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The geochemical associations of nitrate and naturally formed perchlorate in the Mojave Desert, California, USA

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Abstract

Perchlorate is a widely studied environmental contaminant that may adversely affect human health, and whose natural occurrence has emerged as a subject of great interest. Naturally formed perchlorate has been found to co-occur with nitrate in arid environments worldwide, but the relationship is not fully understood in the desert soils of the southwestern United States. The main objective of this research was to explore the origin, pedogenic distribution, and possible preservation of perchlorate and nitrate in the Mojave Desert mud hill deposits of California and to determine if the co-occurrence of putatively natural perchlorate was significantly correlated with nitrate in these soils. We identified 39 soil horizons in the Mojave Desert, California that contained reportable levels of perchlorate (MRL >165 $\mu g \, kg^{-1}$) with a maximum concentration of 23 mg kg^{-1}. A weak yet significant correlation was observed between perchlorate and nitrate ($r^2 = 0.321^{***}$), which could be indicative of similar mechanisms of accumulation. When compared to published data for the Atacama Desert, the Mojave Desert perchlorate concentrations were remarkably lower for a given nitrate concentration. Oxygen isotopes in the nitrate were examined to identify variation within the Mojave Desert field sites, and to compare with the available literature for the Atacama Desert. The Mojave Desert $\Delta^{17}O$ values ranged from 7‰ to 13‰, indicating a mixture of biologically and atmospherically-derived nitrate. An investigation of the distribution of perchlorate among soil horizons revealed that over sixty percent of the samples containing perchlorate were from C horizons while only twenty percent of the samples were from B horizons and even fewer in the overlying A horizons. Soil chemical, morphologic, and geologic characteristics of the soils suggest that the perchlorate, nitrate and/or other soluble salts have moved in a "bottom–up" manner wherein the salts were deposited in strata through geological time and have since been redistributed and evapo-concentrated into the upper soil horizons by capillary rise.
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1. INTRODUCTION

Perchlorate (ClO_4^-) is a contaminant that has both natural and anthropogenic sources, is mobile, abiotically stable, and has permeated the environment (Parker, 2009).

Perchlorate is a strong oxidant that has been widely produced for use in rocket propellants, pyrotechnics, and munitions (Gullick et al., 2001; Trumpolt et al., 2005). Improvements in analytical technology have allowed for the detection of perchlorate at much lower concentrations, thereby stimulating research focused on its widespread distribution in soils, plants, and water sources (Koester et al., 2000; Gullick et al., 2001; Rajagopalan et al., 2006; Rao et al., 2007; Parker et al., 2008; Parker, 2009). Recent studies have suggested several atmospheric production pathways of perchlorate (Dasgupta et al., 2005; Roberts, 2009; Furdui and Tomassini, 2010) with the most comprehensive ozone-based generation mechanism described by Rao et al. (2010). Atmospherically generated perchlorate is subse-

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quently deposited onto the landscape surface (soil, water bodies) through wet (Parker et al., 2008; Rajagopalan et al., 2009) and dry deposition (Rao et al., 2007). The environmental importance of natural perchlorate once it reaches the landscape surface is poorly constrained, but perchlorate appears to be transported under typical arid, oxic conditions where leaching to groundwater is minimal.

Until recently, the hyper arid environment of the Atacama Desert, Chile (precipitation <5 mm yr^{-1}) was the only known source of natural perchlorate salts (Ericksen, 1981, 1983). The Atacama's hyper-aridity has led to landscape stability and the accumulation of soluble salts, such as nitrate and perchlorate, near the ground surface (Ericksen, 1981, 1983; Prellwitz, 2007; Jackson et al., 2010). Perchlorate and nitrate accumulation have also been found in two dry, ultraxerous valleys of Antarctica (Kounaves et al., 2010). The occurrence of naturally formed perchlorate has now been quantified in several semi-arid and arid regions of the United States including Texas, New Mexico, Nevada, Utah, and California (Jackson et al., 2004, 2010; Rajagopalan et al., 2006; Rao et al., 2007). Significant correlations exist between natural perchlorate and nitrate in the Atacama Desert caliche deposits (Grossling and Ericksen, 1971; Ericksen, 1981, 1983; Prellwitz, 2007; Jackson et al., 2010) and in the dry desert soils of Antarctica (Kounaves et al., 2010), but explanations for the co-occurrence and whether this phenomenon is common to all desert soils are still ambiguous. In dry region sites of the southwest United States, Rao et al. (2007) noted perchlorate bulges (1.6–13 μg kg^{-1} dry solid) that corresponded to peaks in chloride (84–630 mg kg^{-1}) and, when present, nitrate (2–1000 mg kg^{-1}). Other groundwater-based studies in the southwestern United States revealed no significant correlation between perchlorate and nitrate (Jackson et al., 2004; Rajagopalan et al., 2006). In a stable isotopic investigation of perchlorate and nitrate, Jackson et al. (2010) provides the only modern perchlorate analyses for the near ore-grade Mojave Desert nitrate deposits, but the correlation between perchlorate and nitrate is not significant ($r^2 = 0.0005$, $n = 5$). The soil perchlorate-nitrate relationship in the Mojave Desert is not well established and has not been assessed by soil morphologic characterizations or via large sample sets to explore the heterogeneity of the deposits.

The origin of natural nitrate deposits in the United States was first investigated in the early 1900s, through extensive USGS-funded reconnaissance work. In the Amargosa River valley, California, clay-hill nitrate deposits originate from ancient saline lake bed sediments (Miocene–Pleistocene age), but may also contain remnants of wind-transported sediments from ancient salt marshes, nearby playas and other clay-hill deposits (Ericksen et al., 1988). The largest nitrate concentrations were found in the clay-hill deposits of Death Valley, California. Noble and Mansfield (1922) surveyed several field areas in the Mojave varying in geologic origin and they concluded that the arrangement of soils in these hills followed a general pattern: a "blistered" surface crust, a relatively shallow zone of clayey, efflorescent soil material, and upturned beds of clay shale and sandstone bedrock covered by a nitrate-rich "caliche" layer. Ericksen et al. (1988) followed up this work

with mineralogical and chemical analyses on the nitrate-rich caliches, and made additional observations on the distribution of the nitrate and other soluble salts present at the Mojave sites. The analytical techniques of the time could not detect quantifiable concentrations of perchlorate in these deposits or determine the source(s) of the natural nitrate (Ericksen et al., 1988). Subsequent research has explored the isotopic compositions and origins of perchlorate and nitrate on select Mojave Desert samples (Böhlke et al., 1997; Michalski et al., 2004; Jackson et al., 2010).

