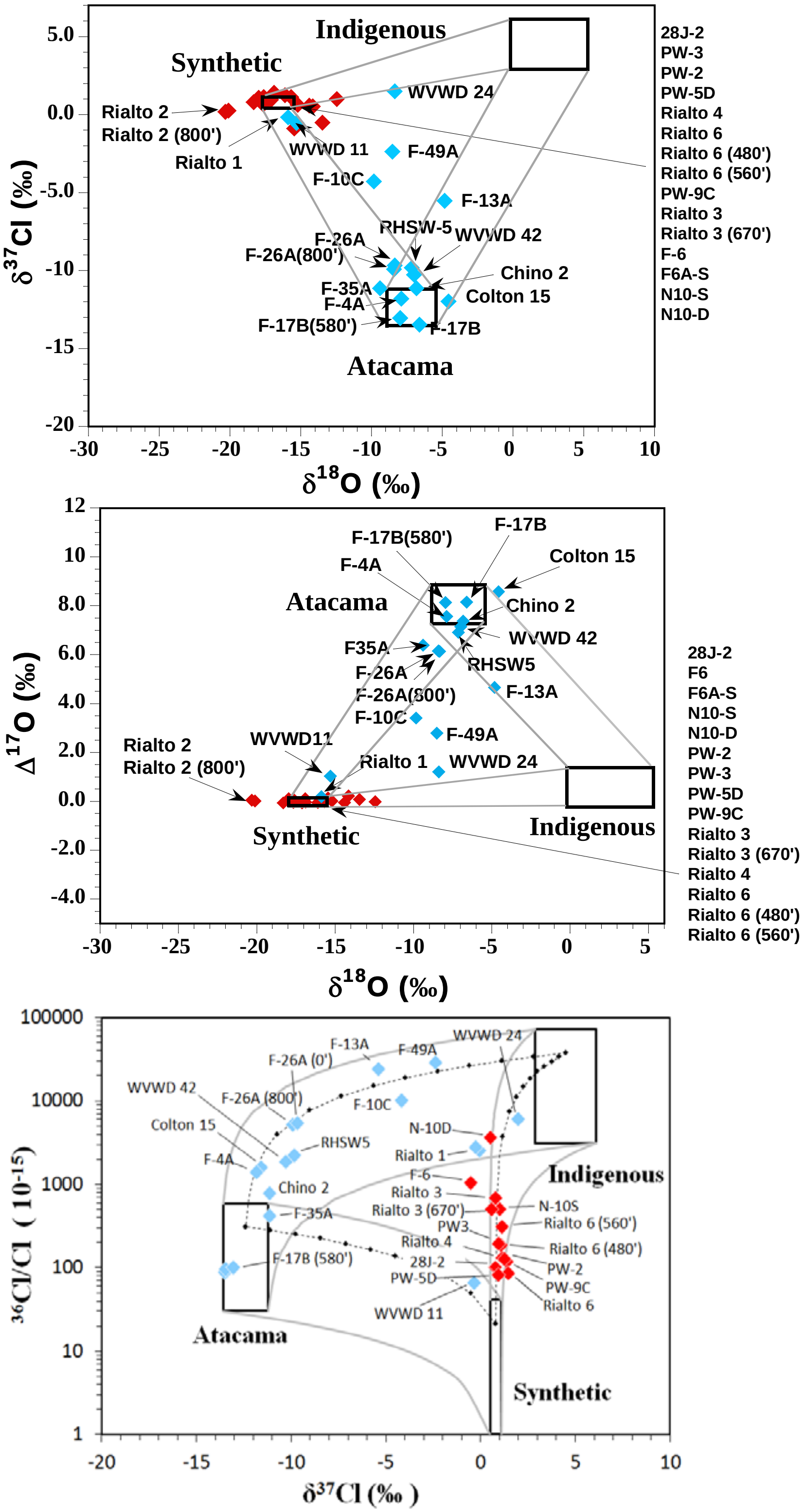


Figure 3.5. Comparison of δ^{37}Cl versus δ^{18}O (top panel); Δ^{17}O versus δ^{18}O (middle panel) and δ^{37}Cl versus ^{36}Cl/Cl (bottom panel) in ClO_4^- from Study Area groundwater samples (symbols as in Figure 3.2). The sides of each box represent the endmember value ± 2-sigma error and the gray lines represent mixing zones between the endmember regions. The endmember values were determined as detailed in the accompanying text and are provided in Table 3.2. The dotted lines in the bottom panel are hypothetical mixing curves between the three endmembers with tick marks shown every 10% as a function of increasing ^{36}Cl/Cl ratio in the mixture (note log scale of y-axis).

Table 3.2. Isotopic compositions of hypothetical endmembers used for analysis of dominant sources in Study Area groundwater. The values in parentheses are 2-sigma errors based on regression analysis of local data (δ^{37}Cl, δ^{18}O, Δ^{17}O for Atacama and synthetic endmembers) or based on published data (δ^{37}Cl, δ^{18}O, Δ^{17}O for the indigenous endmember and ^{36}Cl/Cl for all endmembers). See text for explanation and sources of data.

Isotope parameter	**Atacama ClO_4^-**	**Synthetic ClO_4^-**	**Indigenous ClO_4^-**
δ^{37}Cl (‰)	-12.4 (1.2)	0.8 (0.3)	4.5 (1.6)
δ^{18}O (‰)	-7.2 (1.7)	-16.7 (1.1)	2.5 (2.8)
Δ^{17}O (‰)	8.1 (0.8)	0.1 (0.1)	0.6 (0.8)
^{36}Cl/Cl x 10^{-15}	310 (280)	21 (20)	37,200 (34,000)

Table 3.3. Mixing fractions of Atacama, Synthetic, and Indigenous perchlorate based on δ^{37}Cl vs δ^{18}O stable isotope data for samples collected from wells in the Study Area, June 2010 to February 2012. Values provided are the 95% confidence limits calculated using IsoError1_04.xls with as described in Phillips and Gregg, (2001). Endmember values are given in Table 3.2.

State well number	Local well name	Atacama mixing fraction 95% confidence limits		Synthetic mixing fraction 95% confidence limits		Indigenous mixing fraction 95% confidence limits	
		maximum	minimum	maximum	minimum	maximum	minimum
Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-28J2	28J-2	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-29H1	F6	0.3	-0.1	1.1	0.5	0.3	-0.1
1N/5W-29H3	F6A-S	0.3	-0.1	1.0	0.6	0.2	0.0
1N/5W-33B2	N-10S	0.2	0.0	1.1	0.5	0.4	0.0
Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-21N2	PW-2	0.1	-0.1	1.1	0.7	0.2	0.0
1N/5W-21P2	PW-3	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-33B1	N-10D	0.2	0.0	1.1	0.5	0.3	-0.1
1N/5W-34B2	Rialto 02	0.2	0.0	1.1	0.9	0.0	-0.2
1N/5W-34B2	Rialto 02 (800')	0.2	0.0	1.1	0.9	0.0	-0.2
1N/5W-34G4	PW-5D	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-34M1	Rialto 03	0.2	0.0	1.0	0.6	0.3	-0.1
1N/5W-34M1	Rialto 03 (670')	0.2	0.0	1.0	0.6	0.3	-0.1
1S/5W-02B3	PW-9C	0.2	0.0	1.1	0.7	0.3	-0.1
1S/5W-02G1	Rialto 06	0.2	0.0	1.1	0.7	0.2	0.0
1S/5W-02G1	Rialto 06 (480')	0.2	0.0	1.1	0.7	0.2	0.0
1S/5W-02G1	Rialto 06 (560')	0.2	0.0	1.1	0.7	0.3	-0.1
1S/5W-03A1	Rialto 04	0.2	0.0	1.0	0.8	0.2	0.0
Wells outside the mapped plume							
1N/5W-17K2	WVWD 24	0.3	-0.1	0.8	0.2	0.5	0.3
1N/5W-27D1	Rialto 01	0.3	-0.1	1.0	0.6	0.2	0.0
1N/5W-33N1	F-49A	0.5	0.1	0.7	0.1	0.5	0.1
1S/4W-18G1	Colton 15	1.1	0.9	0.1	-0.1	0.1	-0.1
1S/5W-02K1	WVWD 11	0.2	0.0	1.0	0.6	0.3	-0.1
1S/5W-05A5	F-10C	0.6	0.2	0.7	0.1	0.4	0.0
1S/5W-13B5	13B1-5 (RHSW 5)	0.9	0.7	0.2	0.0	0.2	0.0
1N/5W-32A1	F-13A	0.7	0.5	0.2	0.0	0.4	0.2
Wells in the Chino (or Arlington) subbasins							
1N/5W-32N1	F-26A	0.9	0.7	0.3	0.1	0.1	-0.1
1N/5W-32N1	F-26A (800')	0.9	0.7	0.3	0.1	0.1	-0.1
1S/5W-04N1	F-4A	1.1	0.9	0.2	0.0	0.1	-0.1
1S/5W-04N1	F-4A (J613; 2007 sample)	1.1	0.9	0.2	0.0	0.1	-0.1
1S/5W-07R1	F-35A	1.0	0.8	0.3	0.1	0.1	-0.1
1S/5W-14B1	Chino 02	1.0	0.8	0.2	0.0	0.2	0.0
1S/6W-23D2	F-17B	1.1	0.9	0.1	-0.1	0.1	-0.1
1S/6W-23D2	F-17B (580')	1.1	0.9	0.1	-0.1	0.1	-0.1
	WVWD 42	1.0	0.8	0.2	0.0	0.2	0.0

Table 3.4. Mixing fractions of Atacama, Synthetic, and Indigenous perchlorate based on Δ^{17}O vs δ^{18}O stable isotope data for samples collected from wells in the Study Area, June 2010 to February 2012. Values provided are the 95% confidence limits calculated using IsoError1_04.xls as described in Phillips and Gregg, (2001). Endmember values are given in Table 3.2.

State well number	Local well name	Atacama mixing fraction 95% confidence limits		Synthetic mixing fraction 95% confidence limits		Indigenous mixing fraction 95% confidence limits	
		maximum	minimum	maximum	minimum	maximum	minimum
Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-28J2	28J-2	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-29H1	F6	0.2	0.0	1.0	0.6	0.5	-0.1
1N/5W-29H3	F6A-S	0.2	0.0	1.1	0.7	0.3	-0.1
1N/5W-33B2	N-10S	0.2	0.0	1.1	0.5	0.5	-0.1
Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-21N2	PW-2	0.2	0.0	1.1	0.7	0.3	-0.1
1N/5W-21P2	PW-3	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-33B1	N-10D	0.2	0.0	1.0	0.6	0.4	0.0
1N/5W-34B2	Rialto 02	0.2	0.0	1.1	0.9	0.0	-0.2
1N/5W-34B2	Rialto 02 (800')	0.2	0.0	1.1	0.9	0.0	-0.2
1N/5W-34G4	PW-5D	0.2	0.0	1.0	0.8	0.2	0.0
1N/5W-34M1	Rialto 03	0.2	0.0	1.0	0.6	0.4	0.0
1N/5W-34M1	Rialto 03 (670')	0.2	0.0	1.0	0.6	0.4	0.0
1S/5W-02B3	PW-9C	0.2	0.0	1.0	0.8	0.3	-0.1
1S/5W-02G1	Rialto 06	0.2	0.0	1.0	0.6	0.3	-0.1
1S/5W-02G1	Rialto 06 (480')	0.2	0.0	1.0	0.8	0.3	-0.1
1S/5W-02G1	Rialto 06 (560')	0.2	0.0	1.0	0.6	0.3	-0.1
1S/5W-03A1	Rialto 04	0.2	0.0	1.0	0.8	0.2	0.0
Wells outside the mapped plume							
1N/5W-17K2	WVWD 24	0.4	0.0	0.6	0.4	0.5	0.3
1N/5W-27D1	Rialto 01	0.2	0.0	1.0	0.6	0.3	-0.1
1N/5W-33N1	F-49A	0.5	0.1	0.5	0.3	0.6	0.0
1S/4W-18G1	Colton 15	1.1	0.9	0.1	-0.1	0.2	0.0
1S/5W-02K1	WVWD 11	0.4	0.0	1.0	0.6	0.3	-0.1
1S/5W-05A5	F-10C	0.7	0.1	0.5	0.3	0.4	0.0
1S/5W-13B5	13B1-5 (RHSW 5)	0.9	0.7	0.2	0.0	0.2	0.0
1N/5W-32A1	F-13A	0.9	0.3	0.2	0.0	0.4	0.2
Wells in the Chino (or Arlington) subbasins							
1N/5W-32N1	F-26A	0.9	0.7	0.3	0.1	0.2	0.0
1N/5W-32N1	F-26A (800')	0.9	0.7	0.3	0.1	0.2	0.0
1S/5W-04N1	F-4A	1.1	0.9	0.2	0.0	0.1	-0.1
1S/5W-04N1	F-4A (J613; 2007 sample)	1.1	0.9	0.2	0.0	0.1	-0.1
1S/5W-07R1	F-35A	1.0	0.8	0.3	0.1	0.1	-0.1
1S/5W-14B1	Chino 02	1.0	0.8	0.1	-0.1	0.2	0.0
1S/6W-23D2	F-17B	1.1	0.9	0.1	-0.1	0.1	-0.1
1S/6W-23D2	F-17B (580')	1.1	0.9	0.1	-0.1	0.1	-0.1
1S/5W-23A1	WVWD 42	1.0	0.8	0.1	-0.1	0.2	0.0

Table 3.5. Mixing fractions of Atacama, Synthetic, and Indigenous perchlorate based on ^{36}Cl/Cl abundance vs δ^{37}Cl stable isotope data for samples collected from wells in the Study Area, June 2010 to February 2012. Values provided are the 95% confidence limits calculated using IsoError1_04.xls as described in Phillips and Gregg, (2001). Endmember values are given in Table 3.2.

