

Date: May 15, 2007
To: Project Team
From: Neil C. Sturchio
Subject: Interpretation of Results of Stable Isotope Analyses of Perchlorate from Groundwater, Jet Propulsion Laboratory and Vicinity, Pasadena, CA

Introduction

This memorandum summarizes and interprets stable isotope ratio measurements of oxygen and chlorine in perchlorate extracted from groundwaters in the vicinity of the Jet Propulsion Laboratory (JPL) in Pasadena, California. Historic waste disposal practices at JPL contributed perchlorate to the groundwater beneath JPL, which is in the Monk Hill Subarea of the Raymond Basin. These measurements were performed as part of the work defined in the *Operable Unit 3 Remedial Investigation Addendum Work Plan* (NASA, 2004). In this memorandum, reference is made freely to information and data reported in the January 31, 2007 Technical Memorandum describing the *Additional Investigation Results* (NASA, 2007). The reader is referred to those two NASA reports for additional background pertaining to the context of this memorandum.

Background on Perchlorate Isotopic Compositions

Recent work has shown that there are significant differences in the stable oxygen (O) and chlorine (Cl) isotope ratios of perchlorate from different sources (Bao and Gu, 2004; Böhlke et al., 2005; Sturchio et al., 2006). The cited studies also demonstrate that trace amounts of perchlorate can be extracted from different matrices, including Chilean nitrate salts and groundwaters, for accurate and precise isotopic analyses. These extractions use a highly perchlorate-selective bifunctional anion exchange resin developed at Oak Ridge National Laboratory (Gu et al., 2001).

Oxygen isotopes. Oxygen has three stable isotopes, ^{16}O , ^{17}O , and ^{18}O , which occur in the ratio ~2000:4:1. These three isotopes are normally fractionated by mass-dependent processes so that the information obtained by measuring $^{17}\text{O}/^{16}\text{O}$ is identical to that obtained by measuring $^{18}\text{O}/^{16}\text{O}$, therefore only the $^{18}\text{O}/^{16}\text{O}$ ratio is normally measured and is expressed in per mil deviation from the $^{18}\text{O}/^{16}\text{O}$ ratio of Vienna Standard Mean Ocean Water ($\delta^{18}\text{O}_{\text{VSMOW}}$) as follows:

$$\delta^{18}\text{O} (\text{‰}) = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}} - 1 \right] \times 1000$$

For synthetic perchlorate, which is produced by electrolysis of NaCl brine, the range of $\delta^{18}\text{O}$ values is -24.7 to -16.1‰ , whereas the range of $\delta^{18}\text{O}$ values for natural perchlorate is -9.3 to -4.2‰ (Bao and Gu, 2004; Böhlke et al., 2005; Sturchio et al., 2006). The $\delta^{18}\text{O}$ values of natural perchlorate are 10 to 15‰ higher than those of synthetic perchlorate. Typical analytical precision of $\delta^{18}\text{O}$ measurements on perchlorate is ± 0.1 to 0.3‰ .

In addition to measuring the $^{18}\text{O}/^{16}\text{O}$ ratio of perchlorate, the $^{17}\text{O}/^{16}\text{O}$ ratio provides a diagnostic indication of natural perchlorate. This is because of the discovery that natural perchlorate has an excess amount of ^{17}O relative to that expected from oxygen having normal terrestrial mass-dependent fractionation in which $\delta^{17}\text{O} \approx 0.52 \times \delta^{18}\text{O}$ (Bao and Gu, 2004). The reason for this ^{17}O -excess is that the natural perchlorate is produced in the atmosphere by reaction of ozone (O_3) with volatile chlorine (e.g., HCl). Natural perchlorate thus inherits its ^{17}O -excess from atmospheric O_3 , which is known to have a large ^{17}O -excess (Thiemens, 1999). The amount of excess ^{17}O is expressed relative to that expected from mass-dependent isotope fractionation, as follows:

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

The $\Delta^{17}\text{O}$ values of all synthetic perchlorate measured to date are $0.0 \pm 0.2\text{‰}$, whereas the reported $\Delta^{17}\text{O}$ values of natural perchlorate are generally in the range from $+8$ to $+10\text{‰}$. Typical analytical precision of $\Delta^{17}\text{O}$ measurements on perchlorate is ± 0.1 to 0.2‰ .