Oxygen isotopes have been used to determine the source(s) of natural nitrate found in soils, an important consideration for better understanding the perchlorate–nitrate relationship. Nitrate is formed naturally by biological oxidation of ammonia (nitrification), or by photochemical N fixation and oxidation in the atmosphere (atmospheric nitrate). Atmospheric nitrate forms when lightning-generated NO and ozone (O_3) react to form NO_2 which is then converted to NO_3^- (Galloway et al., 2004; Schumann and Huntrieser, 2007). Ozone has a distinct, photochemically induced $\Delta^{17}O$ isotopic signature (Thiemens and Heidenreich, 1983; Thiemens, 1999; Thiemens et al., 2001), which can be used to distinguish between atmospherically derived and biologically fixed nitrate (Michalski et al., 2002, 2003). The $\Delta^{17}O$ method has been used to conclude that long-term deposition of atmospheric nitrate is the predominate source of nitrate in the Atacama (Böhlke et al., 1997; Michalski et al., 2004) and very little is derived from nitrification. In contrast, investigations of several soils from the Mojave Desert suggested near equal mixtures of biologically fixed and atmospherically derived nitrate (Böhlke et al., 1997; Michalski et al., 2004; Jackson et al., 2010). Böhlke et al. (1997) used $\delta^{15}N$ and $\delta^{18}O$ measurements on ~15 bulk soil and salt samples to estimate that 20–100% of the nitrate in the clay-hill deposits resulted from atmospheric deposition. Michalski et al. (2004) re-analyzed 4 of these samples and found $\Delta^{17}O$ values spanning +7‰ to +13‰, suggesting a mixture of biologic and atmospheric nitrate. On a set of 5 samples encompassing 4 of the major Mojave Desert clay-hill provenances, Jackson et al. (2010) identified a similar range for nitrate ($\Delta^{17}O = +8‰$ to +15.5‰) and high perchlorate $\Delta^{17}O$ values (+8.6‰ to 18.4‰), suggestive of a distinct, and at least partial, atmospheric ozone-derived perchlorate formation mechanism. A more extensive investigation of nitrate sources in the Mojave using geochemical and stable oxygen isotopes is required to better constrain the site specific source variation and how it may relate to the co-occurrence of perchlorate.

The main objective of this research was to explain the sources, pedogenic distribution, and preservation of perchlorate and nitrate in the Mojave Desert deposits of California using geochemical, isotopic, soil morphologic geologic properties. In addition, we sought to determine if the co-occurrence of putatively natural perchlorate was significantly correlated to the nitrate contained in the Mojave Desert clay-hill deposits (Noble and Mansfield, 1922; Ericksen et al., 1988) and whether these deposits were analogous to the perchlorate-containing nitrate deposits in the Atacama. Lastly, the number of soils analyzed for geochemical and nitrate oxygen isotope analysis was greatly expanded to

evaluate nitrate and perchlorate co-accumulation across the clay hill provenances described in the literature (Noble and Mansfield, 1922; Ericksen et al., 1988) and to assess whether these nitrate salts are of biologic or atmospheric origin.

2. MATERIALS AND METHODS

2.1. Study area and site descriptions

The study was conducted at six distinct field areas in the Amargosa River valley, located in the southernmost region of Death Valley, Mojave Desert, California (Fig. 1, Table A.1). This region has an aridic soil moisture regime with a mean annual rainfall of approximately 40 mm/year, falling mostly during the winter months. The arid conditions made Death Valley an ideal location for analyzing the natural abundance of water-soluble salts in soils.

This project was composed of three parts: an initial reconnaissance field survey to locate samples containing nitrate and/or perchlorate, an in-depth analysis of the physical soil and site properties related to a subset of the initially sampled soil pits, and an isotopic investigation of 17 ni-

trate-rich samples to determine the origin of the nitrate salts in the sediments. Field sites for the reconnaissance work were chosen based on site accessibility and chemical data published from earlier geologic explorations of the region for nitrates and other water soluble salts.

2.2. Site characterization

Specific site, caliche, geologic characteristics and accompanying photographs related to the six field areas investigated in this study have been summarized in B.2. A brief overview of the common properties associated with all field sites is given here. Estimated age ranges and geologic formations of each field area were determined from geologic maps and the available literature and are summarized in Table 1.

The clay hills sampled in this study are lightly-colored and support little to no vegetation presumably because of the high salt content of the sediments. Soluble salts have accumulated in "caliche" layers overlying clay beds that range in age from Miocene to Pleistocene. Noble and Mansfield (1922) hypothesized that the saline and gypsiferous clays and sands composing these formations were once
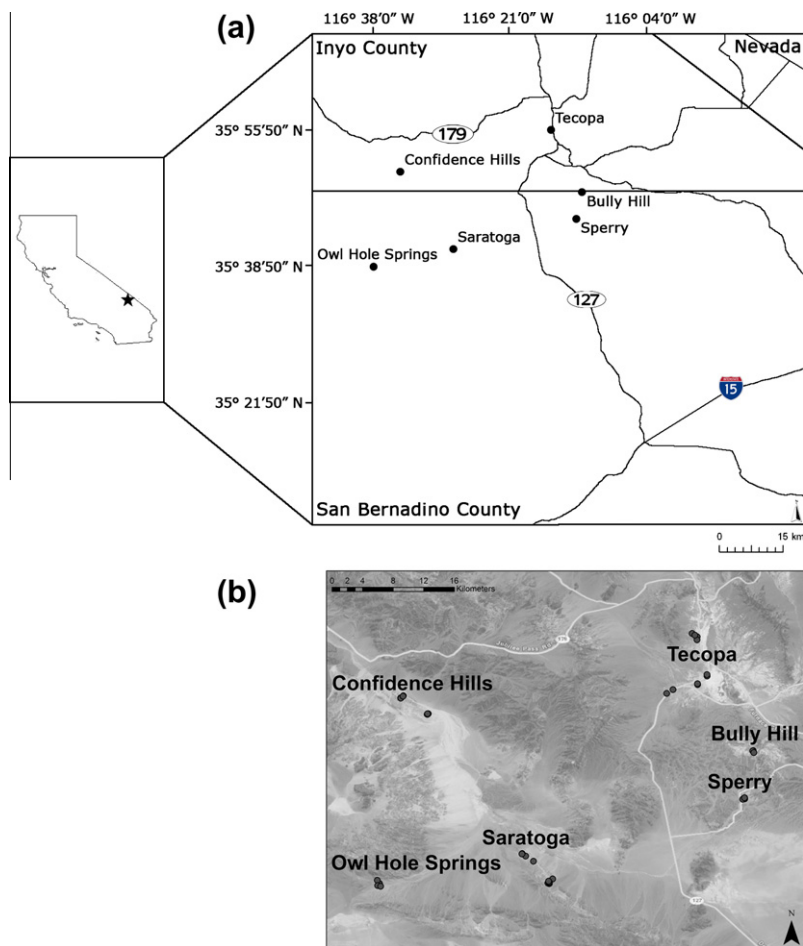