State well number	Local well name	Atacama mixing fraction *95% confidence limits* maximum	minimum	Synthetic mixing fraction *95% confidence limits* maximum	minimum	Indigenous mixing fraction *95% confidence limits* maximum	minimum
Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-28J2	28J-2	0.2	0.0	1.0	0.8	0.002	0.001
1N/5W-29H1	F6	0.3	0.0	1.0	0.7	0.03	0.02
1N/5W-29H3	F6A-S	NA*	NA	NA	NA	NA	NA
1N/5W-33B2	N-10S	0.2	0.0	1.0	0.8	0.02	0.01
Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-21N2	PW-2	0.2	0.0	1.0	0.8	0.004	0.002
1N/5W-21P2	PW-3	0.2	0.0	1.0	0.8	0.006	0.003
1N/5W-33B1	N-10D	0.3	0.0	0.9	0.8	0.12	0.07
1N/5W-34B2	Rialto 02	NA	NA	NA	NA	NA	NA
1N/5W-34B2	Rialto 02 (800')	NA	NA	NA	NA	NA	NA
1N/5W-34G4	PW-5D	0.2	0.0	1.0	0.8	0.002	0.001
1N/5W-34M1	Rialto 03	0.2	0.0	1.0	0.8	0.02	0.01
1N/5W-34M1	Rialto 03 (670')	0.2	0.0	1.0	0.8	0.02	0.01
1S/5W-02B3	PW-9C	0.2	0.0	1.0	0.8	0.005	0.002
1S/5W-02G1	Rialto 06	0.2	0.0	1.0	0.8	0.003	0.001
1S/5W-02G1	Rialto 06 (480')	0.2	0.0	1.0	0.8	0.007	0.002
1S/5W-02G1	Rialto 06 (560')	0.2	0.0	1.0	0.8	0.02	0.00
1S/5W-03A1	Rialto 04	0.2	0.0	1.0	0.8	0.004	0.002
Wells outside the mapped plume							
1N/5W-17K2	WVWD 24	0.2	0.0	0.9	0.8	0.2	0.1
1N/5W-27D1	Rialto 01	0.3	0.0	0.9	0.8	0.09	0.05
1N/5W-33N1	F-49A	0.5	0.4	0.0	-0.2	1.0	0.6
1S/4W-18G1	Colton 15	1.0	0.9	0.06	0.02	0.04	0.03
1S/5W-02K1	WVWD 11	0.3	0.0	1.0	0.7	0.001	0.000
1S/5W-05A5	F-10C	0.6	0.4	0.4	0.2	0.3	0.2
1S/5W-13B5	13B1-5 (RHSW 5)	0.9	0.7	0.2	0.1	0.07	0.04
1S/5W-23A1	F13A	0.7	0.6	0.0	-0.1	0.8	0.5
Wells in the Chino (or Arlington) subbasins							
1N/5W-32A1	WVWD 42	0.9	0.8	0.2	0.0	0.05	0.03
1N/5W-32N1	F-26A	0.9	0.7	0.1	0.0	0.2	0.1
1N/5W-32N1	F-26A (800')	0.9	0.8	0.1	0.0	0.2	0.1
1S/5W-04N1	F-4A	1.0	0.9	0.1	0.0	0.04	0.02
1S/5W-04N1	F-4A (J613; 2007 sample)	NA	NA	NA	NA	NA	NA
1S/5W-07R1	F-35A	1.0	0.8	0.2	0.0	0.01	0.00
1S/5W-14B1	Chino 02	1.0	0.8	0.2	0.0	0.02	0.01
1S/6W-23D2	F-17B	1.1	1.0	0.0	-0.1	0.00	-0.01
1S/6W-23D2	F-17B (580')	1.05	0.97	0.03	-0.04	0.00	-0.01

*NA - data not available.

Some data from wells within the mapped contaminant plume indicate minor components (0 % to ~ 10 %) of natural indigenous ClO_4^-, based upon the values of $^{36}Cl/Cl$ in the samples compared to synthetic ClO_4^- sources (Table 3.5). Minor indigenous components were difficult to resolve in the stable isotope endmember mixing model results, because these fractions were small compared to the uncertainties associated with the mixing calculations (Tables 3.3 and 3.4). However, hypothetical mixing curves for $^{36}Cl/Cl$ and $\delta^{37}Cl$ with endpoints in synthetic, Atacama, and natural indigenous ClO_4^- in Figure 3.5 (bottom panel) highlight an apparent trend of increasing indigenous ClO_4^- in the data array from PW5D (0 %) to N10-D (~ 10 %). $\delta^{18}O$ values slightly higher than the proposed synthetic endmember (with a $\delta^{18}O$ value of $-16.7 \pm 1.1‰$) are also consistent with varying fractions of indigenous natural ClO_4^- in some of the same samples. This general relation is apparent for samples within the mapped plume areas for which both $\delta^{18}O$ and $^{36}Cl/Cl$ values are available (Figure 3.6).

Within the mapped plume areas, samples with larger apparent fractions of indigenous ClO_4^- based on elevated $\delta^{18}O$ and $^{36}Cl/Cl$ ratios (Figure 3.6) tended also to have lower total ClO_4^- concentrations (Figure 3.7), consistent with varying fractions of a low-concentration background source. According to a regional statistical study (Fram and Belitz, 2011), in the absence of anthropogenic sources or localized flushing of ClO_4^- from the vadose zone by irrigation or other artificial recharge processes, concentrations of indigenous natural ClO_4^- in groundwater in arid/semiarid areas of the southwestern U.S. are likely to be less than 1 µg/L. Where accumulated salts are flushed from the vadose zone, natural ClO_4^- concentrations can be much higher, sometimes exceeding 4 µg/L and occasionally reaching > 50 µg/L, as reported for irrigated agricultural regions of the SHP (Jackson et al., 2005; Rajagopalan et al., 2006; Rao et al., 2007). Some of the variability observed in Figures 3.6 and 3.7 may reflect differing concentrations of natural background ClO_4^- in these wells and variability in synthetic and indigenous endmember isotope values; nevertheless, the general relations are consistent with relatively low background concentrations (<0.5 µg/L). The sample from N-10D, with total ClO_4^- concentration of 1.6 µg/L, had a larger apparent fraction of indigenous natural ClO_4^- (~ 10 %, based on its $^{36}Cl/Cl$ ratio) than most other wells in the mapped plume area, possibly indicating this sample included groundwater from beneath the contaminant plume, which would be consistent with the deeper screened interval from which the sample was collected.

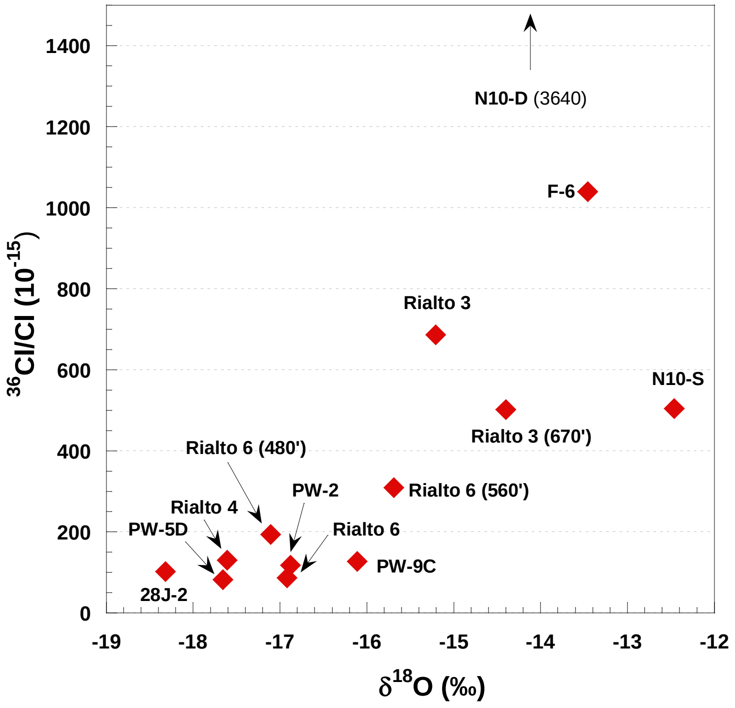


Figure 3.6. Comparison of δ^{18}O values (‰) and ^{36}Cl/Cl ratios for wells located within the mapped ClO_4^- plumes areas for which both values are available.

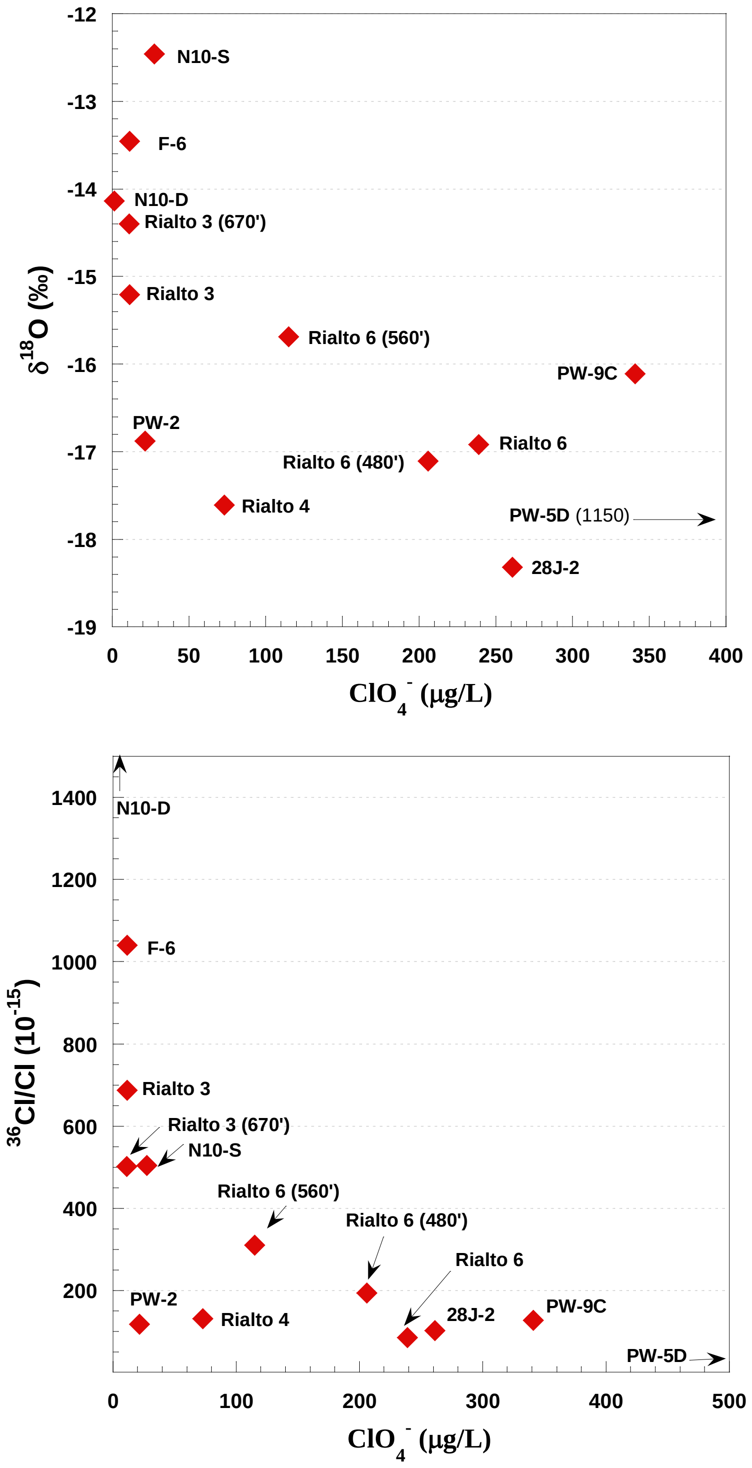


Figure 3.7. Comparison of $\delta^{18}O$ value (‰) versus ClO_4^- concentration (top panel) and $^{36}Cl/Cl$ ratio vs ClO_4^- concentration (bottom panel) for all wells located within the mapped ClO_4^- plume areas for which both values are available.

Downgradient from the two mapped plumes in the southeastern direction, parallel to the Rialto-Colton Fault, the dominant source of ClO_4^- appears to shift from synthetic to Atacama, presumably because of past fertilizer use in the recharge areas for these groundwaters. The ClO_4^- in WVWD 11 appeared to be predominantly synthetic ($\geq$ 60 % based on mixing fraction analysis), but with a significant fraction of Atacama ClO_4^- based upon its $\Delta^{17}O$ value of ~ +1 ‰, compared to < +0.2 ‰ for all other samples collected in the mapped plume area. WVWD 11 also had a lower $\delta^{37}Cl$ value (-0.5 ‰) than most of the wells that appeared to have predominantly synthetic ClO_4^- (average + 0.6 ± 0.6 ‰). Farther downgradient, wells 13B1-5 (RHSW-5) and Colton 15 appeared to have had ClO_4^- that was predominantly Atacama ($\geq$ 70 %), based upon their low $\delta^{37}Cl$ values (-9.8 and -12.3 ‰, respectively) and elevated $\Delta^{17}O$ values (+6.9 and +8.6 ‰, respectively). The combination of low $\delta^{37}Cl$ values and high $\Delta^{17}O$ values in these samples is characteristic of Atacama-derived ClO_4^- (Böhlke et al., 2005, 2009; Jackson et al., 2010; Sturchio et al., 2011, 2012, 2014). The non-Atacama ClO_4^- in these samples (RHSW-5, Colton 15) appears to be largely indigenous, based upon elevated $^{36}Cl/Cl$ values and other correlations.

Samples from the Chino subbasin, southwest of the Rialto-Colton Fault, including those from wells WVWD 42, F-17B, F-35A, F-4A, Chino 2, and F-26A, also had isotopic characteristics indicating predominantly Atacama ClO_4^- ($\geq$ 70 % based on mixing fraction calculations), including elevated values of $\Delta^{17}O$ (+ 6.1 to + 8.2 ‰) and low values of $\delta^{37}Cl$ (-9.7 to -13.5 ‰) (Figures 3.3-3.5, Tables 3.3 and 3.4). The finding of ClO_4^- derived from Atacama fertilizer in the Chino subbasin is consistent with data from previous studies examining ClO_4^- sources in the western region of this subbasin using the stable isotope approach (Sturchio et al., 2008, 2011, 2014). Similarly, Atacama ClO_4^- was recently identified in a number of wells in Riverside, CA in the vicinity of the San Bernardino Airport to the southeast of the Study Area using the stable isotope approach Sturchio et al., (2011, 2012). In the latter case, Atacama ClO_4^- was identified in wells outside a plume of synthetic ClO_4^-. Minor components of indigenous natural ClO_4^- also were indicated in some of the Riverside wells based on the stable isotope values.

The detection of Atacama ClO_4^- in the Study Area on both sides of the Rialto-Colton Fault and across the Chino subbasin is consistent with the past agricultural history of this area, and with anecdotal evidence of the application of Atacama nitrate fertilizer throughout this region (Sturchio et al., 2008, 2011, 2012, 2014). A 1949 land use map showing agricultural regions in the Chino Basin, and covering a substantial portion of the Study Area, is provided in Figure 3.8. This map shows the locations of irrigated vineyards, and irrigated and non-irrigated citrus, within the Study Area. Based on the history of this region, it is likely that these areas were in agriculture for at least a few decades before this 1949 map, when application of Atacama fertilizer was common. Additional historical citrus production along Lytle Creek that is not shown on this figure has also been documented (Geologic Associates, 2002). Peak citrus production in the Chino Basin occurred during the period 1930-1950 (USDA, 2013).