Chlorine isotopes. Chlorine has two stable isotopes, ^{35}Cl and ^{37}Cl , which occur in the ratio of $\sim 3:1$. Chlorine isotope ratios are normally reported in terms of per mil deviation relative to Standard Mean Ocean Chloride (SMOC), as follows:

$$\delta^{37}\text{Cl} (\text{‰}) = \left[\frac{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{sample}}}{(^{37}\text{Cl}/^{35}\text{Cl})_{\text{SMOC}}} - 1 \right] \times 1000$$

The range of reported $\delta^{37}\text{Cl}$ values for synthetic perchlorate compounds (including NH_4ClO_4 , NaClO_4 , $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, KClO_4 , RbClO_4 , and CsClO_4) is -3.1 to $+2.3\text{‰}$ (Ader et al., 2001; Böhlke et al., 2005; Sturchio et al., 2006). The range of reported $\delta^{37}\text{Cl}$ values for natural perchlorate is -14.5 to -11.8‰ (Böhlke et al., 2005; Sturchio et al., 2006), and is based on analyses of Chilean nitrate salts and derived fertilizer products. From these data it appears that $\delta^{37}\text{Cl}$ values of natural perchlorate are 10 to 15‰ lower than those of synthetic perchlorate. Typical analytical precision of $\delta^{37}\text{Cl}$ measurements on perchlorate is ± 0.2 to 0.3‰ .

A comparison of the $\delta^{18}\text{O}$ and $\delta^{37}\text{Cl}$ values for synthetic and natural perchlorates is shown in Figure 1. The restricted isotopic compositions of synthetic and natural perchlorate in this diagram provide a useful tool for identifying the source of perchlorate in the environment. A comparison of the $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values for synthetic and natural perchlorates is shown in Figure 2, which shows that these two types of perchlorate can also be readily distinguished by their $\Delta^{17}\text{O}$ values. Thus, there are effectively three isotopic tracers present in the perchlorate molecule, ^{17}O , ^{18}O and ^{37}Cl , each of which can be used independently to distinguish the source of perchlorate. Perchlorate samples having compositions outside the established ranges for synthetic and natural perchlorate may be mixtures of synthetic and natural perchlorate, or perchlorate that has been affected by biodegradation (Sturchio et al., 2007).

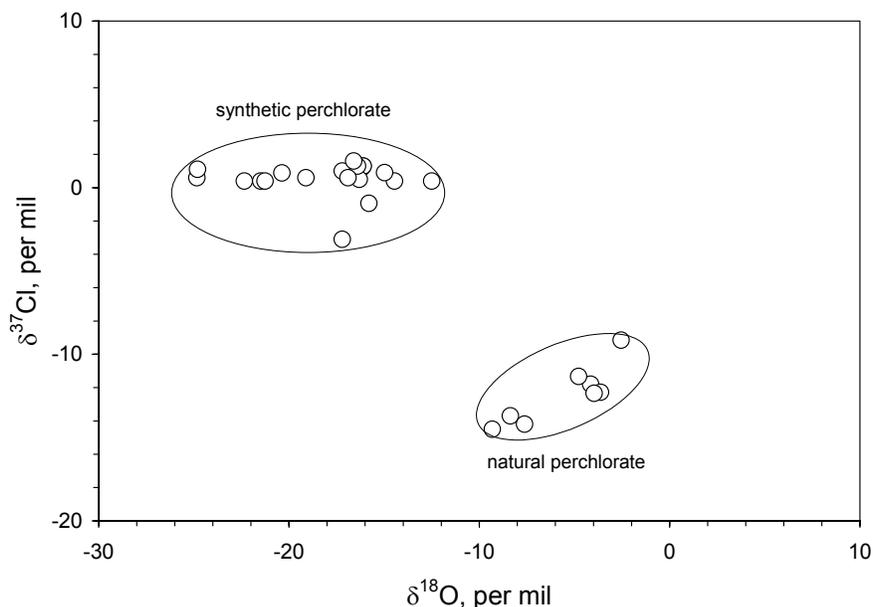


Figure 1. Relationship of representative $\delta^{37}\text{Cl}$ (‰) and $\delta^{18}\text{O}$ (‰) values for synthetic and natural perchlorate samples from known sources analyzed to date, including: synthetic perchlorate used in aerospace and military applications, fireworks, and road flares; natural perchlorate from Chilean nitrate salts and derived fertilizers; and groundwaters known to be contaminated by either synthetic perchlorate or natural perchlorate (data from Böhlke et al., 2005; Sturchio et al., 2006, and some unpublished results of work in progress). Perchlorate samples having compositions outside these ranges may be mixtures of synthetic and natural perchlorate and/or perchlorate that has been affected by biodegradation.