Fig. 1. (a) A general map of the field area located in southeastern California and (b) a more detailed site map depicting individual soil pedons sampled in the Amargosa River valley of the Mojave Desert, CA.

Table 1
Summary of sites investigated, number of samples collected, estimated age ranges and geologic formations described in the literature for the six field areas investigated in this project.

Field area	Sites	Samples	Estimated age range (Ma)[a]	Geologic formation[a]
Bully Hill	6	24	1.8–0.01	China Ranch Formation
Confidence Hills	10	35	>2.15–<1.79	Upper member of Confidence Hills Formation
Owl Hole Springs	14	39	11.3–2.6	Owl Hole Springs Formation
Saratoga	10	33	11.3–1.8	Central redbeds of eastern assemblage (also known as the Noble Hills assemblage)
Sperry	10	40	1.8–0.01	China Ranch Formation
Tecopa	10	36	2.02–0.60	NA[b]
Total	60	207		

[a] Age ranges and available geologic formations were determined from literature and were detailed in B.2.
[b] No geologic formation information found for site.

deposited as nearly flat beds in playas, or evaporating lakes. Over time, coarser sands and gravel materials from nearby alluvial slopes buried the playas. Since the time of deposition, these beds have been deformed by faulting and folding and have become exposed in some areas by washes, streams, and other drainages (Noble and Mansfield, 1922).

The caliches varied in chemical composition, occurrence, depth from surface, and mechanical strength across the six field areas. Each site also contained thin, blistered surface crusts that blanketed the soil and bedrock deposits (Fig. 2a). The color, composition, and structural features of the surface crusts varied slightly among locations, but all exhibited the general appearance shown in Fig. 2a. There was widespread evidence of gully and rill erosion as well as intricate drainage networks that were created during the intense, infrequent rain events that occur in Death Valley (Fig. 2b, Fig. B.2.1c).

2.3. Soil sampling techniques and chemical analyses

Soils were excavated and collected from each site by morphologic and geologic horizons. The samples were prepared for chemical analysis using a dilute extraction method (1000:1) to ensure that all soluble salts in the sample were solubilized. All extracts were prepared using Type I deionized water (18 MΩ cm or better). The fine-earth soil fractions (<2 mm) were crushed and homogenized. One hundred milligrams of each soil sample was placed in a 50 mL centrifuge tube along with deionized water (30 mL for the first extraction, 15 mL for subsequent extractions), shaken for 15 min using an automated shaker (Burnell, Pittsburgh, PA), centrifuged for 20 min, and decanted into a 100 mL volumetric flask. This process was repeated three times or until the electrical conductivity of the supernatant was less than 100 μS cm^{-1}.

The decanted solution was brought to 100 mL and analyzed for perchlorate on a Dionex ion chromatograph using electrospray-ionization-mass-spectrometry (IC–ESI-MS) and a $Cl^{18}O_4^-$ internal standard (Dionex Corp, 2003a; Environmental Protection Agency, 2005). Perchlorate was separated using an IonPac AS16 analytical column with an IonPac AG16 guard column (Dionex, Sunnyvale, CA). Ion chromatography was used with a Dionex IonPac
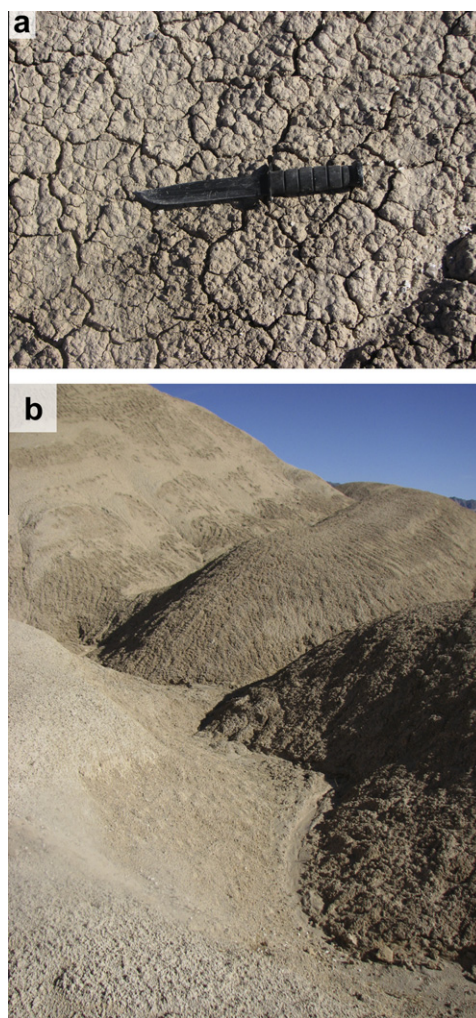
Fig. 2. Characteristics common to Mojave Desert field areas include (a) blistered, lightly colored surface crusts and (b) evidence of surface erosion.

AS18 analytical column (2 × 250 mm) and IonPac AG18 guard column (2 × 50 mm) to determine major anion concentrations (sulfate, nitrate, and chloride) in each sample

(Dionex Corp, 2003b). Both columns are hydroxide-selective anion columns that use KOH as an eluent. Base cations were determined by ICP-OES (PerkinElmer, Waltham, MA). Total dissolved solids (TDS) was measured on approximately 40 mL of each sample extract using an established method of gravimetric analysis (Rhoades, 1996).