Well WVWD 24 was initially selected for sampling as a possible representative of uncontaminated ("background") conditions, based upon its location far upgradient of the two ClO_4^- plume source areas, its low ClO_4^- concentration (~ 0.3 μg/L), and its potential for recharge from the San Gabriel Mountains (Izbicki et al., 2014). It was presumed that wells in this part of the Study Area were most likely to contain local indigenous natural ClO_4^-, rather than synthetic or Atacama ClO_4^-. Three additional wells (F-27A, F-33A, and F-42A) located to the north of WVWD 24 were considered for background sampling, but ClO_4^- concentrations in these wells, all of which were monitoring wells, were considered to be too low to obtain adequate ClO_4^- for isotopic analysis (0.10, 0.11, and 0.14 μg/L, respectively).

Based on our endmember selections for mixing analysis, isotope data for ClO_4^- from WVWD 24 indicated that this well contained a mixture composed primarily of indigenous natural ClO_4^- and synthetic ClO_4^- (Figures 3.3-3.5, Table 3.3 and 3.4). The sample had a $\delta^{18}O$ value of -8.4, which is between the estimated endmember values of synthetic ClO_4^- (-16.7 ‰) and indigenous natural ClO_4^- (+2.5 ‰) listed in Table 3.2. The WVWD 24 sample had a $\Delta^{17}O$ value of +1.5 ‰, which is within the range reported for indigenous natural ClO_4^- in the southwest US (Jackson et al., 2010) and slightly lower than that for eastern Oregon (Hatzinger et al., 2012) or the Great Lakes (Poghosyan et al., 2014). Finally, the $^{36}Cl/Cl$ ratio of WVWD 24 (6021×10^{-15}) placed it within the lower end of the range reported for indigenous natural ClO_4^- (Sturchio et al., 2009; Poghosyan et al., 2014). All of these observations could be consistent with a synthetic-indigenous mixture in WVWD 24. Tritium (^3H) was detected in this well at 10.6 pCi/L (Izbicki et al., 2014), indicating that it contained at least some modern (post-bomb) recharge water.

Because WVWD-24 is located upgradient from the identified source areas of the two mapped ClO_4^- plumes (Figure 3.1) it is unlikely to have acquired synthetic ClO_4^- from those source areas by groundwater flow (Izbicki et al., 2014). If synthetic ClO_4^- was present in WVWD 24, as indicated by the isotope data, it may have originated from other commercial sources, such as road flares, fireworks, or blasting explosives, each of which could have contributed to groundwater contamination in this area, as they apparently have elsewhere in the U.S. (e.g., Böhlke et al., 2009; Munster and Hanson, 2009; Munster, 2008; Munster et al., 2008; Aziz et al., 2007).

An alternative hypothesis is that the sample from WVWD 24 represents a local indigenous natural component that is different from the one proposed in the mixing analysis. Additional regional sampling would be required to further evaluate this hypothesis. Moreover, whether ClO_4^- from WVWD 24 was entirely or only partly natural (i.e., indigenous mixed with synthetic), it could represent a regional background ClO_4^- that is present in varying proportions in other wells in the Study Area that are not within the mapped plumes.

Three wells not discussed above, F-13A, F-49A, and F-10C, all had low ClO_4^- concentrations ranging from 0.4 to 0.9 μg/L and appeared to represent mixed ClO_4^- sources. In map view (Figure 3.1), well F-13A is located along Barrier H, to the south of the 160 Acre Site, well F-49A is located to the east of Barrier H, and well F-10C is located east of the Rialto-Colton Fault and west of Barrier H. Wells F-10C and F-49A were observed to have perched groundwater cascading downward and mixing with deeper water in the well casing (Izbicki et al., 2014). The perched groundwater may have carried ClO_4^- that was not present in deeper groundwater in these wells. Evaluating all three stable isotopes ($\delta^{18}O$, $\delta^{37}Cl$, $\Delta^{17}O$), and assuming the characteristics of Atacama, synthetic, and indigenous end members as previously described, the ClO_4^- in well F-13A would appear to be composed largely of Atacama and indigenous ClO_4^-, whereas wells F10-C and F49-A would appear to have ClO_4^- from all three endmember sources, with no individual component dominating the mixture (Tables 3.3 and 3.4). If isotope data from WVWD 24 represented a widespread mixed (indigenous + synthetic) background ClO_4^- type, then data from F10-C and F49-A could be consistent with mixtures of Atacama and that mixed background type.

Relations between $^{36}Cl/Cl$ and $\delta^{37}Cl$ values (Figure 3.5, bottom panel) generally support the observations above for these wells, but would appear to indicate somewhat larger fractions of indigenous ClO_4^- and smaller fractions of synthetic ClO_4^-. These apparent differences could be due to variability associated with the $^{36}Cl/Cl$ ratio of natural ClO_4^-. Alternatively, it could indicate contributions of anomalously ^{36}Cl-enriched indigenous ClO_4^- from the brief period of thermonuclear bomb tests in the western Pacific (1952-1964). Poghosyan et al. (2014) propose that ClO_4^- having $^{36}Cl/Cl$ ratios around 1,000,000 x 10^{-15} was widely deposited during that time. Most of the samples analyzed in the current study, with the exception of bulk discharge from well F-17B, had measurable ^3H (Izbicki et al., 2014), indicating at least a portion of the water precipitated after 1952. Any bomb-pulse ClO_4^- contribution (if present) would likely be most evident in the lowest-concentration samples (i.e., F-10C, F-13A, F-49A, and WVWD 24); these are the samples having the highest $^{36}Cl/Cl$ ratios in the present study. A potential bomb-pulse contribution is partially accounted for in the indigenous endmember used for mixing calculations (Table 3.2) by inclusion of data from the Great Lakes (Poghosyan et al. 2014). However, it is possible that the $^{36}Cl/Cl$ ratio was actually higher than that assumed for our mixing calculations or that the specific bomb-pulse contribution varied on a well by well basis in relation to varying local recharge conditions.

The origin of the apparent synthetic ClO_4^- component in wells F-10C and F-49A (based on stable isotope data) is uncertain, as it contributed a maximum of only about 0.6 and 0.2 μg/L, respectively, to the mixtures in the wells based on stable isotope mixing fraction estimates (Table 3.3 and Table 3.4). Sources of such low concentrations could include upgradient background groundwater (as in WVWD 24), plume-related or non-plume-related ClO_4^- in perched groundwater, or other local contamination. Alternatively, if the ClO_4^- in WVWD 24 was isotopically representative of natural indigenous ClO_4^- in the Study Area, then the apparent synthetic components in wells F-10C and F-49A would be reduced or eliminated, as these wells fall reasonably in a mixing line between WVWD 24 and the Atacama endmember based on stable isotope values (Figure 3.5). In this case, however, the $^{36}Cl/Cl$ ratios in these two samples would be expected to fall between that of WVWD 24 and the Atacama endpoint, rather than being higher, particularly in the case of well F-49A.

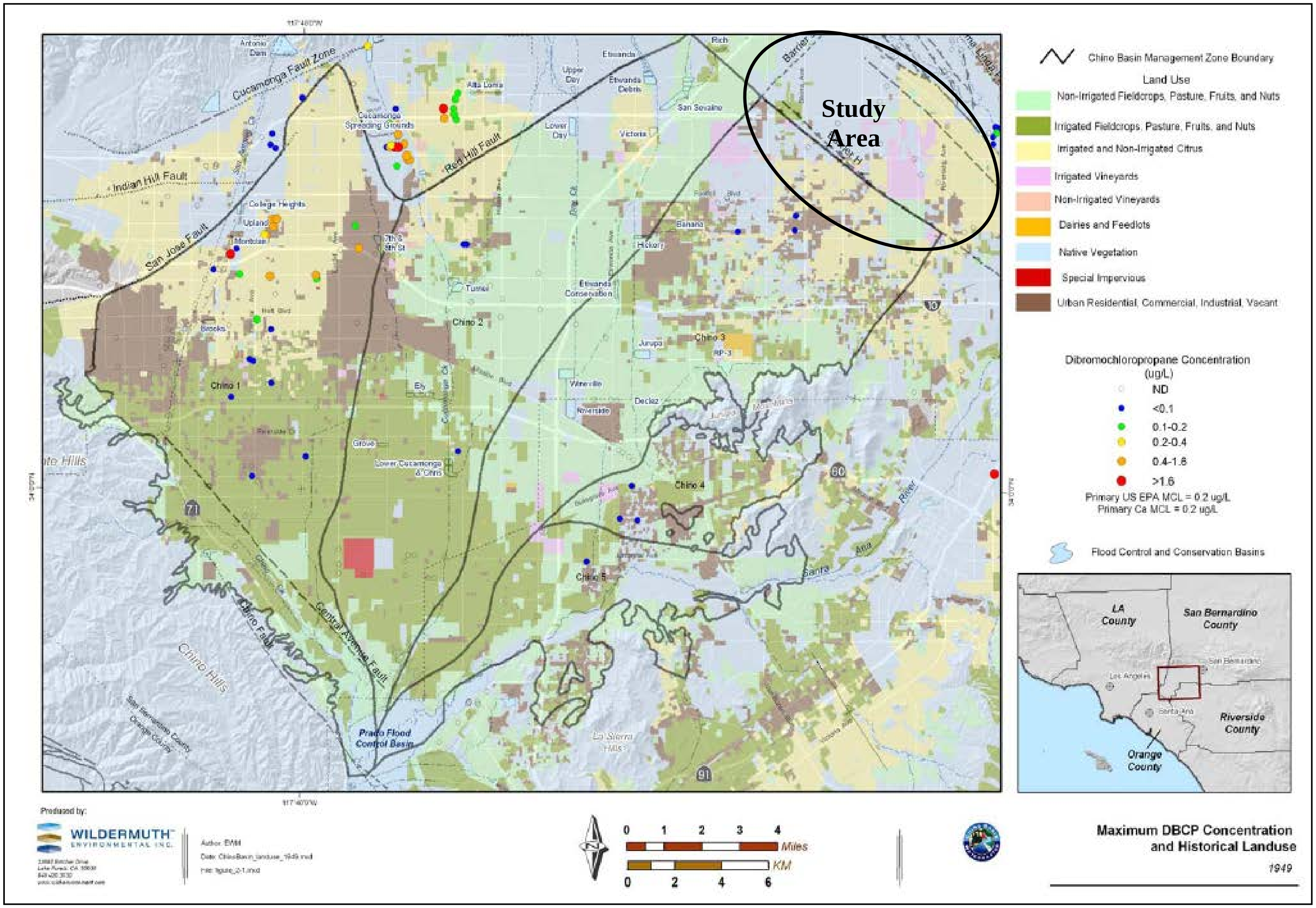


Figure 3.8. Map of land use characteristics in 1949 in the Chino Basin Management Zone. The Study Area is shown in the top right corner. Figure from Sturchio et al. (2008).

3.3. Depth-Dependent Isotope Samples

Depth-dependent groundwater sampling and isotopic analysis was conducted on five of the production wells in the Study Area: F-17B, F-26A, Rialto 2, Rialto 3, and Rialto 6. This work was conducted as part of the coupled well-bore flow and depth dependent water quality data analysis described by Izbicki et al. (2014). The primary objective of sampling ClO_4^- isotopes with depth in these wells was to determine whether different sources were entering the wells at different depth intervals in the aquifer(s) (e.g., synthetic ClO_4^- at the top of the well screen and indigenous ClO_4^- at a deeper screened interval).

Overall, the results showed that the source(s) of ClO_4^- collected from the bulk discharge of each of the wells was similar to that collected from a deep interval within the well, or in the case of Rialto 6, from two different depth intervals (Table 3.1; Figure 3.9). There were small differences in $\delta^{18}O$ between F-17B (580') and F-17B (bulk discharge) and between Rialto 6 (480') and Rialto 6 (560'), but these differences did not indicate substantial differences in ClO_4^- source fractions. In general, the major-ion composition of the wells with depth also was similar to the surface discharge from each well, with the exception of dissolved oxygen (DO), which generally decreased with depth. Biological degradation of ClO_4^- and associated fractionation of Cl and O isotopes in ClO_4^- are possible under anoxic conditions, particularly if organic carbon or other electron donors are available for growth of perchlorate-reducing bacteria (e.g., Sturchio et al., 2007). However, depth-dependent discharge data indicate deeper groundwater with low DO may not contribute substantially to the total discharge from the wells (Izbicki et al., 2014). No evidence of ClO_4^- isotopic fractionation was apparent in the depth-dependent samples. Similarly, no evidence of NO_3^- isotopic fractionation that might be associated with NO_3^- reduction was apparent in the same set of samples (Izbicki et al., 2014). For wells F-26A, F-17B, and Rialto 6, both the deep sampled interval and the bulk discharge had high DO concentrations (> 8 mg/L; Izbicki et al., 2014), indicating the bulk of the sampled groundwater was from the upper oxic part of the aquifer. The DO concentration was low for Rialto 3 at 670' (0.2 mg/L) but there was no evidence for biological fractionation of ClO_4^- isotopes in this sample. Dissolved oxygen data were not available for Rialto 2 with depth.

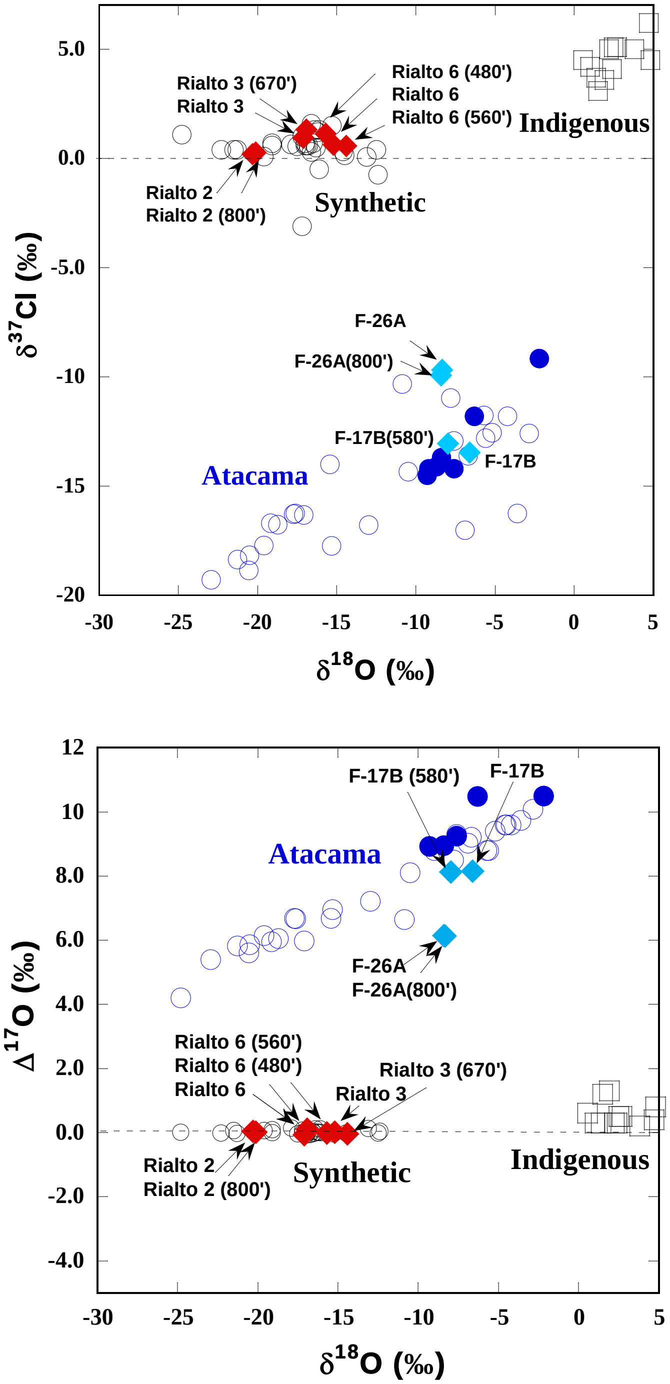


Figure 3.9. Comparison of δ^{37}Cl versus δ^{18}O (top panel) and Δ^{17}O versus δ^{18}O (bottom panel) in ClO_4^- from Study Area groundwater depth-dependent samples (symbols as in Figure 3.2) with published data for indigenous natural ClO_4^- of the SHP and MRGB (black open squares), natural Atacama ClO_4^-, (open blue circles for field samples and closed blue circles for Atacama nitrate fertilizer samples) and synthetic ClO_4^- (open black circles). Sources of ClO_4^- isotope data for Atacama, Synthetic and Indigenous as described in Figure 3.2.