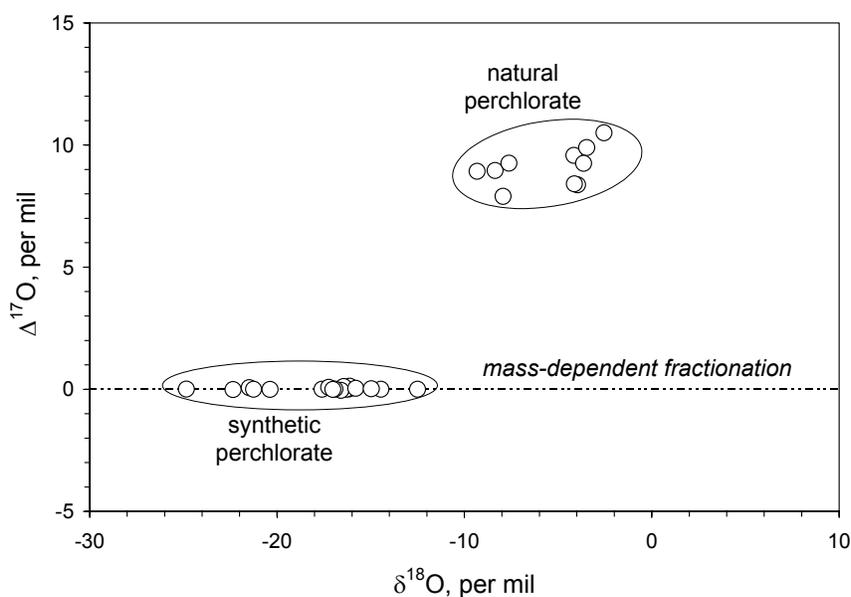


Figure 2. Relationship of $\Delta^{17}\text{O}$ (‰) vs. $\delta^{18}\text{O}$ (‰) values of synthetic and natural perchlorates. These data are for the same samples for which data are shown in Figure 1.

It may be possible to distinguish synthetic perchlorates from different manufacturers by their characteristic $\delta^{18}\text{O}$ values. For example, stable isotope data for synthetic perchlorate manufactured at three separate, known locations (in southern Nevada, southwestern Utah, and northern New Jersey) are shown in Figure 3. This diagram shows that perchlorate from each location has a distinct $\delta^{18}\text{O}$ value, which is roughly correlated with the mean monthly $\delta^{18}\text{O}$ value of tap water in the region (Bowen et al., 2007). However, the $\delta^{18}\text{O}$ value of the perchlorate is not identical to that of the local tap water, but is about 6 to 8‰ lower than the $\delta^{18}\text{O}$ value of the tap water because of oxygen isotopic fractionation that occurs during perchlorate synthesis. The $\delta^{37}\text{Cl}$ values of synthetic perchlorate are only slightly higher than that of seawater chloride, which has $\delta^{37}\text{Cl} = 0.0\text{‰}$ by definition, because Cl is mainly conserved during the synthesis of perchlorate from NaCl brine solutions. With additional data for perchlorate manufactured at other locations, it may eventually be possible to constrain the source of synthetic perchlorate in groundwater at a given location.