2.4. Method detection limit (MDL)

The method detection limit for perchlorate was determined by analyzing ten replicate samples containing 250 ng L^{-1} perchlorate in a 1 g L^{-1} sodium nitrate matrix using IC–ESI-MS. These replicate samples were bracketed by blank samples of the same matrix. The MDL was calculated using the method described in the EPA Method 314.0 (Environmental Protection Agency, 1999):

$$MDL = ts \qquad (1)$$

where $t = 2.82$ for nine degrees of freedom and s is the standard deviation of the perchlorate concentrations measured in the ten replicate samples. The minimum reporting limit (MRL) is defined as being three times greater than the MDL. The calculated minimum reportable and method detection limits for this study were 165 µg/kg^{-1} and 55 µg kg^{-1}, respectively.

2.5. Soil morphological analyses

Of the 60 soil pits sampled, 10 were selected for soil morphological analyses. These selections were made based on important chemical correlations observed between nitrate and perchlorate, and to make pertinent comparisons between soils sampled in the same field area. Dry and wet soil colors were determined using the Munsell Color Chart. All of the soil descriptions were made using established guidelines (Thien, 1979; Schoeneberger et al., 2002). The conventional saturated paste method was used to determine electrical conductivity and pH. The saturated paste extracts were prepared by first adding deionized water to soil samples until complete saturation was reached. The samples were then equilibrated for 18 h before measurements were made (US Salinity Laboratory, 1953). Electrical conductivity was measured using a CDM 83 Conductivity Meter (Radiometer, Copenhagen, Denmark) and pH with an AR25 Dual Channel pH/Ion Meter (Fisher Scientific, Pittsburgh, PA).

2.6. Nitrate stable isotope analysis

Samples were purified for oxygen isotope analysis using established methods (Silva et al., 2000; Michalski, 2010). The chemical constituents of the soil were extracted with a 1:1 soil and deionized water extract. Excess BaCl$_2$ was used to precipitate the SO$_4^{2-}$ and PO$_4^{3-}$ from solution. The cations were removed by passing the extract through 4 mL of Bio-Rad 100–200 mesh AG 50 W X8 cation exchange resin in the H+ form (Silva et al., 2000). Extensively washed Ag$_2$O was added to precipitate AgCl and to neutralize the solution. The remaining AgNO$_3$ solution was freeze–dried, rehydrated, filtered with a 0.2 µm syringe filter, and freeze–dried again (Michalski, 2010). The purified AgNO$_3$ was then used for isotopic analysis using the thermal decomposition method (Michalski et al., 2002) at the Purdue Stable Isotope Facility. All samples analyzed were calibrated to measurements of USGS reference materials.

3. RESULTS

3.1. Perchlorate and nitrate content of the clay hill deposits

Table 1 summarizes sites visited and samples analyzed for all field areas studied in the project. The perchlorate and nitrate deposits are summarized in Fig. 3 and detailed in Table C.3. Perchlorate concentrations greater than the MRL (165 µg kg^{-1}) were found in 39 out of the 207 soil samples (19%). There were 31 samples with perchlorate concentrations less than the MRL and greater than the MDL (55 µg kg^{-1}) and 137 samples (66%) were <MDL. Samples with perchlorate concentrations between the MDL and MRL and the samples containing perchlorate < MDL were all classified as non-detectable and set to half of the MDL, which was 24.7 µg kg^{-1} (Environmental Protection Agency, 1999).

All six general field areas contained at least one sample with reportable levels of perchlorate and/or nitrate (Table C.3). The nitrate in the Mojave samples ranged from non-detectable (0.015 mg g^{-1}) to an ore-grade (61.5 mg g^{-1}) concentration at Bully Hill (BH1), compared to a range of 1.8–28 mg g^{-1} in Jackson et al. (2010). Sperry (SP 8) contained the horizon with the highest perchlorate value of 23 mg kg^{-1}, substantially greater than the previously reported maximum of 1.7 mg kg^{-1} (Jackson et al., 2010). More specifically, reportable perchlorate concentrations ranged from 0.21 mg kg^{-1} to 3.42 mg kg^{-1} ($n = 9$) at Bully Hill, 0.28–0.42 mg kg^{-1} ($n = 2$) at Confidence Hills, 0.19–3.15 mg kg^{-1} ($n = 9$) at Owl Hole Springs, 0.20–23.40 mg kg^{-1} ($n = 14$) at Sperry, and 0.17–2.24 mg kg^{-1} ($n = 4$) at Tecopa (Fig. 3; Table C.3). There was only one Saratoga sample with a reportable perchlorate concentration (3.03 mg kg^{-1}). This is also the only site where perchlorate did not correspond to a high nitrate concentration (0.10 mg g^{-1}). There were no significant correlations observed between perchlorate and the other ions, including chloride, investigated in the project (Table C.3). The Mojave Desert perchlorate values reported in Jackson et al. (2010) spanned 0.25–1.7 mg kg^{-1}, which were similar in magnitude to Confidence Hills and lower than the maximum concentrations found at Bully Hill, Owl Hole Springs, Saratoga, Sperry and Tecopa.