3.4 Data Quality and Reproducibility

As described in the Methods section, several different procedures were implemented to ensure data quality and reproducibility. These procedures included (1) collection of replicate columns from ~ 30 % of the wells to establish column to column variability; (2) analysis of purified samples multiple times when large enough quantities were available to establish analytical variability; (3) routine analysis of ClO_4^- isotopic reference materials for consistency of IRMS data calibration; (4) analysis of $\delta^{18}O$ and $\delta^{17}O$ by O_2-DI-IRMS(-N_2) in addition to O_2-DI-IRMS(+N_2) to evaluate levels of contaminants and co-products of ClO_4^- decomposition; (5) analysis of select samples by by CO-CF-IRMS for independent quantification of $\delta^{18}O$; and (6) preparation and analysis of ClO_4^- isotopic reference materials loaded onto IX columns to assess effects of routine sample processing on stable isotope values.

3.4.1 Results from Replicate Columns

The data from individual replicate columns are provided in Table 3.6. For $\delta^{18}O$ and $\Delta^{17}O$, differences between replicate columns were $\leq$ 0.5 ‰ for all samples tested. For $\delta^{37}Cl$ differences in replicates were $\leq$ 1.0 ‰. For well F-17B, four IX columns were processed and analyzed independently, and the differences among replicates were $\leq$ 0.2 ‰ for $\delta^{37}Cl$, $\leq$ 0.4 ‰ for $\delta^{18}O$ and $\leq$ 0.2 ‰ for $\Delta^{17}O$. Similarly, for the four replicate columns from F-17B, $^{36}Cl/Cl$ ratios varied by $< 10 \times 10^{-15}$.

3.4.2 $\delta^{18}O$ from O_2-DI-IRMS(+N_2), O_2-DI-IRMS(-N_2), and CO-CFIRMS

All samples were analyzed by O_2-DI-IRMS(+N_2) and those results are the reported values (Table 3.1). Most samples also were analyzed by O_2-DI-IRMS(-N_2) to evaluate contaminants and co-products of ClO_4^- decomposition such as CO_2. A subset of samples also were analyzed independently by CO-CF-IRMS, which includes measurement of the relative amount of N_2 as an indication of potential contamination by air or N-O salts such as NO_3^-. For most samples, $\delta^{18}O$ values from O_2-DI-IRMS(+N_2) were slightly lower than $\delta^{18}O$ values from CO-CF-IRMS and O_2-DI-IRMS(-N_2) (Figure 3.10; Table 3.7). Several different processes could have contributed to differences between results of these methods including the following: (1) isotopic fractionation of O_2 by partial oxidation of reduced C in the samples (both O_2-DI-IRMS methods); (2)

isotopically anomalous O_2 produced by fragmentation of CO_2 in the IRMS (O_2-DI-IRMS(-N_2)); (3) contamination by O with elevated $\delta^{18}O$ (all three methods); (4) isotopic exchange between O_2 and CO_2 in the reaction tubes (both O_2-DI-IRMS methods); and (5) analytical artifact of elevated CO_2 in the ion source (O_2-DI-IRMS(-N_2)). Linear fits through the $\delta^{18}O$ data have R^2 values of 0.993-0.994 and intercepts between 0.4 and 0.6 ‰ indicating data from different methods are well correlated. Values of $\Delta^{17}O$ were indistinguishable between the two O_2-DI-IRMS methods, with R^2 of 0.999 and intercept of 0.0 ‰. To illustrate these effects in context of ClO_4^- source identification, data from all three methods are plotted together with ClO_4^- source data in Figure 3.11. In most cases, the symbols for isotopic values from each well by each of the three methods overlap. More importantly, the interpretation of sources for all of the wells is the same irrespective of the analytical technique used to measure $\delta^{18}O$ and/or $\delta^{17}O$. Data reported in Table 3.1 (from O_2-DI-IRMS(+N_2)) represent approximately 100 analyses of separate sample aliquots. A total of three analyses of this type (one from Rialto 4 and two from WVWD 42) were eliminated as outliers (small aliquots, highly fractionated); larger aliquots of those samples subsequently were purified and analyzed. All other analyses were included in the averages.

3.4.3 Perchlorate Extraction and Purification – Method Tests for QA/QC

Quality Assurance/Quality Control (QA/QC) tests were conducted using the USGS37 and USGS38 $KClO_4$ reference materials to evaluate the extent of Cl and/or O isotopic fractionation caused by the laboratory extraction and purification methods. The methods and results from these tests are presented in Appendix A. Here, isotope data are given for samples subjected to extraction and purification procedures after normalization to analyses of pure reference materials in order to isolate the effects of sample preparation. In summary, values of $\delta^{18}O$, $\Delta^{17}O$, and $\delta^{37}Cl$ of USGS37 that had been loaded on IX columns and purified by typical procedures at UIC were within the stated analytical uncertainties of ±0.2, ±0.2, and ±0.1 ‰, respectively, of the assumed reference values for USGS37. For USGS38, which was intentionally synthesized with unnaturally elevated values of $\delta^{18}O$ (+52.5 ‰) and $\Delta^{17}O$ (+73.3 ‰) and low value of $\delta^{37}Cl$ (-87.2 ‰), deviations of -2.1, -1.9 ‰, and +0.6 ‰, respectively, were observed for $\delta^{18}O$, $\Delta^{17}O$, and

δ^{37}Cl. Contraction of the apparent O isotope scale (factor of approximately 0.97) is consistent with the presence of small quantities of oxygen-bearing impurities with more normal δ^{18}O and δ^{17}O values in the prepared samples. The observed deviations in the USGS38 tests, when spread over the entire range of the calibration between USGS37 and USGS38, would not cause significant changes to δ values within the ranges of the samples analyzed in this study.

3.4.4 Secondary Ion Mass Spectrometry (SIMS)

An independent analysis of a subset of the purified Study Area ClO_4^- samples was conducted by SIMS at the Caltech Microanalysis Center (John Eiler, unpublished data). An advantage of the SIMs method is that much smaller quantities of ClO_4^- are required for a SIMS analysis than for traditional IRMS. However, the method has not been validated for complete stable isotope analysis of Cl and O isotopes in ClO_4^-, and is considered experimental. The data from the SIMS analysis are compared to those from IRMS for split samples in Appendix B.

Table 3.6. Perchlorate Cl and O isotope data for replicate sample columns from wells in the Study Area, June 2012 to February 2012.

State well number	Local well name	Date	δ^{37}Cl (‰)	δ^{18}O (‰)	Δ^{17}O (‰)	^{36}Cl ^{36}Cl/Cl x 10^{-15}	Column identification number
Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-28J2	28J-2	07/01/10	0.8 ± 0.1	-18.2	-0.1	101 (5)	242
1N/5W-28J2	28J-2	07/01/10	0.8	-18.4	-0.1	103 (6)	248
Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume							
1N/5W-21N2	PW-2	08/11/10	1.4 ± 0.2	- 16.9 ± 0.3	0.0 ± 0.2	118 (4)	230
1N/5W-21N2	PW-2	08/11/10	1.4	- 16.8 ± 0.5	-0.1 ± 0.1	NA	231
1S/5W-03A1	Rialto 04	10/20/10	1.1±0.0	-17.7 ± 0.1	0.0 ± 0.2	131 (3)	269
1S/5W-03A1	Rialto 04	10/20/10	1.1 ± 0.1	-17.5 ± 0.2	0.0 ± 0.3	NA	277
Wells outside the mapped plume							
1N/5W-17K2	WVWD 24	06/29/10	2.0	-8.7	1.1	6021 (110)	223+224+250+251
1N/5W-17K2	WVWD 24	06/29/10	1.3 ± 0.0	-8.2 ± 0.2	1.3 ± 0.2	NA	259+260+261+262
1N/5W-27D1	Rialto 01	05/18/11	0.0 ± 0.0	-16.1 ± 0.0	0.2 ± 0.0	2570 (50)	324
1N/5W-27D1	Rialto 01	05/18/11	-0.3 ± 0.1	-15.7 ± 0.0	0.2 ± 0.1	2750 (40)	325
1S/4W-18G1	Colton 15	07/08/10	-12.6 ± 0.4	-4.6 ± 0.1	8.6 ± 0.1	NA	245
1S/4W-18G1	Colton 15	07/08/10	-11.6	-4.5 ± 0.0	8.6 ± 0.1	1590 (40)	246
1S/5W-02K1	WVWD 11	06/30/10	-0.3 ± 0.1	-15.4 ± 0.0	1.0 ± 0.2	66 (3)	232
1S/5W-02K1	WVWD 11	06/30/10	-0.7 ± 0.4	-15.2 ± 0.7	1.1 ± 0.2	NA	240
1N/5W-32A1	F-13A	05/11/11	-5.4	-4.9	4.4	NA	320
1N/5W-32A1	F-13A	05/11/11	-5.7	-4.8 ± 0.0	4.8 ± 0.1	24200 (1200)	322
Wells in the Chino (or Arlington) subbasins							
1S/5W-23A1	WVWD 42	07/08/10	-10.3	NA	NA	1690 (110)	225
1S/5W-23A1	WVWD 42	07/08/10	-10.3	NA	NA	1880 (90)	226
1S/5W-23A1	WVWD 42	07/08/10	-10.4	-7.0 ± 0.0	7.1 ± 0.1	NA	225 + 226
1S/6W-23D2	F-17B	06/17/10	-13.4	-6.5 ± 0.2	8.2 ± 0.1	92 (6)	238
1S/6W-23D2	F-17B	06/17/10	-13.5	-6.5 ± 0.3	8.2 ± 0.1	88 (5)	239
1S/6W-23D2	F-17B	06/17/10	-13.5	-6.6 ± 0.3	8.0 ± 0.0	88 (6)	243
1S/6W-23D2	F-17B	06/17/10	-13.6 ± 0.2	-6.9 ± 0.3	8.2 ± 0.1	96 (6)	244
1S/5W-04N1	F-4A	07/28/10	-11.8 ± 0.3	-7.9 ± 0.2	7.6 ± 0.1	1380 (30)	255
1S/5W-04N1	F-4A (J613; 2007 sample)	03/09/07	-11.9	-8.0	7.6	NA	mpg31

NA - data not available.

Means and standard deviations are provided for replicate runs on individual columns. When individual values are provided, samples were analyzed once.

For WVWD-24, columns 223, 224, 250, 251 were combined into a single sample and 259, 250, 261, 262 were combined into a second sample.

The two samples were then treated independently.

Columns 225 & 226 from WVWD 42 were independently analyzed for δ^{37}Cl and ^{36}Cl but combined form δ^{18}O and Δ^{17}O analysis.

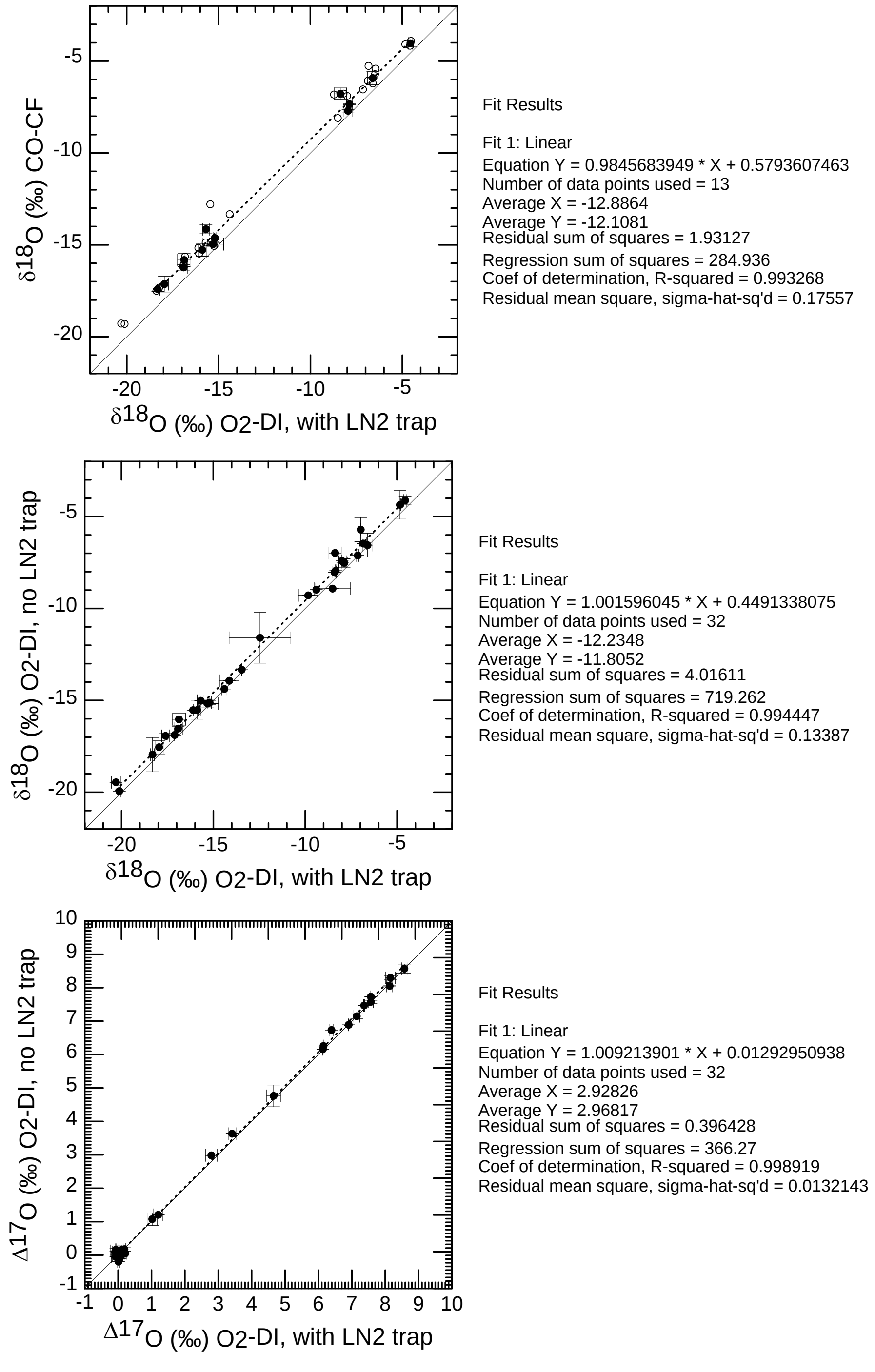
For ^{36}Cl, values in parentheses are laboratory reported unceratinty for individual samples.