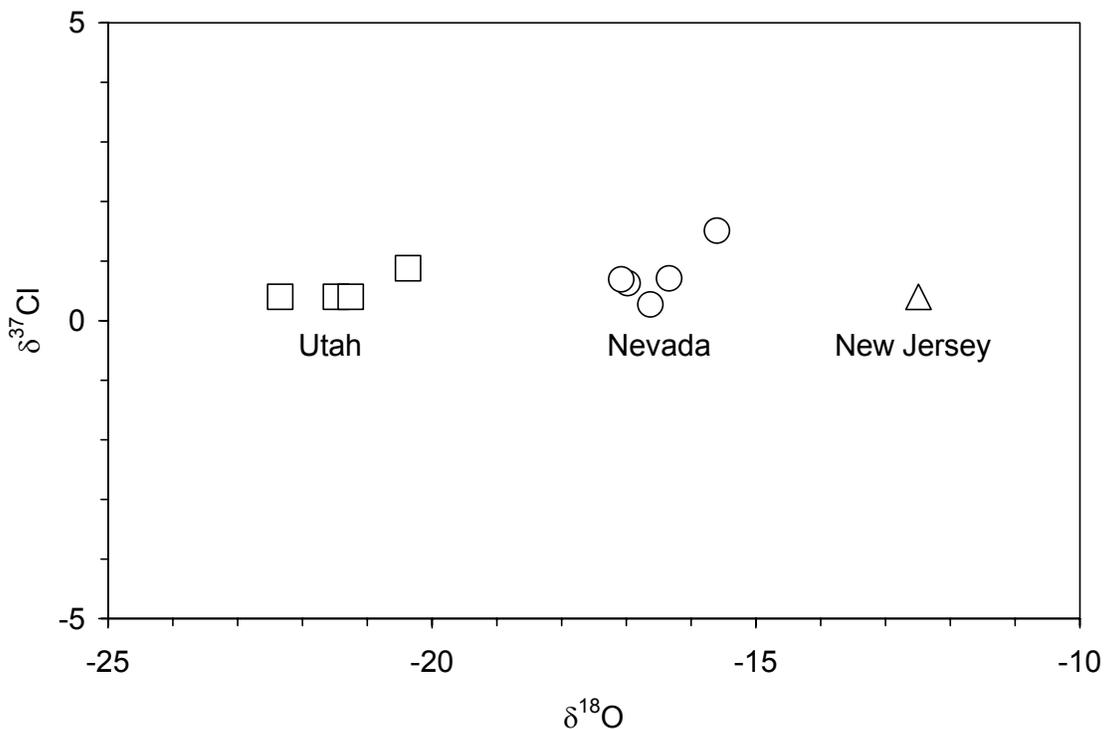


Figure 3. *Isotopic compositions of synthetic perchlorates manufactured at separate, known locations (data from Böhlke et al., 2005; Sturchio et al., 2006; and unpublished data from ongoing ESTCP project). The $\delta^{18}\text{O}$ value of the perchlorate is correlated with that of local tap water used in its synthesis (Bowen et al., 2007).*

Isotopic Composition of Perchlorate in Groundwater from the JPL and Vicinity

There are three important questions that can be addressed directly using stable isotope ratio measurements of perchlorate extracted from groundwaters in the study area: (1) Is there evidence for multiple sources of synthetic perchlorate? (2) Is there evidence for natural perchlorate that may have been derived from past application of Chilean nitrate fertilizer products? (3) Is perchlorate undergoing any change in isotopic composition during transport, either by physical processes or through natural attenuation caused by microbial reduction in the aquifer? Answers to these questions can be obtained by considering perchlorate isotopic data in conjunction with other information, including data on land use, water importation, and aquifer geochemistry in the study area. For reference, sample location maps are shown in the Appendix.

Perchlorate isotopic data ($\delta^{37}\text{Cl}$ vs. $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$) for groundwater samples collected for this study are shown in Figures 4 and 5, respectively. The following salient features of the isotopic data provide answers to the above questions:

- The isotopic composition of perchlorate from the JPL source area (MW-16, MW-16R, and OU-1N) and from a nearby off-facility (less than 1 mile from JPL) production well (LAWC#3) which captures JPL groundwater, and an intervening monitoring well (MW-17), is distinct from that of all other off-facility perchlorate samples. The perchlorate from these wells, which are within the rectangle labeled “JPL Source” in Figures 4 and 5, must be derived at least partly from a source that is less abundant or absent in all other wells measured for this study. This indicates clearly that there must be multiple sources for the perchlorate in the groundwater of the study area.
- The isotopic compositions of samples from Bangham, Garfield, and MW-25 all have positive $\Delta^{17}\text{O}$ values, indicating the presence of some natural perchlorate. This is likely to reflect a contribution from the historic use of Chilean nitrate fertilizer products on orchards in the basin. According to the California Department of Agriculture, more than 477,000 metric tons of Chilean nitrate were used in the State as fertilizer between 1923 and 1998 (California Department of Food and Agriculture, 1999). Although man-made nitrogen sources are now used in most fertilizer applications, more than 55,000 metric tons of the Chilean nitrate material was shipped to California between 1995 and 2000, primarily for fertilizer application. The concentration of perchlorate in processed Chilean nitrate fertilizer was reported to range from approximately 1,750 to 7,700 mg/kg (US EPA, 2001). Thus, one metric ton of this material can contain as much as 7.7 kg of perchlorate; enough to contaminate more than 340 million gallons of groundwater to above the current California Action level of 6 mg/L. However, since 1999 the primary exporter of this material (SQM Corp.) has changed its production process to reduce the perchlorate concentration to below 100 mg/kg. In addition to the perchlorate found in Chilean nitrate and other natural salt deposits, natural background levels of perchlorate up to 2 micrograms/liter have been reported in samples of rain, snow and groundwater (DasGupta et al., 2005;