Perchlorate was found in fewer of the Mojave Desert lake deposits, had lower concentrations, and a weaker correlation with nitrate content compared to soils in the Atacama Desert (Prellwitz, 2007; Jackson et al., 2010). Significant correlations exist between perchlorate and nitrate at both locations. The weak but significant correlations between these anions in the Mojave Desert suggest that their accumulation is not controlled by exactly the same factors.
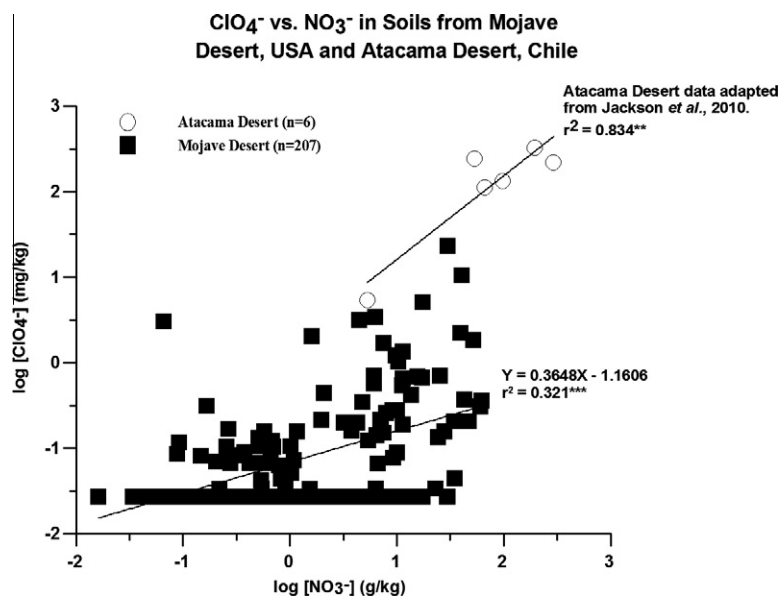
Fig. 3. Correlations between perchlorate and nitrate in soils collected in the Mojave Desert, California and Atacama Desert, Chile. The Atacama Desert data was adapted from Jackson et al. (2010). Separate linear regressions were performed on the perchlorate and nitrate data collected from the two locations. The linear regression equations and r^2 values are given for each location. The superscripts associated with the r^2 values denote the significance where $^{***}P < 0.001$, $^{**}P < 0.01$ and $^*P < 0.05$.

3.2. Soil nitrate $\Delta^{17}O$ isotopic measurements

The $\Delta^{17}O$ method was used to determine the contributions of atmospheric and biologic nitrate in the Mojave Desert. The $\Delta^{17}O$ measurements for the Mojave Desert field areas ranged from 7.0‰ to 13.2‰, showing that these samples contained a mixture of atmospherically derived and biologically fixed nitrate (Table 2, Fig. 4). $\Delta^{17}O$ values for Bully Hill were 7–7.7‰, similar to the 7.2‰ measurements noted in the literature (Michalski et al., 2004; Jackson et al., 2010). The $\Delta^{17}O$ measurements for the Confidence Hills (10.4–13.2‰) extended the lower boundary of the isotopic ranges reported previously for this area, which were 12.4–13.1‰ (Michalski et al., 2004) and 12.7–15.5‰ (Jackson et al., 2010). The single Saratoga $\Delta^{17}O$ value of 12.0‰ was analogous to Michalski et al., 2004 reporting of 12.4‰. The $\Delta^{17}O$ values measured for Sperry ($\Delta^{17}O =$ 8.2–8.8‰) and Owl Hole Springs ($\Delta^{17}O = 10.3‰$) are the first to be reported for these field areas and fall within the isotopic compositions expected for soils composed of biologic and atmospheric nitrate mixtures. Little variation was seen in the sites sampled with depth (e.g. BH1 to BH1-4 and SP8-2 to SP8-6). Standard deviations were lowest for the Bully Hill and Sperry field areas (<0.30‰) where

samples were collected from soil pedons similar to one another in geologic origin and soil morphology. The two samples analyzed from the Confidence Hills field areas differ in soil chemical, geomorphological, and soil morphological properties.

The $\Delta^{17}O$ and $\delta^{18}O$ values of the Mojave and Atacama Deserts are plotted in Fig. 4. Michalski et al., 2004 showed that Atacama Desert nitrate samples cluster together in a relatively small group of $\Delta^{17}O$ and $\delta^{18}O$ values, suggesting a similar origin related to atmospheric deposition (Fig. 4). Nitrate from the Mojave Desert has a broader range of $\Delta^{17}O$ and $\delta^{18}O$ values that represent a mixture of atmospheric and biologically fixed nitrate specific to each field area analyzed (Table 2, Fig. 4). These findings suggest that there are other geologic differences in landform age and stability that are crucial to understanding the co-occurrence of nitrate and perchlorate between the two locations, as well as the differences observed between field areas in the Mojave Desert.

3.3. Soil profile and site characteristics

Detailed soil and site descriptions for ten of the sites sampled in the Mojave Desert have been summarized in Table D.4. Electrical conductivity values of the soils ranged

Table 2
Mean, range and standard deviation values of $\Delta^{17}O$ measurements for samples collected from five field areas in the Mojave Desert, California.

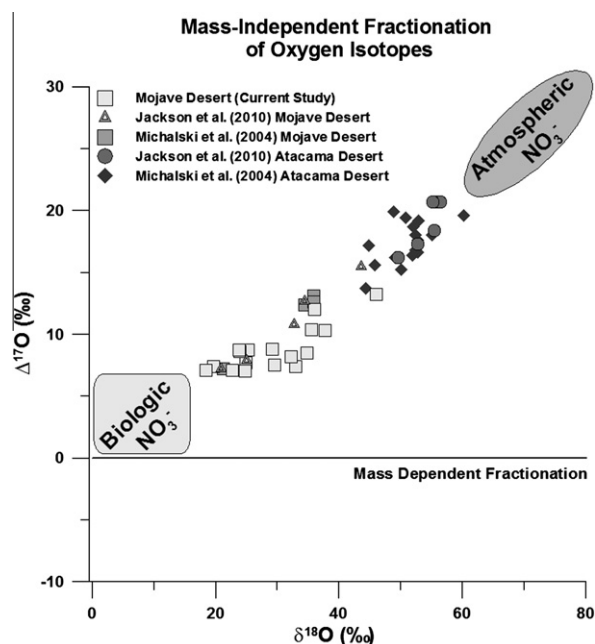| Field area	Mean (‰)	n	Range (‰)	Standard deviation (‰)
Bully Hill	7.31	7	7.0–7.7	0.25
Confidence Hills	11.8	2	10.4–13.2	1.98
Owl Hole Springs	10.3	1	NA[a]	NA[a]
Saratoga	12	1	NA[a]	NA[a]
Sperry	8.6	6	8.2–8.8	0.21

[a] NA = Not applicable.