Table 3.7. Perchlorate isotope data using three different methods of O stable isotope analysis for samples collected from wells in the Study Area, June 2012 to February 2012.

State	Local			O_2-DI-IRMS(+N_2)		O_2-DI-IRMS(-N_2)		CO-CFIRMS
well	well		$\delta^{37}Cl$	$\delta^{18}O$	$\Delta^{17}O$	$\delta^{18}O$	$\Delta^{17}O$	$\delta^{18}O$
number	name	Date	(‰)	(‰)	(‰)	(‰)	(‰)	(‰)
Wells in the perched aquifer in the Rialto-Colton subbasin within the mapped plume								
1N/5W-28J2	28J-2	07/01/10	0.8 ± 0.1	-18.3 ± 0.1	-0.1 ± 0.0	-18.0 ± 0.9	0.2 ± 0.0	-17.4 ± 0.1
1N/5W-29H1	F6	07/20/10	-0.5	-13.5	0.1	-13.3	0.0	NA
1N/5W-29H3	F6A-S	07/22/10	-0.9	-15.5 ± 0.3	0.2 ± 0.1	NA	NA	NA
1N/5W-33B2	N-10S	07/21/10	1.0 ± 0.0	-12.5 ± 1.7	0.0 ± 0.1	-11.6 ± 1.4	0.0 ± 0.1	NA
Wells in the Regional aquifer in the Rialto-Colton subbasin within the mapped plume								
1N/5W-21N2	PW-2	08/11/10	1.4 ± 0.1	-16.9 ± 0.4	0.0 ± 0.1	16.0 ± 0.3	0.0 ± 0.2	15.8 ± 0.4
1N/5W-21P2	PW-3	08/10/10	1.1 ± 0.2	-18.0 ± 0.2	0.1 ± 0.1	-17.6 ± 0.4	0.1 ± 0.1	-17.1 ± 0.4
1N/5W-33B1	N-10D	05/19/11	0.5	-14.1 ± 0.5	0.2 ± 0.0	-13.9	0.1	NA
1N/5W-34B2	Rialto 02	02/25/12	0.2	-20.3 ± 0.2	0.0 ± 0.0	-19.5	-0.1	NA
1N/5W-34B2	Rialto 02 (800')	02/25/12	0.3	-20.1 ± 0.1	0.0 ± 0.0	-19.9	-0.2	NA
1N/5W-34G4	PW-5D	08/04/10	0.7 ± 0.4	-17.6 ± 0.6	0.0 ± 0.1	NA	NA	NA
1N/5W-34M1	Rialto 03	03/15/11	0.6 ± 0.3	-15.2 ± 0.1	0.0 ± 0.2	-15.1 ± 0.1	0.1 ± 0.1	-14.6 ± 0.2
1N/5W-34M1	Rialto 03 (670')	03/15/11	0.6	-14.4 ± 0.1	0.0 ± 0.0	-14.4	0.0	NA
1S/5W-02B3	PW-9C	08/05/10	1.3	-16.1 ± 0.3	0.0 ± 0.1	-15.5	0.0	NA
1S/5W-02G1	Rialto 06	03/11/11	1.3 ± 0.3	-16.9 ± 0.2	0.1 ± 0.1	-16.5 ± 0.1	0.2± 0.1	-16.2 ± 0.2
1S/5W-02G1	Rialto 06 (480')	03/11/11	1.0	-17.1 ± 0.0	-0.1 ± 0.1	-16.9	0.0	NA
1S/5W-02G1	Rialto 06 (560')	03/11/11	1.1	-15.7 ± 0.2	0.0 ± 0.1	-15.0	0.0	-14.2 ± 0.2
1S/5W-03A1	Rialto 04	10/20/10	1.1 ± 0.1	-17.6 ± 0.2	0.0 ± 0.2	-16.9 ± 0.1	0.1 ± 0.1	NA
Wells outside the mapped plume								
1N/5W-17K2	WVWD 24	06/29/10	1.5 ± 0.4	-8.4 ± 0.3	1.2 ± 0.1	-7.0	1.2	-6.8 ± 0.3
1N/5W-27D1	Rialto 01	05/18/11	-0.2 ± 0.1	-15.9 ± 0.2	0.2 ± 0.0	-15.5 ± 0.5	0.2 ± 0.1	-15.3 ± 0.4
1N/5W-33N1	F-49A	04/23/11	-2.4 ± 0.0	-8.5 ± 1.0	2.8 ± 0.2	-8.9	3.0	NA
1S/4W-18G1	Colton 15	07/08/10	-12.3 ± 0.7	-4.6 ± 0.1	8.6 ± 0.1	-4.1 ± 0.2	8.6 ± 0.1	-4.0 ± 0.2
1S/5W-02K1	WVWD 11	06/30/10	-0.5 ± 0.4	-15.3 ± 0.6	1.0 ± 0.2	-15.2 ± 0.2	1.1 ± 0.2	-15.0 ± 0.1
1S/5W-05A5	F-10C	04/18/11	-4.3 ± 0.2	-9.8 ± 0.5	3.4 ± 0.1	-9.3	3.6	NA
1S/5W-13B5	13B1-5 (RHSW 5)	08/12/10	-9.8	-7.1 ± 0.1	6.9 ± 0.0	-7.1	6.9	NA
1N/5W-32A1	F-13A	05/11/11	-5.5 ± 0.2	-4.8 ± 0.0	4.7 ± 0.2	-4.8 ± 0.3	4.5 ± 0.1	NA
Wells in the Chino (or Arlington) subbasins								
1S/5W-23A1	WVWD 42	07/08/10	-10.3 ± 0.1	-7.0 ± 0.0	7.1 ± 0.1	-5.7 ± 0.7	7.1 ± 0.1	NA
1N/5W-32N1	F-26A	12/12/10	-9.7	-8.3 ± 0.0	6.1 ± 0.0	-7.9	6.2	NA
1N/5W-32N1	F-26A (800')	12/12/10	-9.9	-8.4 ± 0.1	6.2 ± 0.0	-8.0	6.3	NA
1S/5W-04N1	F-4A	07/28/10	-11.8 ± 0.3	-7.9 ± 0.2	7.6 ± 0.1	-7.5 ± 0.2	7.6 ± 0.0	-7.3 ± 0.0
1S/5W-04N1	F-4A (J613; 2007 sample)	03/09/07	-11.9	-8.0	7.6	-7.4	7.7	NA
1S/5W-07R1	F-35A	07/27/10	-11.1	-9.4 ± 0.1	6.4 ± 0.1	-9.0	6.7	NA
1S/5W-14B1	Chino 02	07/22/10	-11.1	-6.8 ± 0.2	7.4 ± 0.0	-6.5	7.5	NA
1S/6W-23D2	F-17B	06/17/10	-13.5 ± 0.0	-6.6 ± 0.3	8.2 ± 0.1	-6.6 ± 0.6	8.3 ± 0.1	-5.9 ± 0.4
1S/6W-23D2	F-17B (580')	06/17/10	-13.0 ± 0.2	-8.0 ± 0.2	8.1 ± 0.1	-7.5 ± 0.0	8.1 ± 0.0	-7.7 ± 0.1

NA - data not available.

Means and standard deviations are provided for all individual analyses per well . When individual values are provided samples were analyzed once.



```
Fit Results

Fit 1: Linear
Equation Y = 0.9845683949 * X + 0.5793607463
Number of data points used = 13
Average X = -12.8864
Average Y = -12.1081
Residual sum of squares = 1.93127
Regression sum of squares = 284.936
Coef of determination, R-squared = 0.993268
Residual mean square, sigma-hat-sq'd = 0.17557
```

```
Fit Results

Fit 1: Linear
Equation Y = 1.001596045 * X + 0.4491338075
Number of data points used = 32
Average X = -12.2348
Average Y = -11.8052
Residual sum of squares = 4.01611
Regression sum of squares = 719.262
Coef of determination, R-squared = 0.994447
Residual mean square, sigma-hat-sq'd = 0.13387
```

```
Fit Results

Fit 1: Linear
Equation Y = 1.009213901 * X + 0.01292950938
Number of data points used = 32
Average X = 2.92826
Average Y = 2.96817
Residual sum of squares = 0.396428
Regression sum of squares = 366.27
Coef of determination, R-squared = 0.998919
Residual mean square, sigma-hat-sq'd = 0.0132143
```

Figure 3.10. Comparison of O isotope results from different methods. Abbreviations for methods are: "CO-CF" = Conversion of O in ClO_4^- sample to CO with isotopic analysis of CO by continuous-flow (CF) isotope-ratio mass spectrometry (IRMS); "O2-DI" = Conversion of O in ClO_4^- to O_2 with isotopic analysis by dual-inlet (DI) IRMS; "with LN2 trap" = liquid N_2 trap in place to remove condensable gases (e.g., CO_2, H_2O) at the inlet to the mass spectrometer; "no LN2 trap" = liquid N_2 trap removed, admitting condensable gases into the mass spectrometer. Solid lines indicate 1:1 slope (perfect agreement). Dashed lines are linear fits to the data. Open symbols in the upper panel represent samples prepared with TPA and not pre-baked, potentially containing excess C or N (not included in the fit).

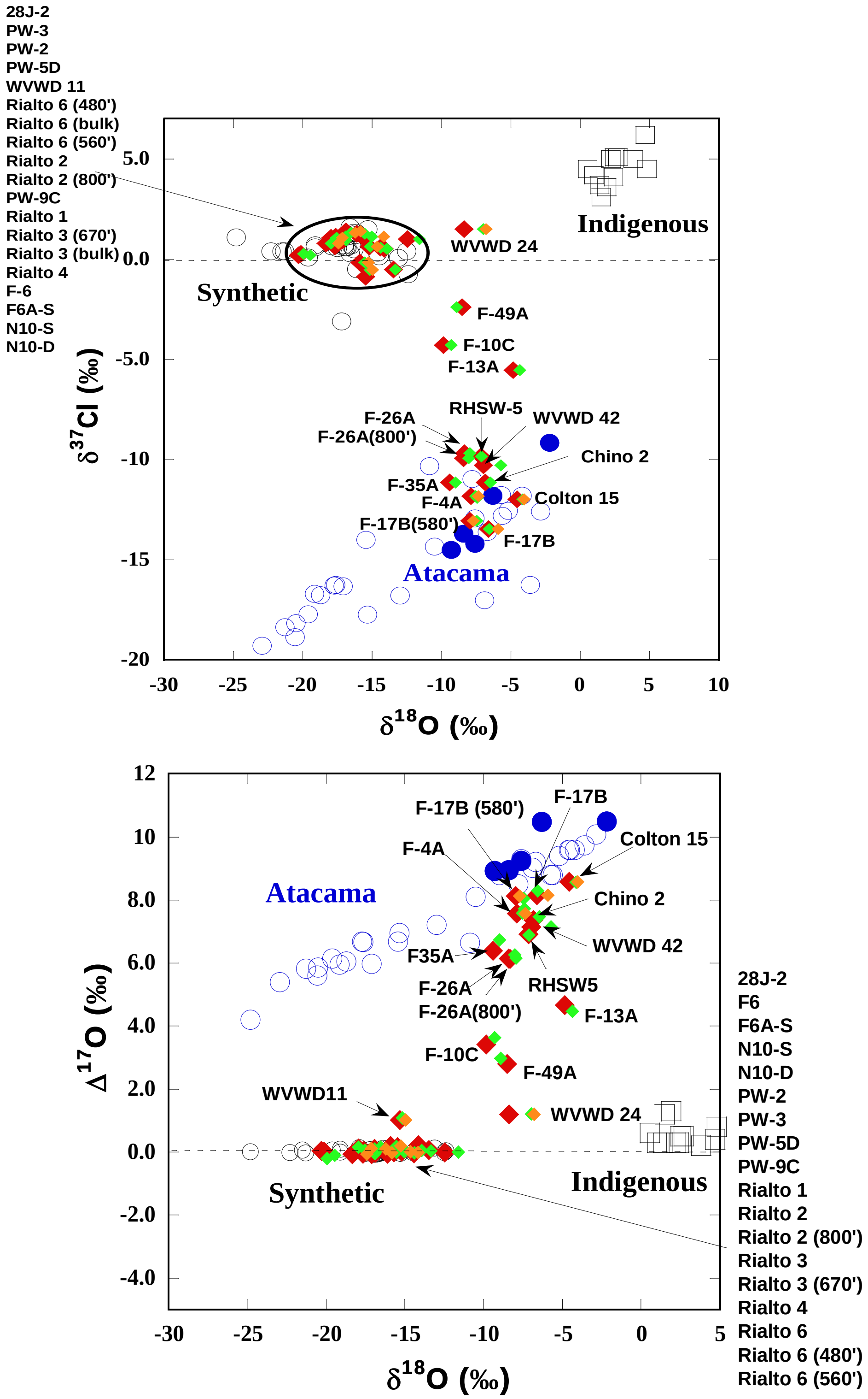


Figure 3.11. Comparison of $\delta^{37}Cl$ versus $\delta^{18}O$ (top panel) and $\Delta^{17}O$ versus $\delta^{18}O$ (bottom panel) in ClO_4^- from individual Study Area groundwater samples analyzed for O isotopes by O_2-DI-IRMS(+N_2) (closed red diamonds), O_2-DI-IRMS(-N_2) (closed green diamonds), or CO-CFIRMS (closed orange diamonds) with published data for natural indigenous ClO_4^- of the US (open black squares), natural Atacama ClO_4^-, (open blue circles and closed blue circles for actual fertilizer samples) and synthetic ClO_4^- (open black circles). Sources of ClO_4^- isotope data for Atacama, Synthetic and Indigenous as described in Figure 3.2.