Plummer et al., 2006). The percentage of natural perchlorate in the samples from Bangham, Garfield, and MW-25 can be estimated at 10 to 20%; the remainder of the perchlorate in these wells is synthetic perchlorate from at least two sources.

- The isotopic composition of JPL perchlorate apparently does not change during transport. This is demonstrated by the fact that perchlorate isotopic compositions of MW-16 (in the JPL source area) and MW-17-3 (approximately 3,000 feet downgradient of MW-16) are indistinguishable. None of the perchlorate isotopic compositions appears to have been strongly affected by biodegradation, because either they are all within the established field of synthetic perchlorate, or they are mixtures of synthetic and natural perchlorate (i.e., Bangham, Garfield, and MW-25). This conclusion is supported by other chemical and genomics data for the groundwater in the study area (NASA, 2007).

Other sources of synthetic perchlorate that may have entered the groundwater in the study area, outside the JPL source area, include:

- (1) Colorado River water imported by the Metropolitan Water District for aquifer recharge in the Raymond Basin. It is well documented that this water has been contaminated for many years with large amounts of synthetic perchlorate from former perchlorate-manufacturing plants at the BMI complex in Henderson, NV, where large-scale perchlorate production began in 1945. Over 30% of the water used in the Raymond Basin between 1952 and 2002 was imported from the Colorado River.
- (2) Fireworks - from dissolution of unexploded fireworks in display areas (e.g., Wilkin et al., 2007).
- (3) Road flares – from dissolution of unburnt portions of road flares left on roadways.
- (4) Bleach used for water disinfection and general cleaning purposes. The main ingredient of bleach is a sodium hypochlorite solution which normally contains trace amounts of perchlorate.
- (5) Chlorate used as a defoliant or herbicide normally contains trace amounts of perchlorate.
- (6) Other undocumented industrial usage/disposal of perchlorate (e.g., explosives, electroplating solutions, etc.).

It is difficult to quantify the proportions of these other sources of synthetic perchlorate in the groundwater because of overlap in their isotopic compositions and because there is not yet an exhaustive database for the isotopic compositions of all commercially available synthetic perchlorates. There are no archived data for the concentration and isotopic composition of perchlorate in the Colorado River (except for the analysis of one

sample taken at Las Vegas Wash), though it is presumably derived mainly from the BMI Complex in Henderson, NV. Archived samples of perchlorate manufactured at the BMI Complex in the late 1980's, as well as contaminated groundwater and surface water samples from that site, have $\delta^{18}\text{O}$ values ranging from -14.5 to -17.1‰ , which are significantly higher than those of the JPL Source samples (-21.8 to -19.3‰) (Figures 4 and 5). These values for perchlorate derived from the BMI Complex are consistent with such perchlorate being a major source of the off-facility perchlorate in the Raymond Basin groundwater. Other sources of synthetic perchlorate, such as fireworks and road flares, also have isotopic compositions consistent with those measured in off-facility groundwater (Figures 4 and 5), but complete documentation of all such historic uses of perchlorate in the Raymond Basin is not available.