Fig. 4. Mass-independent fractionation of oxygen isotopes in nitrate salts of samples collected in the Mojave Desert, California. Additional nitrate oxygen isotope data from the Mojave Desert and the Atacama Desert are referenced from Michalski et al. (2004) and Jackson et al. (2010).
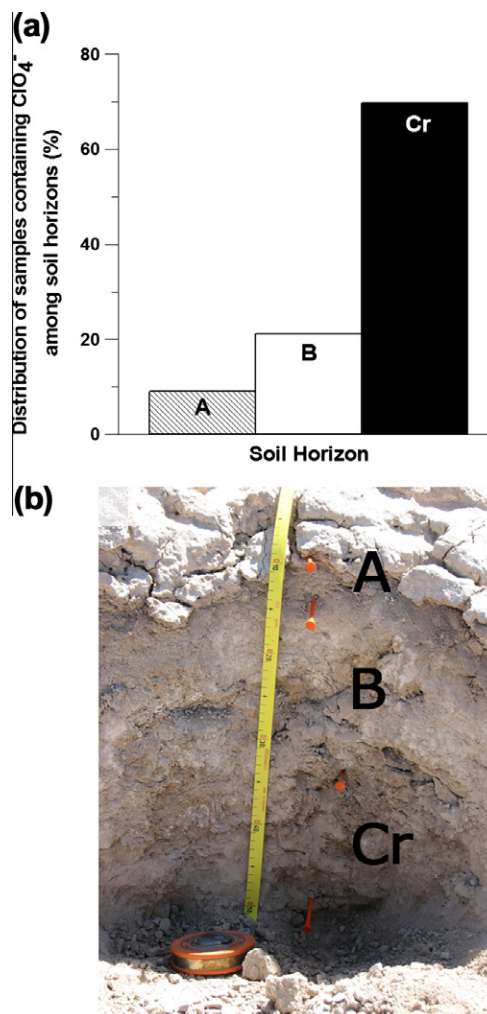

Fig. 5. (a) Distribution of samples containing perchlorate among soil horizons and (b) a soil profile illustrating the use of soil horizon designations in this project.

from 3.28 dS m^{-1} to 207 dS m^{-1} and generally increased with depth (Table D.4). In some profiles, the electrical conductivity values of the caliche and weathered bedrock horizons were near thirty times higher than the accompanying surface soils (Table D.4). The pH of the soil horizons fell in the neutral to alkaline range, 6.00–9.75 and did not correlate with the occurrence of nitrate or perchlorate. Perchlorate concentrations did not correlate with electrical conductivity, most likely due to the much higher levels of chloride, sulfate and other ions present in the soils.

While perchlorate was not present in reportable concentrations at all of the sites visited, a general trend was observed for the occurrence of perchlorate amongst soil horizons (Fig. 5a). When present, the highest concentrations of perchlorate were found in the Cr horizons, a delineation used to describe weathered bedrock (Fig. 5a, b). The B horizons, zones of illuviation, had the second highest percentage of samples containing perchlorate while the A horizons had the least. Fig. 5b represents how the soil horizon designations were made for this soil environment.

4. SOLUBLE SALT ACCUMULATION IN THE MOJAVE DESERT

4.1. Bottom–up accumulation model

Two general hypotheses were explored to explain how nitrate, perchlorate and other soluble salts accumulated at the field areas in the Mojave Desert. The first hypothesis describes a "bottom–up" mechanism where the salts were deposited in stratified layers of mudstone and sandstone formed in ancient inland lakes. Over time, the deposits were subject to folding, faulting and other forms of tectonic activity (Noble and Mansfield, 1922). Thin soil mantles developed by weathering and slopewash now overly the strata. In current arid environments of the Mojave, wetting fronts are shallow (<1m) due to short, sporadic rain events with minimal leaching (Nimmo et al., 2009) (Fig. 6). As the soils dry after a rain event, capillary rise redistributes and evapo-concentrates soluble salts into the upper soil and weathered bedrock horizons.

The second hypothesis is a "top-down" approach where salts were deposited onto a rough, stable soil surface through aerosol deposition and have concentrated in the subsoil over time. This mechanism has been used to explain reservoirs of nitrate found in arid, landscapes (Hunter et al., 1982; Walvoord et al., 2003; Graham et al., 2008). In the Mojave Desert, these nitrate pools are typically associated with desert pavement landscapes and are found on stable geomorphic surfaces with a cap of alluvial gravel or basalt. The rough surfaces of the surface materials trap eolian fine-textured sediments, which are then washed
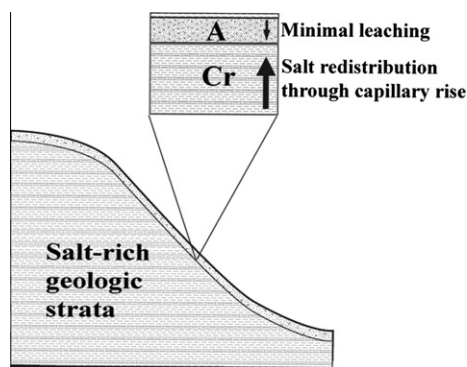
Fig. 6. A general depiction of the "bottom–up" salt redistribution model describing how perchlorate, nitrate and other soluble salts have accumulated at the field areas in the Mojave Desert, California. Soil depths and soil horizon thicknesses are not drawn to scale.

beneath or to the sides of the rubble during intense episodic rain events (Wells et al., 1985). Over thousands of years, the eolian deposits accumulate and lift a thin mosaic of clasts from alluvial fill or the rubble zone of a basalt flow to form a desert stone pavement. These clasts stabilize over time, which significantly decreases infiltration, increases surface run off and allows for the accumulation of soluble salts beneath the surface.

Many of the sites visited during the study lacked depositional surfaces, such as an alluvial or basalt mosaic pavement, that would allow for the leaching and concentration of soluble salts over time. Most of the field areas contained erosional surfaces with minimal gravel cover that could serve as dust traps for eolian deposition (Fig. 2). SP9 and BH5, the two depositional desert pavement surface cover sites sampled in this study, did not concentrate more nitrate or perchlorate than the erosional sites (A3). For example, the desert pavement site at Sperry, SP9, contained no reportable perchlorate and a maximum nitrate concentration of 6.4 mg g^{-1} compared to SP8, an erosional site in the same field area containing maximum perchlorate and nitrate concentrations of 23.4 mg kg^{-1} and 29.6 mg g^{-1}, respectively. In addition, the soil morphologic characterization of the sites revealed that >60% of the samples containing detectable perchlorate originated from geologic parent material (C horizons) compared to ~30% from the A and B horizons combined (Fig. 5a). If the soluble salts were leached via a top–down mechanism then the illuvial B and/or upper C horizons would accumulate substantial amounts of perchlorate, nitrate and other soluble salts, more so than the underlying, relatively un-altered C horizons where over half of the perchlorate-containing soils were found. Soluble salts can concentrate beneath depositional surfaces in arid environments as described in the literature (Graham et al., 2008); however, evidence supporting the top–down accumulation of soluble salts beneath the erosional surface sites was not observed in the study.