3.5 Summary and Conclusions

Samples were collected from wells throughout the Study Area to evaluate Cl and O stable isotope ratios and ^{36}Cl abundances in ClO_4^-. The dominant source(s) of ClO_4^- in each of these samples was evaluated based on the isotopic data. The data indicate that synthetic, Atacama, and indigenous natural ClO_4^- were present in groundwater in the Study Area. In general, data for samples with relatively high ClO_4^- concentrations were consistent with either synthetic or Atacama ClO_4^- being dominant, whereas data for samples with low concentrations were more likely to indicate mixtures including substantial indigenous natural ClO_4^- fractions. The stable isotope data from nearly all samples from wells within two mapped ClO_4^- contaminant plume areas, including those located in the perched aquifer (28J-2, F6, F6A-S, N-10S) and those in the regional aquifer (PW-2, PW-3, Rialto 2, Rialto 2 (880'), PW-5D, Rialto 3, Rialto 3 (670'), PW-9C, Rialto 6, Rialto 6 (480'), Rialto 6 (560'), and Rialto 4) were consistent with a dominant synthetic ClO_4^- source in groundwater. The ^{36}Cl and δ^{18}O data indicate that some of these samples also contained smaller fractions of indigenous natural ClO_4^-. Downgradient from the mapped plume areas at wells 13B1-5 and Colton 15, and across the Rialto-Colton Fault to the southwest (Chino 2, WVWD 42, F-4A, F-35A, F-17B, F-26A, F-26A (800')), the dominant source of ClO_4^- in analyzed samples was Atacama, presumably from historical application of fertilizers imported from the Atacama Desert of Chile. Past agricultural land use in these areas is consistent with the use of such fertilizers.

A sample from an upgradient well (WVWD 24) appeared to contain a mixture of synthetic and indigenous ClO_4^- based upon all isotopic measures. This sample indicated that other synthetic sources may be present in the Study Area besides those originating from the two mapped plume source locations. There is also a possibility that the ClO_4^- in this sample represented a pure indigenous natural source, with isotopic characteristics (primarily δ^{18}O) that differ from the assumed values; however, the presence of tritium in this sample indicates a synthetic component cannot be ruled out. Interpretation of dominant sources in most samples did not differ substantially if one assumes that WVWD 24 represents a pure indigenous source, although this assumption is likely to affect the estimated fractions of indigenous ClO_4^- in mixing calculations.

Isotopic data for samples from wells outside the mapped plume areas with very low ClO_4^- concentrations (F-13A, F-49A, and F-10C) indicated mixed ClO_4^- sources. ClO_4^- from F-13A apparently was composed largely of Atacama and indigenous ClO_4^-, with a relatively large fraction of indigenous ClO_4^-. A small fraction of synthetic ClO_4^- was also possible based upon the $\delta^{18}O$ value. Based on the stable isotope values, ClO_4^- from F-10C and F-49A appeared to be composed of mixtures of all three sources. However, relations between $^{36}Cl/Cl$ and $\delta^{37}Cl$ values could also indicate mixtures of indigenous and Atacama ClO_4^-, with no apparent contribution from synthetic ClO_4^-. Uncertainties in the interpretation of ClO_4^- sources in these low-concentration samples are related in part to uncertainty and possibly local variability in the isotopic characteristics of indigenous natural ClO_4^-.

Depth-dependent sampling was conducted in several production wells to determine if different sources of ClO_4^- were present in these wells at different depth intervals (e.g., synthetic ClO_4^- in shallow groundwater and indigenous ClO_4^- in deep groundwater). The isotopic data generally were similar between the bulk discharge of the well and the depth dependent sample(s), indicating little or no variation in major ClO_4^- source(s) with depth in these wells.

4.0 Acknowledgments

The project team gratefully acknowledges the financial and technical support provided for this project by the DoD Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP). We also acknowledge the USGS National Research Program. We thank Dr. Andrea Leeson and Dr. Jeff Marqusee from SERDP/ESTCP for their guidance. The authors also thank the local stakeholders, their staff, and their consultants who provided data, access to wells, and input to the project through the Technical Advisory Committee (TAC). Other major contributors to this work included Stanley Mroczkowski (USGS), Linnea Heraty, Abe Beloso Jr., and Armen Poghosyan (University of Illinois at Chicago; UIC), Anthony Soto and Randi Rothmel (CB&I Federal Services, LLC; CB&I). Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

5.0 References Cited

Alpers, C.N.; Brimhall G.H. 1988. Middle Miocene climatic change in the Atacama Desert, northern Chile—evidence from supergene mineralization at La-Escondida, *Geol. Soc. Am. Bull.* 100:1640–1656.

Angert, A.; Cappa, C.D.; DePaolo, D.J. 2004. Kinetic ^{17}O effects in the hydrologic cycle: indirect evidence and implications. *Geochim. Cosmochim. Acta* 68:3487-3495.

Argento D.C.; Stone J.O.; Fifield L.K.; Tims S.G. 2010. Chlorine-36 in seawater. *Nucl. Inst. Meth. Phys. Res B*. 268:1226–1228.

Assonov, S.S.; Brenninkmeijer, C.A.M. 2005. Reporting small Δ^{17}O values: existing definitions and concepts. *Rapid Com. Mass Spectr*. 19:627-636.

Aziz, C.E.; Hatzinger, P.B. 2008. Perchlorate Sources, Source Identification, and Analytical Methods. In *In Situ Bioremediation of Perchlorate.* H.F. Stroo and C.H. Ward, (Eds). Springer, New York, pp 55-77.

Aziz, C; Borsch, R.; Nicholson, P; Cox, E. 2006. Alternative Causes of Wide-Spread, Low Concentration Perchlorate Impacts to Groundwater. In *Perchlorate Environmental Occurrences, Interactions, and Treatment*. B. Gu and J.D. Coates, (Eds). Springer, New York, pp 71-88.

Bao H.; Gu B. 2004. Natural perchlorate has a unique isotopic signature. *Environ. Sci. Technol.,* 38:5073-5077.

Bentley, H.W.; Phillips, F.M.; Davis, S.N. 1986. ^{36}Cl in the Terrestrial Environment, In *Handbook of Environmental Geochemistry, Vol. 2b*, P. Fritz and J.-Ch. Fontes (Eds). Elsevier Science, New York, pp. 422-475.

Böhlke, J.K.; Hatzinger, P.B.; Sturchio, N.C.; Gu, B.; Abbene, I.; Mroczkowski, S.J. 2009. Atacama perchlorate as an agricultural contaminant in groundwater: Isotopic and chronologic evidence from Long Island, New York. *Environ. Sci. Technol.* 43:5619-5625.

Böhlke, J.K.; Sturchio, N.C.; Gu, B.; Horita, J.; Brown, G.M.; Jackson, W.A.; Batista, J.R.; Hatzinger, P.B. 2005. Perchlorate isotope forensics: *Anal. Chem.* 77:7838 -7842.

Böhlke, J.K.; Mroczkowski, S.J.; Coplen, T.B. 2003. Oxygen isotopes in nitrate: new reference materials for ^{18}O:^{17}O:^{16}O measurements and observations on nitrate-water equilibration. *Rapid Comm. Mass Spec.* 17:1835-1846.

Böhlke, J.K.; Ericksen, G.E.; Révész, K. 1997. Stable isotope evidence for an atmospheric origin of desert nitrate deposits in northern Chile and southern California. *Chem. Geol.* 136:135-152.

Brand, W.A.; Coplen, T.B.; Aerts-Bijma, A. T. A.; Böhlke, J.K.; Gehre, M.; Geilman, H.; Gröning, M.; Jansen, H.G.; Meijer, H. A. J. ; Mroczkowski, S. J.; Qi, H.; Soergel,K.; Stuart-Williams, H.; Weise, S.M.; Werner, R.A. 2009. Comprehensive inter-laboratory calibration of reference materials for δ^{18}O versus VSMOW using various on-line high-temperature conversion techniques. *Rapid Com. Mass Spec.* 23:999–1019.

California Department of Food and Agriculture. 1999. *Fertilizing Materials Tonnage Report*, July-December 1999, Sacramento, CA.

Catling, D.C.; Clair, M.W.; Zahnle, K.J.; Quinn, R.C.; Clarc, B.C.; Hecht, M.H.; Kounaves S.P. 2010. Atmospheric origins of perchlorate on Mars and in the Atacama. *J Geophys. Res.* 115: E00E11.

Coplen, T.B., 1994, Reporting of stable hydrogen, carbon, and oxygen isotopic abundances. *Pure Appl. Chem.* 66:273-276.

Coplen, T.B.; Böhlke, J.K.; De Bièvre, P.; Ding, T.; Holden, N.E.; Hopple, J.A.; Krouse, H.R.; Lamberty, A.; Peiser, H.S.; Révész, K.; Rieder, S.E.; Rosman, K.J.R.; Roth, E.; Taylor, P.D.P.; Vocke, R.D.Jr.; Xiao, Y.K.. 2002. Isotope-abundance variations of selected elements. *Pure Appl. Chem*. 74:1987-2017.

Cunniff, S.E.; R.J. Cramer; Maupin, H.E. 2006. Perchlorate: Challenges and lessons. In *Perchlorate Environmental Occurrences, Interactions, and Treatment*. B. Gu and J.D. Coates, (Eds). Springer, New York, pp 1-14.

Dasgupta, P.K.; Dyke, J.V.; Kirk, A.B.; Jackson, W.A. 2006. Perchlorate in the United States. Analysis of relative source contributions to the food chain. *Environ. Sci. Technol.* 40:6608-6614.

Dasgupta, P.K.; Martinelango, P.K.; Jackson, W.A.; Anderson, T.A.; Tian, K.; Tock, R.W.; Rajagopalan, S. 2005. The origin of naturally occurring perchlorate: The role of atmospheric processes. *Environ. Sci. Technol.* 39:1569-1575.

Davis, S.N.; Moysey, S; Cecil, L.D.; Zreda, M. 2003. Chlorine-36 in groundwater of the United States: empirical data. *Hydrogeol. J.* 11:217-227.

Eldridge, J.E.; Tsui, D.T.; Mattie, D.R.; Crown, J.; Scott, R. 2000. Perchlorate in Fertilizers. U.S. Air Force Research Laboratories. Wright Patterson AFB, OH.

Eastoe, C.J.; Peryt, T.M.; Petrychenko, O.Y.; Geisler-Cussy, D. 2007. Stable chlorine isotopes in Phanerozoic evaporites. *Appl. Geochem.* 22: 575-588.

Eggenkamp, H.G.M. 1994. *The Geochemistry of Chlorine Isotopes.* PhD Thesis, University of Utrecht, Utrecht, the Netherlands. Geological Ultraiectina, No. 116: 149p.

Ericksen, G. E. 1981. *Geology and Origin of the Atacama Nitrate Deposits,* Prof. Paper 1188; U.S. Geological Survey: Washington, D.C.

Ericksen, G.E. 1983. The Atacama nitrate deposits. *Amer. Sci.* 71:366-374.

Fram, M.S.; Belitz, K. 2011. Probability of detecting perchlorate under natural conditions in deep groundwater in California and the southwestern United States. *Environ. Sci. Technol.* 45:1271-1277.

GeoLogic Associates (in association with Bryan A. Stirrat & Associates). 2002. Environmental Audit, Potential Sources of Perchlorate Impacts, Rialto-Colton Groundwater Basin, San Bernardino, California, Anaheim, Calif., variously paged.

GeoLogic, Associates. 2003. Perchlorate Investigation in the Vicinity of the Mid Valley Sanitary Landfill, San Bernardino, California. Report prepared for the County of San Bernardino Waste System Division. Anaheim, Calif., variously paged.

GeoLogic Associates. 2013. First Quarter (Winter) 2013 Monitoring Report Rialto GWTS Perchlorate and VOC Investigation, San Bernardino County, California. Anaheim, Calif., variously paged.

Godon, A.; Jendrzejewski, N.; Eggenkamp, H.G.M.; Banks, D.A.; Ader M.; Coleman M.L.; Pineau F. 2004. An international cross calibration over a large range of chlorine isotope compositions. *Chem. Geol.* 207:1-12.

Gonfiantini, R. 1978. Standards for stable isotope measurements in natural compounds: *Nature* 271:534-536.

Gu B., Brown G. M., Maya L., Lance M. J., and Moyer B. A. 2001. Regeneration of perchlorate (ClO_4^-)-loaded anion exchange resins by novel tetrachloroferrate ($FeCl_4^-$) displacement technique. *Environ. Sci. Technol.* 35, 3363-3368.

Gu, B.; Böhlke, J.K.; Sturchio, N.C.; Hatzinger, P.B.; Jackson, W.A.; Beloso, Jr., A.D.; Heraty, L.J.; Bian, Y; Jiang, X. Brown, G.M. 2011. Removal, recovery and fingerprinting of perchlorate by ion exchange processes In *Ion Exchange and Solvent Extraction: A Series of Advances*, 20th Ed., Taylor and Francis Group, New York, pp. 117-144.

Hartley A.J.; Chong G. 2002. Late Pliocene age for the Atacama Desert: Implications for the desertification of western South America, *Geology* 30:43–46.

Hatzinger, P.B. 2005. Perchlorate biodegradation for water treatment. *Environ. Sci. Technol.* 39: 239A-247A.

Hatzinger, P.B.; Böhlke, J.K.; Sturchio, N.C.; Gu, B. 2011. Guidance Document: Validation of Chlorine and Oxygen Isotope Ratios to Differentiate Perchlorate Sources and Document Perchlorate Biodegradation. Environmental Security Technology Certification Program. 107 pp. Online: http://www.clu in.org/download/contaminantfocus/perchlorate/ Perchlorate-ER-200509-GD.pdf.

Hatzinger, P.B.; Böhlke, J.K.; Sturchio, N.C.; Gu, B. 2013. Validation of Chlorine and Oxygen Isotope Ratios to Differentiate Perchlorate Sources and Document Perchlorate Biodegradation. Final Report. Environmental Security Technology Certification Program. 176 pp. Online: http://www.serdp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-200509.

Hecht, M.H.; Kounaves, S.P.; Quinn, R.C.; West, S.J.; Young, S.M.M.; Ming, D.W.; Catling, D.C.; Clark, B.C.; Boynton, W.V.; Hoffman, J.; DeFlores, L.P.; Gospodinova, K.; Kapit, J., Smith, P.H. 2009. Detection of perchlorate and the soluble chemistry of martian soil at the Phoenix lander site. *Science* 325: 64– 67.

Holt, B.D.; Sturchio, N.C.; Abrajano, T.A.; Heraty, L.J. 1997. Conversion of chlorinated volatile organic compounds to carbon dioxide and methyl chloride for isotopic analysis of carbon and chlorine. *Anal. Chem.* 69:2727-2733.