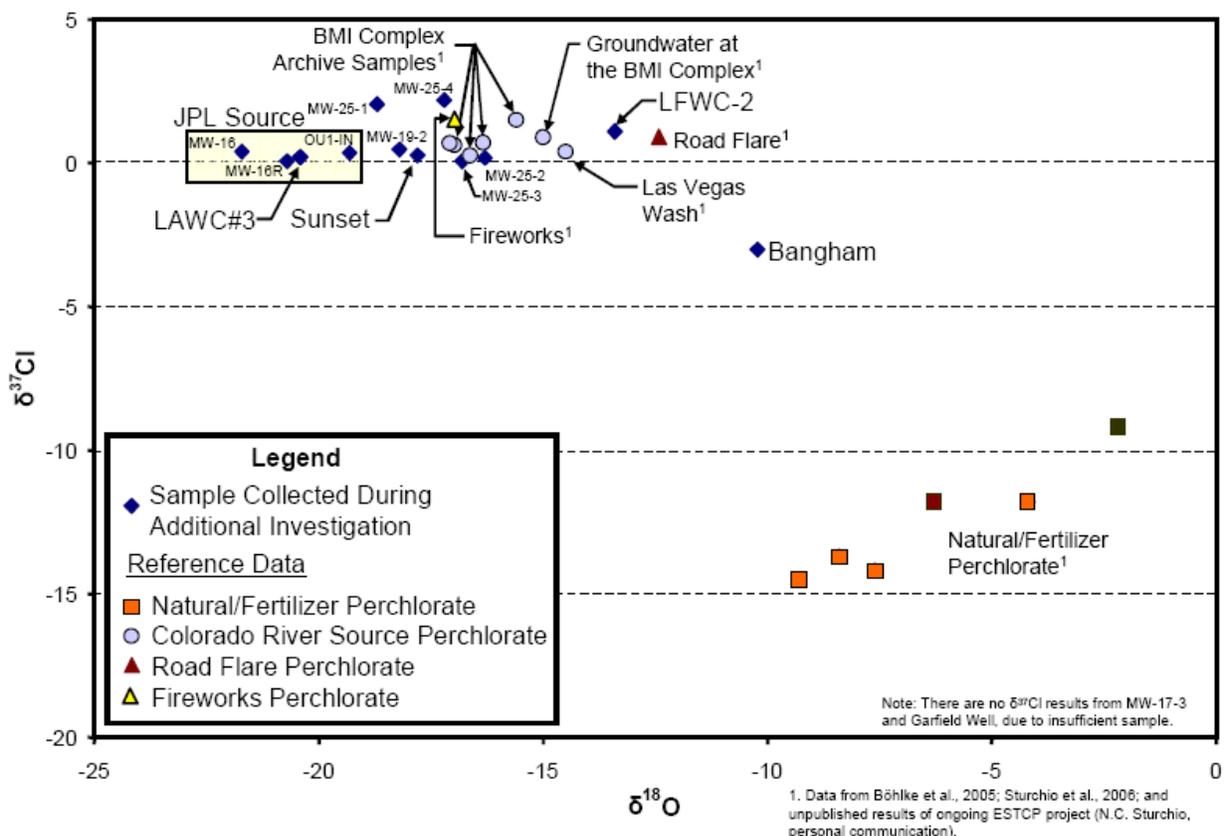


Figure 4. Diagram showing $\delta^{37}\text{Cl}$ (‰) vs. $\delta^{18}\text{O}$ (‰) values for perchlorate in groundwater collected from the JPL study area, in relation to representative data for other potential perchlorate source materials (i.e., fireworks, road flares, Chilean nitrate fertilizer products, and archived synthetic perchlorate produced at the BMI complex in Henderson, NV which is known to have contaminated Lake Mead and the lower Colorado River. (This is identical to Figure 16 in the January 31, 2007 NASA Technical Memorandum.)

Despite the difficulty in identifying all sources of synthetic perchlorate in the study area, it is possible to combine different lines of evidence to reach conclusions about relationships between the sources of perchlorate in different parts of the study area. For example, the perchlorate in Sunset well is isotopically indistinguishable from that of

MW-19 but isotopically distinct from that at the JPL source area. MW-19 is cross-gradient from JPL (i.e., not within the flow path of a particle originating from JPL), and groundwater flows downgradient from MW-19 toward Sunset, therefore these two wells may contain synthetic perchlorate from a single source (other than JPL). In contrast, the local heterogeneity of the perchlorate sources in the Sunset Reservoir well-field is remarkable when comparing MW-25, Sunset, Bangham, and Garfield, which are within about a mile of each other yet have a wide range in both $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ values. Almost as wide a range in isotopic composition is found between MW-19 and LFWC-2, also within about a mile of each other. Such isotopic variability emphasizes the diversity of perchlorate sources in the Raymond Basin. In this context, JPL is apparently but one local source of perchlorate in this basin. JPL's influence, as evidenced by the isotopic compositions of perchlorate measured in groundwaters of the study area, is apparently constrained to a relatively small area that is defined by the JPL site on the upgradient end and by the capture zone to the nearby Monk Hill Subarea production wells such as LAWC#3 on the downgradient end. There is no compelling evidence for the presence of JPL-derived perchlorate in groundwater outside this area.