The "bottom–up" hypothesis is supported by local topography at several of the field sites. According to the general catena model (Birkeland, 1999), the upper positions of a steep-sided, erosional hillslope are not conducive to the accumulation of soluble salts, clays, and minerals. These

materials move from the summit position of a hillslope to the lower, more energetically favorable foot and toeslope positions. Water availability and slope control overland and throughflow catena processes thereby dictating how much accumulation occurs in lower hillslope positions (Tardy et al., 1973). Sperry, SP8, was located on a narrow ridge with a slope >20% and would not be expected to accumulate salts based on the catena model yet this site contains the highest perchlorate concentration (Table D.4, Fig. B.2.5a). Likewise, at the Confidence Hills site, CH6, the single horizon containing a reportable concentration of perchlorate and percent level nitrate was located at the summit of a steep-sided hillslope. Conversely, the Confidence Hills sites sampled at the toeslope positions contained no perchlorate and only one sample in the toe slope position contained >1% nitrate. In addition, deformed and folded rock strata exposed at the Confidence Hills reveal a complex geologic history that is too unstable for the top–down concentration of soluble salts (Fig. B.2.2b). The soil-topography relationship observed at Saratoga, SA9, also provides strong support for the bottom–up hypothesis (Table D.4). SA9 was located on a steep backslope landscape position with a slope of 43%. There was a thin, eroded soil surface overlying steeply upturned strata (Fig. B.2.4). While non-detectable in surface soils, the only reportable perchlorate occurred in steeply upturned cemented sandstone (27–56 cm) where nitrate concentrations were negligible (Table C.3). These topographic observations and geochemical data reinforce the bottom-up hypothesis where perchlorate, nitrate, and other soluble salts previously accumulated in geologic strata. The salts have since been subsequently incorporated into overlying soils through a "bottom–up" weathering mechanism.

4.2. Sources and preservation of nitrate and perchlorate in the Mojave Desert, CA

The isotope data suggests that the nitrate in the Mojave Desert soil is a mixture of atmospheric and biologic nitrate (Fig. 4). The $\Delta^{17}O$ isotopic signature of nitrate derived from photochemical oxidation of nitrogen oxides averages ≈24‰ (Thiemens, 1999; Michalski et al., 2004). This is in contrast to nitrification that generates nitrate with $\Delta^{17}O \approx 0‰$. Based on these observations, a simple two-member isotope mixing model was used to estimate the atmospheric fraction of nitrate (f_{atm}) in the soils using $\Delta^{17}O_{soil} = f_{atm}(24‰) + (1-f_{atm})(0‰)$. The atmospheric nitrate input at our study sites ranged from 31% to 50%. While the sources of biologically fixed nitrate in these soils are not well understood, the significant fraction of atmospheric nitrate in the soil would argue for the top–down hypothesis unless there was a paleoclimatic mechanism incorporating atmospheric nitrate into geologic strata. We suggest a two-part hypothesis that might explain the concentration of nitrate and perchlorate in these lacustrine deposits. First, a flush of solutes from an arid, but biologically active, watershed may have subsequently accumulated and been preserved in a low-lying playa setting. Secondly, there may have been direct deposition and accumulation of atmospheric nitrate and perchlorate in a paleolacustrine system where biologic activity was minimal.

4.2.1. Incomplete nitrogen cycling in playas

The first part of the hypothesis involving the flushing of an arid, but biologically active, watershed and the subsequent accumulation and preservation of solutes in a playa setting is based on N cycling dynamics of soil crusts in modern deserts. Biological soil crusts generally form on bare, shallow, fine-textured and sometimes rocky soils (Belnap et al., 2001). Recent work by Johnson et al. (2007) documented the incomplete cycling of nitrogenous compounds in biological soil crusts resulting in the potential net export of nitrate, ammonium and organic nitrogen. The abundance and diversity of the organisms living in biological soil crusts has been found to increase when formed on calcareous and gypsum-rich sediments (Belnap et al., 2001). These conditions were likely present when climate change at the end of the Pleistocene desiccated many extensive pluvial lake systems in the Mojave Desert, leading to the formation of closed basin dry lake playas at the lowest points on the landscape (Enzel et al., 2003). The desiccation of the lake systems exposed mudstone and sandstone lacustrine sediments to the atmosphere. The exposure of these calcareous and gypsum-rich lacustrine sediments may have provided a suitable paleoenvironment for biological soil crust formation and subsequent biological nitrate formation (Fig. 7). This aridic paleo-climate could have been conducive to the formation of surface soil crusts containing nitrogen-fixing bacteria. There are multiple species of heterocytous cyanobacteria that have been identified in desert biological soil crusts as nitrogen fixers (Yeager et al., 2007), yet there has been a notable absence of denitrifying activity in these same crusts (Johnson et al., 2007). If biological soil crusts containing nitrogen-fixing bacteria existed within the arid paleo-watershed then incomplete nitrogen cycling in biological soil crusts, coupled with atmospheric nitrate and perchlorate deposition, affords a possible explanation as to how perchlorate and a mixture of atmospheric and biologic nitrate was preserved in these ancient lakebed sediments.

4.2.2. Preservation of nitrate and perchlorate in paleoclimate playa systems

In addition to promoting biological nitrogen fixation and the subsequent accumulation of nitrate in lake sediments, the desiccation of pluvial lake systems is a plausible explanation for the concentration of atmospherically derived nitrate and perchlorate. The most detailed perchlorate formation pathway involves a photochemical reaction between a chlorine species and atmospheric ozone, a mechanism similar to chemical N_2 fixation (Rao et al., 2010). Jackson et al. (2010) found Mojave Desert perchlorate to

contain the highest $\Delta^{17}O$ values (8.6‰ to +18.4‰), providing support for an ozone mediated formation mechanism. Biologically formed nitrate combined with atmospheric nitrate and perchlorate deposited on the Earth's surface may have been subsequently leached into the young, newly exposed lacustrine sediments that were further compressed, folded and deformed by later tectonic activity. The preservation of nitrate and perchlorate in ancient playa lakes is another important consideration.