ITRC; Interstate Technology & Regulatory Council. 2008. *Remediation Technologies for Perchlorate Contamination in Water and Soil*. PERC-2, ITRC Perchlorate Team, Washington, D.C. Online: http://www.itrcweb.org/documents/perc-2.pdf.

Izbicki, J.; Teague, N.F.; Hatzinger, P.B.; Böhlke, J.K.; Sturchio, N.C. 2014. Groundwater movement, recharge, and perchlorate occurrence in a faulted alluvial aquifer in California (USA). *Hydrogeology J. (accepted, in press; DOI* 10.1007/s10040-014-1217-y*).*

.

Jackson, W.A.; Böhlke, J.K.; Gu, B.; Hatzinger, P.B.; Sturchio, N.C. 2010. Isotopic composition and origin of indigenous natural perchlorate and co-occurring nitrate in the southwestern United States. *Environ. Sci. Technol*. 44:4869-4876.

Jackson, W.A., Davila, A.F.; Estrada, N,; Lyons, W.B.; Coates, J.D.; Priscu, C.. 2013. Perchlorate and chlorate biogeochemistry in ice-covered lakes of the McMurdo Dry Valleys, Antarctica. *Geochim. Cosmochim Acta*. 98:19-30.

Jackson, W.A.; Anderson,T.A.; Harvey, G.; Orris,G.; Rajagopalan, S.; Namgoo, K. 2006. Occurrence and formation of non-anthropogenic perchlorate. In *Perchlorate Environmental Occurrences, Interactions, and Treatment*. B. Gu and J.D. Coates, (Eds). Springer, New York, pp. 49-66.

Jackson, W.A.; Anandam, S.K.; Anderson, T.; Lehman, T.; Rainwater, K.; Rajagopalan, S.; Ridley, M.; Tock, R. 2005. Perchlorate occurrence in the Texas southern high plains aquifer system. *Ground Water Monit. Remed.* 25:137-149.

Jackson, W.A.; Anderson, T.A.; Lehman, T.; Rainwater, K.A.; Rajagopalan, S.; Ridley, M. Tock, W.R. 2004. *Distribution and Potential Sources of Perchlorate in the High Plains Region of Texas.* Final Report to the Texas Commission on Environmental Quality.

Johnson, D.G.; Jucks, K.W.; Traub, W.A.; Chance, K.V. 2000. Isotopic composition of stratospheric ozone. *J. Geophys. Res. [Atmos.]*. 105:9025-9031.

Kang, N.; Jackson, W.A.; Dasgupta, P.K.; Anderson, T.A. 2008. Perchlorate production by ozone oxidation of chloride in aqueous and dry systems. *Science Total Environ*. 405:301-309.

Kounaves, S.P.; Stroble, S.T.; Anderson, R.M.; Moore, Q.; Catling, D.C.; Douglas, S. McKay, C.P.; Ming, D.W., Smith, P.H.; Tamppari, L.K.; Zent, A.P. 2010. Discovery of natural perchlorate in the Antarctic Dry Valleys and its global implications. *Environ Sci Technol* 44: 2360–2364.

Lybrand, R.A.; Michalski, G.; Graham, R.C; Parker, D.R. 2013. The geochemical associations of nitrate and naturally formed perchlorate in the Mojave Desert, California, USA. *Geochim. Cosmochim. Acta* 104:136-147.

MADEP. 2007. Massachusetts Department of Environmental Protection. *The Evaluation of Perchlorate Contamination at a Fireworks Display, Dartmouth, MA*, Final Report, Boston, MA, 33 pp. Online:http://www.mass.gov/dep/cleanup/sites/umdrep.pdf.

Miller, M.F. 2002. Isotopic fractionation and quantification of ^{17}O anamolies in the oxygen three-isotope system. An appraisal and geochemical significance. *Geochim. Cosmochim. Acta* 66:1881-1889.

Ming D.W.; Smith, P.H.; Tamppari, L.K.; Zent, A.P. 2010. Discovery of natural perchlorate in the Antarctic Dry Valleys and its global implications. *Environ. Sci. Technol* 44:2360–2364.

Munster, J.E. 2008. *Nonpoint Sources of Nitrate and Perchlorate in Urban Land Use to Groundwater, Suffolk County, NY.* PhD Thesis, Stony Book University, Stony Brook, NY, 115 pp.

Munster, J.E.; Hanson, G.N. 2009. Perchlorate and ion chemistry of road runoff. *Environ. Chem.* 6:28-35.

Munster, J., G.N. Hanson, W.Andrew Jackson, and S. Rajagopalan. 2008. The fallout from fireworks: Perchlorate in total deposition. *Water Air Soil Pollut.* 198:149-153.

Murphy, D. M.; Thomson, D.S. 2000. Halogen ions and NO^+ in the mass spectra of aerosols in the upper troposphere and lower stratosphere. *Geophys. Res. Let.* 27:3217-3220**.**

Parker, D.R.; Seyfferth, A.L.; Reese, B.K. 2008. Perchlorate in groundwater: A synoptic survey of "pristine" sites in the conterminous Unites States. *Environ. Sci. Technol*. 42: 1465-1471.

Paulinski, S., 2012. Structural, hydrogeologic framework and textural model of the Rialto-Colton basin and the Chino and North Riverside area. Master of Science Thesis, Department of Geology, California State University, Sacramento, 171 p.

Phillips F.M. 2000. Chlorine-36. In *Environmental Tracers in Subsurface Hydrology,* Cook, P. and Herczeg, A., (Eds), Kluwer Academic Publishers, Boston, pp. 299-348.
Plummer, L.N.; Böhlke, J.K.; Doughten, M.W. 2006. Perchlorate in Pleistocene and Holocene groundwater in north-central New Mexico. *Environ. Sci. Technol.* 40:1757-1763.

Phillips D.L.; Gregg J.W. 2001 Uncertainty in source partitioning using stable isotopes. *Oecologia* 127:171-179.

Poghosyan A.; Sturchio N.C.; Morrison C.G.; Beloso, A.D. Jr.; Guan Y.; Eiler J.M.; Jackson W.A.; Hatzinger P.B. 2014. Perchlorate in the Great Lakes: Isotopic composition and origin. *Environ. Sci. Technol.* 48:11146-11153.

Rajagopalan, S.; Anderson, T.; Cox, S.; Harvey, G.; Cheng, Q. 2009. Perchlorate in wet deposition across North America. *Environ. Sci. Technol.* 43:616–622.

Rajagopalan, S.; Anderson, T.A.; Fahlquist, L.; Rainwater, K.A.; Ridley, M.; Jackson, W.A. 2006. Widespread presence of naturally occurring perchlorate in high plains of Texas and New Mexico. *Environ. Sci. Technol*. 40:3156-3162.

Rao, B.; Anderson, T.A.; Redder, A.; Jackson, W.A. 2010. Perchlorate formation by ozone oxidation of aqueous chlorine/ox-chlorine species: Role of Cl_xO_y radicals. *Environ. Sci. Technol.* 44:2961–2967.

Rao, B.; Anderson, T.A.; Orris, G.J.; Rainwater, K.A.; Rajagopalan, S.; Sandvig, R.M.; Scanlon, B.R.; Stonestrom, D.A.; Walvoord, M.A.; Jackson, W.A. 2007. Widespread natural perchlorate in unsaturated zones of the Southwest United States, *Environ. Sci. Technol.* 41:4522–4528.

SAIC; Science Applications International Corporation. 2004. Final Report: Operational History 1941-1945 Rialto Ammunition Back-Up Storage Point. Report prepared for the U.S Army Corps of Engineers Los Angeles District. Online: http://www.waterboards.ca.gov/rwqcb8/water_issues/programs/perchlorate/docs/dod_report.pdf.

SARWQCB; Santa Ana Regional Water Quality Control Board. 2005. Proposed groundwater monitoring program, Cleanup and Abatement Order (CAO) R8-2003-0013, to Mr. Peter Wulfman, Division Manager, Solid Waste Management Division, County of San Bernardino, Department of Public Works, November 29.

Schilt, A.A. 1979. *Perchloric Acid and Perchlorates.* GFS Chemicals, Columbus, OH, pp 3-4.

Schumacher, J.C. (Ed). 1960. *Perchlorates - Their Properties, Manufacture and Uses*. American Chemical society Monograph Series No. 146. Reinhold Publishing Co., New York.

Slaten, S.; Fields, K.A.; Santos, S.; Barton, A.; Rectanus, H.V., Bhargava, M. 2010. Integrated environmental forensics approach for evaluating the extent of dissolved perchlorate originating from multiple sources. *Environ. Forensics* 11:72-93.

Sturchio, N.C.; Beloso Jr., A.D.; Heraty, L.J.; Wheatcraft, S.; Schumer, R. 2014. Isotopic tracing of perchlorate sources in groundwater from Pomona, California. *Appl. Geochem.*, 43:80-87.

Sturchio, N.C.; Hoaglund III, J.R.; Marroquin, R. J.; Beloso Jr., A.D.; Heraty, L.J.; Bortz, S.E.; Patterson, T.L. 2012. Isotopic mapping of perchlorate plumes. *Groundwater*, 50:94-102.

Sturchio, N.C., Böhlke, J.K.; Gu, B.; Hatzinger, P.B.; Jackson, W.A. 2011. Isotopic tracing of perchlorate in the environment. In *Handbook of Environmental Isotope Geochemistry*, M. Baskaran (Ed), Springer-Verlag, New York, pp. 437-452.

Sturchio, N.C., M Caffee, A.D. Beloso, L. Heraty, J.K. Böhlke, P.B. Hatzinger, W.A. Jackson, B. Gu, J.M. Heikoop and M. Dale. 2009. Chlorine-36 as a tracer of perchlorate origin. *Environ. Sci. Technol*. 43:6934-6938.

Sturchio, N.C.; Beloso, Jr. A.D.; Heraty, L.J; LeClair, J.; Rolfe, T., Manning, K.R. 2008. Isotopic evidence for agricultural perchlorate in groundwater of the Western Chino Basin, California. In Sixth International Conference on Remediation of Chlorinated Solvents, Monterey, CA. 18-22 May.

Sturchio, N.C.; Böhlke, J.K.; Beloso, Jr. A.D.; Streger, S.H.; Heraty, L; Hatzinger, P.B. 2007. Oxygen and chlorine isotopic fractionation during perchlorate biodegradation: Laboratory results and implications for forensics and natural attenuation studies. *Environ. Sci.Technol.* 41:2796-2802.

Sturchio, N.C.; Böhlke, J.K.; Gu, B.; Horita, J.; Brown, G.M.; Beloso, A, Jr.; Patterson, L.J.; Hatzinger, P.B.; Jackson, W.A.; Batista, J.R. 2006, Stable isotopic composition of chlorine and oxygen in synthetic and natural perchlorate, In *Perchlorate Environmental Occurrences, Interactions, and Treatment*. B. Gu and J.D. Coates, (Eds). Springer, New York, pp. 93-109.

Thiemens, M.H. 1999. Mass-independent isotope effects in planetary atmospheres and the early solar system. *Science* 283:341-345.

Trumpolt, C; Crain, M.; Cullison, G.D.; Flanagan, S.J.P.; Siegel, L.; Lathrop, S. 2005. Perchlorate: Sources, uses, and occurrences in the environment. *Remediation*, Winter, 65-89.

Urbansky, E.T.; Brown, S.K.; Magnuson, M.L.; Kelly, C.A. 2001a. Perchlorate levels in samples of sodium nitrate fertilizer derived from Chilean caliche. *Environ. Pollut.* 112:299-302.

Urbansky, E.T.; Collette, T.W.; Robarge, W.P.; Hall, W.L.; Skillen, J.M.; Kane, P.F. 2001b. *Survey of Fertilizers and Related Materials for Perchlorate.* US Environmental Protection Agency. EPA/600/R-01/047. 33 pp.

USDA (US Department of Agriculture) (2013) US Census of Agriculture. Online: http://www.agcensus.usda.gov.

USEPA. 2014. U.S. Environmental Protection Agency, Pacific Southwest Region 9: Superfund. Rockets, Fireworks, and Flares. Website. Online: http://www.epa.gov/region9/rff.

Woolfenden, L.R. 2007. Aquifer susceptibility to perchlorate contamination in a highly urbanized basin, In: Trefry, M.G. (ed.), *Securing Groundwater Quality in Urban and Industrial Environments*. Proceedings of the International Association of Hydrologic Scientists, Groundwater Quality 2007, Fremantle, Western Australia, Dec. 2-7, IAHS Publication 324, p. 156-1,1 CD-ROM.

APPENDIX A

Perchlorate Extraction and Purification – Method Tests for QA/QC

A total of 27 separate Quality Assurance/Quality Control (QA/QC) tests were performed to evaluate the extent of Cl and O isotopic fractionation caused by the laboratory extraction and purification methods. These tests were done in addition to the field replication tests described in Section 3.4.1. The QA/QC tests were performed by the same analysts who processed all of the field samples at UIC (Abelardo Beloso, Jr. and Linnea Heraty). The perchlorates used in these QA/QC tests were the USGS37 and USGS38 $KClO_4$ reference materials. A few of the tests included potential interfering compounds, such as chlorate (ClO_3^-) and organics, to measure their effects on ClO_4^- isotope ratios.

Twelve tests involved the entire procedure: loading the Purolite A530E ion exchange resin column (i.e., field column) with two liters of a $KClO_4$ solution (10 mg/L ClO_4^-), followed by extraction and purification of the ClO_4^- from each column according to the procedures used for the field samples. These tests of the entire procedure used the following initial solutions: (1) four columns prepared by loading pure $KClO_4$ solutions made from deionized water plus USGS37 (two columns) or USGS38 (two columns); (2) four columns loaded with $KClO_4$ solutions made from USGS37 and USGS38 plus added ClO_3^- from reagent $NaClO_3$ (two columns made with USGS37 and two columns made with USGS38, both having ~1,000 mg/L ClO_3^-); and (3) four columns loaded with $KClO_4$ solutions made from USGS37 and USGS38 plus added humic and fulvic acid from commercially available extracts (two columns made with USGS37 and two columns made with USGS38, each having ~50 mg/L humic + fulvic acid). The outcome of these tests for the six column tests having ClO_4^- from USGS37 resulted in little isotopic fractionation (Table A-1). The mean normalized values of $\delta^{18}O$, $\Delta^{17}O$, and $\delta^{37}Cl$ were within the stated analytical uncertainties of ±0.2, ±0.2, and ±0.1 per mil, respectively, for the calibration values of USGS37. For the six column tests having ClO_4^- from USGS38, which was intentionally synthesized with elevated values of $\delta^{18}O$ (+52.5 ‰) and $\mathbf{\Delta}^{17}O$ (+73.3 ‰), and a low value of $\delta^{37}Cl$ (-87.2 ‰), the mean normalized values of $\delta^{18}O$, $\Delta^{17}O$, and $\delta^{37}Cl$ had deviations of -1.8, -1.7, and +0.6 per mil, respectively. The estimated analytical uncertainties for USGS-38 are ±0.5 and ±0.3 for $\delta^{18}O$ and $\delta^{37}Cl$. The relatively large deviations for the O isotopes in the USGS38 tests may reflect the presence of small amounts of O-bearing impurities which are isotopically light relative to

O in USGS38. If these impurities were present in the USGS37 method test samples, they did not significantly affect the resulting values of $\delta^{18}O$ and $\Delta^{17}O$. The deviation of the mean normalized $\delta^{37}Cl$ value for the USGS38 method tests, +0.6 per mil, is about two standard deviations higher than the accepted value and could be caused by small amounts of gaseous impurities in the CH_3Cl used for Cl isotope ratio measurements. However, the observed deviations in the O and Cl isotope ratios of the USGS38 tests, when spread over the entire range of the calibration between USGS37 and USGS38, would not cause significant changes to δ values within the ranges of the samples analyzed in this study.