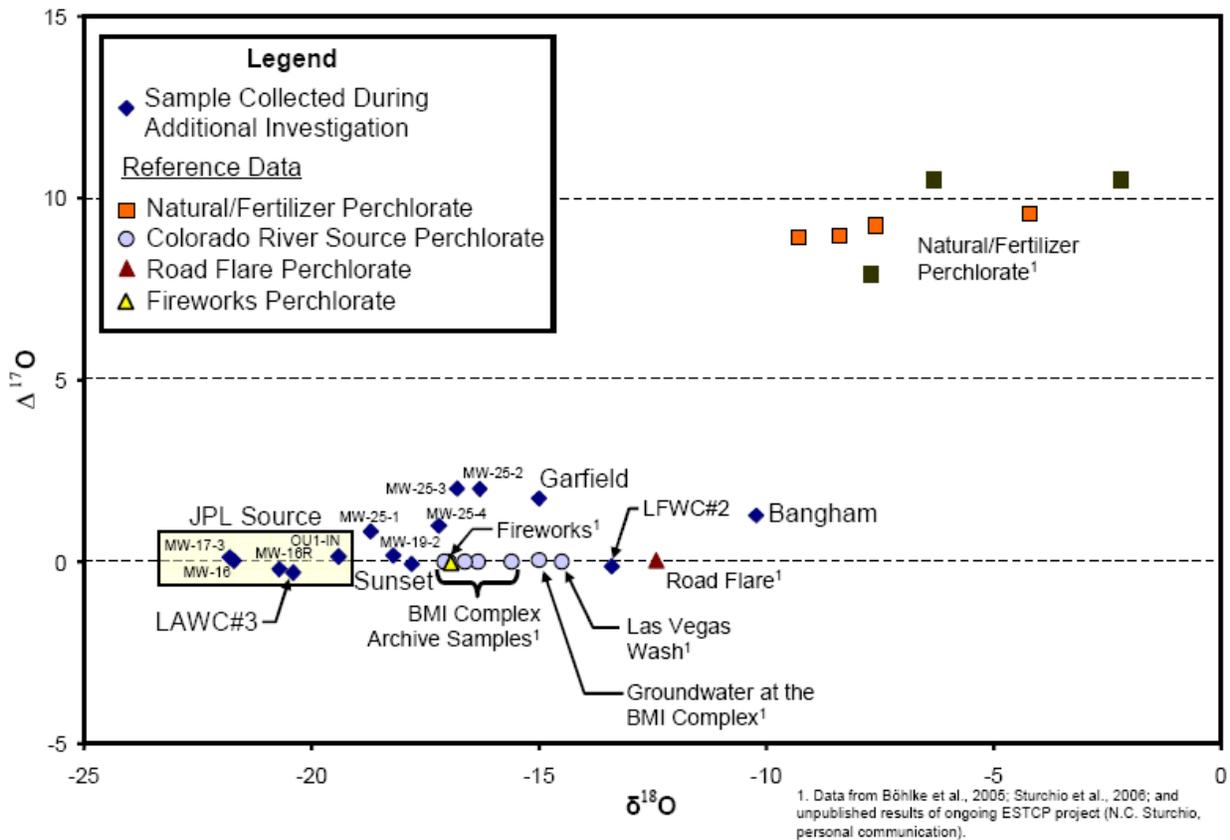


Figure 5. Diagram showing $\Delta^{17}\text{O}$ (‰) vs. $\delta^{18}\text{O}$ (‰) values for perchlorate in groundwater collected from the JPL study area, in relation to representative data for other potential perchlorate source materials (i.e., fireworks, road flares, Chilean nitrate fertilizer products, and synthetic perchlorate produced at the BMI complex in Henderson, NV which is known to have contaminated Lake Mead and the lower Colorado River). (This is identical to Figure 17 in the January 31, 2007 NASA Technical Memorandum.)

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APPENDIX – Location Map