The second component of this hypothesis, also portrayed in Fig. 7, is the preservation and/or formation of nitrate in a paleoclimate playa system. Nitrate has been identified as an important component of today's active playas and the dust generated from playa lake systems throughout the southwest (Blank et al., 1999). Large concentrations of nitrate have been reported both on the surfaces of dry lakes and in the soils below playas (Noble and Mansfield, 1922; Hirmas and Graham, 2011) while the accumulation of perchlorate in playa systems has not been extensively studied. The origins of the nitrate salts in playas are not well understood and have been attributed to both biological and chemical nitrogen fixation sources (Leatham et al., 1983; Böhlke et al., 1997). Nitrate and perchlorate preservation would require low organic matter concentrations in the sediments. Investigations of the degree and/or rates of perchlorate reduction have produced variable results; however, in most instances, the disappearance of perchlorate immediately followed that of nitrate (Parker, 2009). Nitrate is readily denitrified under organic-rich, anaerobic conditions, explaining why few lake or ocean sediments contain nitrate. Therefore, minimal organic matter would be expected in the lacustrine sediments in order for the bottom–up hypothesis to be valid. Hsieh and Murray (1996) noted low organic contents and high sulfate concentrations in the Mojave lacustrine deposits of the Confidence Hills. Modern saline lakes in western China have low organic matter and high nitrate concentrations, suggesting modern-day analogs to the Mojave paleolakes.

4.3. Distribution of perchlorate in geologic strata

The distribution of perchlorate among soil profiles shows that over sixty percent of the samples containing perchlorate were excavated from the Cr horizons (little to no pedogenic alteration), thereby supporting the bottom–up hypothesis (Fig. 5). Only twenty percent of the samples were located in the B horizons and even fewer in the A horizons, suggesting that perchlorate is preserved in the geologic parent material underlying arid land soils. Sperry
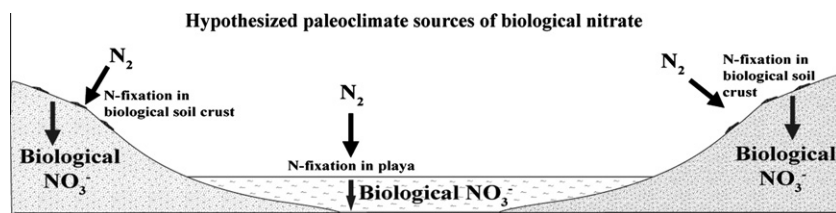

Fig. 7. Diagram representing hypothesized paleoclimate processes that could have served as sources of biologically fixed nitrate.

(SP-8), the site containing the highest known concentration of naturally formed perchlorate (23.40 mg kg^{-1}) in southern California, was also located in a Cr horizon. This research was the first to analyze perchlorate distribution in terms of soil morphology. While this work revealed that perchlorate concentrates in the geologic strata of underlying arid land soils, the mechanisms explaining how this natural perchlorate was atmospherically formed, deposited and preserved in these strata are not well understood and require additional investigation. Furthermore, the proposed hypotheses related to nitrate preservation and the paleoclimate sources of biological nitrate are speculative and more research needs to be conducted before any conclusions can be reached.

4.4. Potential environmental impacts of the Mojave Desert nitrate deposits

The Mojave Desert clay-hill deposits span land used for military bases, desert roads, off-roading areas, recreational parks and other applications. Soils disturbed by human activities are more susceptible to wind and water erosion (Belnap, 1995; Lovich and Bainbridge, 1999). The far-reaching dust generated by the disturbance of fragile arid-land systems impact the biological and hydrologic dynamics of nutrient-limited systems, such as alpine lakes (Ballantyne et al. 2011). Improving the chemical characterization of aridland dust sources, such as the erosional mud hill deposits of the Mojave Desert, is important for understanding the potential biogeochemical impacts of atmospheric deposition on adjacent ecosystems. In addition, substantial increases in urban development and desert agriculture have made general assessments of natural nitrate and perchlorate reservoirs and distributions in arid landscapes a useful exercise. Understanding the impacts of land use change, such as the generation of salt-rich dust by human-induced soil disturbance, is essential in accounting for the risk of contaminating surface and groundwater supplies with naturally formed nitrate and perchlorate. Böhlke et al., (1997) described a nitrate groundwater sample collected near Victorville, California that was isotopically similar to nearby desert nitrate deposits in Barstow, California, suggesting that at least a small portion of surficial natural nitrate had been incorporated into the local groundwater supply. It is crucial to be aware of the occurrence of "background" levels of natural nitrate and perchlorate when assessing the risks and effects of anthropogenic contamination on the environment.

5. CONCLUSIONS

Putatively natural sources of perchlorate appear to have co-accumulated with nitrate in ancient lacustrine sediments and/or paleoclimatic playa systems. These sediments have since been exposed through geological events and are eroding through a hypothesized bottom–up weathering mechanism. The extensive survey of six field areas revealed the first significant correlation between nitrate and perchlorate in the Mojave Desert nitrate deposits and the highest concentration of naturally formed perchlorate in the south-western United States. The relationship between nitrate and perchlorate in the Mojave Desert was weaker than relationships observed for the Atacama Desert, or for the dry valleys of Antarctica. Near-ore-grade nitrate deposits occur in the Mojave Desert, but the perchlorate levels are at least two orders of magnitude lower than the Atacama nitrates.

A $\Delta^{17}O$ isotopic investigation of seventeen samples revealed the origins of the nitrate salts in the soils collected from geologically distinct field areas in the Mojave Desert, California. The Mojave Desert nitrate salts were found to be a mixture between atmospherically derived and biologically fixed nitrate. Each site contained unique $\Delta^{17}O$ isotopic signatures thereby suggesting distinctive nitrate and perchlorate deposition and/or preservation mechanisms. In contrast, previous studies have confirmed that Antarctic and Atacama Desert nitrate salts are dominantly atmospheric in origin.

Soil chemical, morphologic, and geologic data collected in the Mojave Desert soils support a "bottom–up" hypothesis for soluble salt accumulation, specifically perchlorate and nitrate. Here, soluble salts are being redistributed into the upper soil horizons through the weathering of underlying salt-rich geologic strata.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2012.10.028.

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