Other QA/QC tests were done to examine the effects of specific steps in the purification procedure, after the extraction from the Purolite A530E resin (Table A-2). Compared with the deviations described above for the entire extraction and purification procedure, the post-extraction steps caused deviations that were comparable in direction and not significantly different in magnitude from those caused by the entire procedure. This implies that most of the observed isotopic effects associated with extraction and purification of perchlorate samples collected on Purolite A530E resin occur during the post-extraction purification steps, in which there are opportunities for addition of small amounts of O-bearing impurities (or C-bearing impurities that may become oxidized to CO_2 during the high-temperature $KClO_4$ decomposition step) during a number of adsorption, precipitation, and washing steps.

Table A-1. Evaluation of fractionation of Cl and O isotopes during extraction and purification of perchlorate from ion exchange columns.

Test ID	date (mm/yr)	mg ClO4	δ^{37}Cl	δ^{18}O	Δ^{17}O	D37	D18	D17	description of test
UIC-EX1-37C	8/13	3.4	NA	-17.0	0.0	NA	0.0	0.0	USGS-37 solution in DIW, 10 mg/L, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX1-37D	8/13	3.8	0.9	-17.7	0.0	0.3	-0.6	0.0	USGS-37 solution in DIW, 10 mg/L, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX1-38C	8/13	3.3	-86.8	50.6	71.6	0.4	-1.9	-1.7	USGS-38 solution in DIW, 10 mg/L, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX1-38D	8/13	2.8	-86.4	49.3	70.6	0.8	-3.2	-2.7	USGS-38 solution in DIW, 10 mg/L, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX2-37C	8/13	2.9	0.8	-16.8	0.0	0.2	0.2	0.0	USGS-37 solution in DIW, 10 mg/L, plus 1000 mg/L chlorate, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX2-37D	8/13	2.8	0.8	-16.6	-0.1	0.2	0.4	-0.1	USGS-37 solution in DIW, 10 mg/L, plus 1000 mg/L chlorate, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX2-38C	8/13	3.2	-86.5	51.2	72.0	0.7	-1.3	-1.3	USGS-38 solution in DIW, 10 mg/L, plus 1000 mg/L chlorate, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX2-38D	8/13	2.9	-86.7	50.8	71.7	0.5	-1.7	-1.6	USGS-38 solution in DIW, 10 mg/L, plus 1000 mg/L chlorate, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX3-37C	8/13	4.2	0.9	-16.9	0.0	0.3	0.1	0.0	USGS-37 solution in DIW, 10 mg/L, plus 50 mg/L humic and fulvic acid, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX3-37D	8/13	3.8	NA	-17.1	0.1	NA	-0.1	0.1	USGS-37 solution in DIW, 10 mg/L, plus 50 mg/L humic and fulvic acid, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX3-38C	8/13	2.7	-86.7	50.5	71.5	0.5	-2.0	-1.8	USGS-38 solution in DIW, 10 mg/L, plus 50 mg/L humic and fulvic acid, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
UIC-EX3-38D	8/13	4.2	NA	51.6	72.3	NA	-1.0	-1.0	USGS-38 solution in DIW, 10 mg/L, plus 50 mg/L humic and fulvic acid, 2 L solution passed through column, entire procedure including TPA-ClO4 precipitation
				USGS-37	mean	0.2	0.0	0.0	
					stdev	0.1	0.4	0.0	
				USGS-38	mean	0.6	-1.8	-1.7	
					stdev	0.2	0.8	0.6	

D37, D18, and D17 are deviations from reference values.
NA – data not available.
Reference values of δ^{18}O , Δ^{17}O, and δ^{37}Cl for USGS37 are -17.0 ‰, 0.0 ‰, and 0.6‰, respectively.
Reference values of δ^{18}O , Δ^{17}O, and δ^{37}Cl for USGS38 are 52.5 ‰, 73.3 ‰, and -87.2 ‰, respectively.
See Equation 1.4 for definition of Δ^{17}O.

Table A-2. Evaluation of fractionation of Cl and O isotopes during specific steps of perchlorate purification and precipitation.

Test ID	date (mm/yr)	mg ClO_4	δ^{37}Cl	δ^{18}O	Δ^{17}O	D37	D18	D17	description of test
RSIL-4 (125A)	11/11	3.1	0.6	-16.9	0.0	0.0	0.1	0.0	USGS-37 stock solution evaporated into combustion tube
RSIL-4 (125B)	11/11	3.1	0.7	-16.6	-0.1	0.1	0.4	-0.1	USGS-37 stock solution evaporated into combustion tube
RSIL-5 (132A)	11/11	3.1	-86.8	51.9	72.3	0.4	-0.6	-1.0	USGS-38 stock solution evaporated into combustion tube
RSIL-5 (132B)	11/11	3.1	-86.2	51.9	72.4	1.0	-0.6	-0.9	USGS-38 stock solution evaporated into combustion tube
RSIL-4 (81410AA)	11/11	1.7	0.7	-16.5	0.1	0.1	0.5	0.1	USGS-37 stock solution through SPE, precipitation, washing, dissolved in DIW and evaporated into combustion tube
RSIL-4 (81410AB)	11/11	1.5	0.6	-16.0	0.0	0.0	1.0	0.0	USGS-37 stock solution through SPE, precipitation, washing, dissolved in DIW and evaporated into combustion tube
RSIL-5 (92010AA)	11/11	2.1	-87.2	52.1	72.6	0.0	-0.4	-0.7	USGS-38 stock solution through SPE, precipitation, washing, dissolved in DIW and evaporated into combustion tube
RSIL-5 (92010AB)	11/11	2.0	-87.2	51.6	71.8	0.0	-0.9	-1.5	USGS-38 stock solution through SPE, precipitation, washing, dissolved in DIW and evaporated into combustion tube
RSIL-4 (1 mg ppt)	12/12	0.8	0.4	-16.4	-0.2	-0.2	0.6	-0.2	USGS-37 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
RSIL-4 (3 mg ppt)	12/12	2.7	0.6	-16.6	-0.1	0.0	0.4	-0.1	USGS-37 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
RSIL-5 (1 mg ppt)	12/12	0.8	NA	51.2	70.5	NA	-1.3	-2.8	USGS-38 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
RSIL-5 (3 mg ppt)	12/12	2.7	-86.4	51.0	71.8	0.8	-1.5	-1.5	USGS-38 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
UIC RSIL-4	7/13	2.5	1.3	-17.4	0.0	0.7	-0.4	0.0	USGS-37 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
UIC-RSIL-4-Aug-2013	8/13	2.5	0.9	-17.3	-0.1	0.3	-0.3	-0.1	USGS-37 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C
UIC-RSIL-5-Aug-2013	8/13	2.4	-87.0	51.2	72.3	0.2	-1.3	-1.0	USGS-38 stock solution through TPA-ClO4 precipitation, conversion to KClO4, evaporation into combustion tube, bake 10 min @ 400 C

D37, D18, and D17 are deviations from reference values.
NA – data not available.
Reference values of δ^{18}O , Δ^{17}O, and δ^{37}Cl for USGS37 are -17.0 ‰, 0.0 ‰, and 0.6‰, respectively.
Reference values of δ^{18}O , Δ^{17}O, and δ^{37}Cl for USGS38 are 52.5 ‰, 73.3 ‰, and -87.2 ‰, respectively.
See Equation 1.4 for definition of Δ^{17}O.

APPENDIX B

Comparison of Cl and O Stable Isotope Values in ClO_4^- by SIMS and IRMS

A set of sample splits (aliquots of purified $KClO_4$) were sent to Professor John Eiler of Caltech for isotope ratio measurements using the Cameca ims-7f GEO secondary ion mass spectrometer (SIMS), also known as ion microprobe, at the Caltech Microanalysis Center. The primary strength of SIMS stable isotope analysis is that very small sample quantities are required (μg quantitites). However, the method has yet to be fully validated for analysis of Cl and O isotopes in ClO_4^-, so the data and method should be considered experimental for this application. This instrument uses a ~1 nA primary Cs+ ion beam to sputter the sample surface, which generates secondary ions that are accelerated through a magnetic field to a set of detectors for isotope ratio measurement. The $KClO_4$ samples were provided as fine powders and a small amount of each sample was pressed into an indium sample mount for analysis. A thin layer of gold was deposited on the sample surface to prevent sample charging, then the sample mount was placed in the high-vacuum sample chamber of the ion microprobe for isotopic analysis. Analyses were performed by rastering the primary ion beam over a 50 μm x 50 μm area to average out the effects of rough sample surface topography. The measurements of $^{37}Cl/^{35}Cl$ were performed separately from the measurements of $^{18}O/^{17}O/^{16}O$ under slightly different sets of analytical conditions (i.e., beam tuning and counting time) to optimize results. The results of the SIMS analyses are compared with IRMS results in Table B-1. In a memo accompanying the report of these results by Professor Eiler, he concludes that the SIMS method remains experimental and it should be considered less reliable than the IRMS method.

As previously noted, one of the strengths of SIMS is that it can produce isotope ratio measurements from tiny amounts of sample, much smaller than the amounts used for IRMS measurements. However, this can also be a weakness if the sample being measured is not isotopically homogeneous. With respect to measurements of ClO_4^- isotope ratios, the sample is measured in the form of solid $KClO_4$, which is precipitated from an aqueous solution after purification. Because there are small (approximately per mil level) mass-dependent isotopic fractionations of O and Cl between solid $KClO_4$ and aqueous ClO_4^-, isotopic zoning will inevitably occur during precipitation of the solid phase. This can cause the last fraction of $KClO_4$ precipitate to be significantly depleted in the heavier isotopes ^{18}O and ^{37}Cl relative to the cumulative solid $KClO_4$. For example, if the isotopic fractionation factor is such that the solid $KClO_4$ is one per mil enriched in ^{18}O and ^{37}Cl relative to the aqueous ClO_4^-, then when 99% of the aqueous ClO_4^- has been removed from solution, the solid being precipitated at that instant is about 5 ‰ depleted in both ^{18}O and ^{37}Cl relative to the cumulative solid $KClO_4$. Also, at the initial stage of precipitation, the solid phase is one per mil enriched in ^{18}O and ^{37}Cl relative to the aqueous ClO_4^-. In addition, trace contaminants that would have relatively little effect on bulk analysis could be heterogeneously distributed in a sample such that a highly focused ion beam could analyze a highly contaminated small portion of the sample. In contrast, during the IRMS measurements, a sample aliquot is transferred to a glass tube in liquid or bulk powder form and the entire aliquot is converted to O_2 and CH_3Cl for isotopic analysis, thus minimizing effects of trace contaminants or isotopic fractionation during precipitation of the $KClO_4$.

Table B-1. Comparison of IRMS and SIMS results for split samples collected from the Study Area.

Well	Local well name	Analytical method	USGS Sample number[1]	δ^{37}Cl (‰)	δ^{18}O (‰)	δ^{17}O (‰)	Δ^{17}O (‰)
1S/5W-02K1	WVWD 11	IRMS	N17910	-0.4	-15.7	-7.3	1.0
1S/5W-02K1	WVWD 11	SIMS (11/2013)	N17910	-3.4	-20.9	-8.4	2.7
1S/6W-23D2	F-17B	IRMS	N17880	-13.5	-6.6	4.5	8.0
1S/6W-23D2	F-17B	SIMS (7/2013)	N17880	-13.3	-5.3	4.5	7.3
1N/5W-32N1	F-26A	IRMS	N19245	-9.7	-8.3	1.7	6.1
1N/5W-32N1	F-26A	SIMS (7/2013)	NA[2]	-11.9	-9.1	-0.8	4.0
1N/5W-32N1	F-26A	SIMS (11/2013)	N19245	-8.7	-11.3	1.3	7.3
1S/5W-04N1	F4A	IRMS	N17914	-11.6	-8.0	3.4	7.6
1S/5W-04N1	F4A	SIMS (7/2013)	N17914	-13.9	1.6	7.1	6.2
1S/5W-04N1	F-4A (J613; 2007 sample)	IRMS	N19688	-11.9	-8.0	3.3	7.6
1S/5W-04N1	F-4A (J613; 2007 sample)	SIMS (11/2013)	N19688	-10.7/-8.6	-15.1	-1.5	6.5
1N/5W-21N2	PW-2	IRMS	N17906	1.4	-17.2	-9.2	-0.1
1N/5W-21N2	PW-2	SIMS (11/2013)	N17906	-2.2	-15.1	-9.2	-1.2
1S/5W-02G1	Rialto 06	IRMS	N17916	1.3	-16.9	-8.8	0.2
1S/5W-02G1	Rialto 06	SIMS (11/2013)	N17916	-7.6	-12.5	-3.4	3.2
	USGS37	IRMS [3]	standard	0.6	-17.0	-9.0	0.0
	USGS37	SIMS[3]	standard	0.6	-17.0	-9.0	0.0
	USGS38	IRMS [3]	standard	-87.2	52.4	102.4	73.3
	USGS38	SIMS (7/2013)[3]	standard	-91.0	53.3	98.8	69.3
	USGS38	SIMS (11/2013)[3]	standard	-87.9	53.7	102.7	72.8

[1] IRMS data are for specific samples (column + purification aliquot) that were split for SIMS analysis with the exception of F-17B, for which the δ^{37}Cl value is from the same resin column but different purification aliquot (see Table 3.6).

[2] It is unclear from the data report whether the F26A sample analyzed on 7/2013 was N19245.

[3] IRMS measurements were calibrated to both USGS37 and USGS38. Values for the calibration standards are provided.
SIMS measurements were calibrated to USGS37, whereas USGS38 was analyzed as an unknown.
Δ^{17}O values for USGS38 measured by SIMS were recalculated using Equation 1.4 for consistency with other data in this report
(Δ^{17}O values for other samples do not differ significantly with different definitions of Δ^{17}O).