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

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10 Pages, Including 2 tables and 4 figures.

Methods for nitrate stable isotope analysis

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

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

Reporting of perchlorate isotope data

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

Methods for separating and purifying perchlorate for isotopic analysis

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

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

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

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

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

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Table S1. Additional information about soil and caliche samples.

Sample ID	Location	Land Use	Latitude	Longitude	Date Sampled	Sample Depth	Sample Description	Elevation (m)
Confidence Hills 1	Death Valley, California, USA (Clay Hills)	National Park	N 35 50.350	W 116 35.256	2/16/2006	<1 m	Salt-cemented salt and clay	4
Confidence Hills 2			N 35 50.372	W 116 35.47	1/25/2008	~10-30cm	Salt-cemented green and red clay with chunks of mixed salts	40
Saratoga Hills			N 35 40.050	W 116 28.197		~5-30cm	Salt-cemented red clay streaked with white veins	130
Bully Hill			N 35 47.647	W 116 12.346		~5-30cm	Salt-cemented green and red clay with chunks of mixed salts	390
Zabriskie		Bureau of Land Management	N 35 55.103	W 116 16.234		~5-30cm	Salt-cemented green and red clay with chunks of mixed salts	420
P1	Baquedano District, Chile	Surface NO ₃ ⁻ mines	S23 11.863	W69 40.635	10/12/2007	>6m	Salts in fractured andesite	1279
P2			S23 11.863	W69 40.635		>6m	Salts in fractured andesite	1279
P3			S23 12.059	W69 40.205		25cm	Unconsolidated sediments	1304
P4			S23 12.059	W69 40.205		50cm	NaNO ₃ caliche	1304
GJ01	Chile	Unknown	Unknown		Unknown	Unknown	caliche	Unknown
UIC 24	Chile	Railway Cut	S23.16.53	W 69.46.14	11/03/2007	5m	NO ₃ ⁻ vertical vein in regolith	1137

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

	Middle Rio Grande Basin		Southern High Plains					
Well Name	RR8	RR16	MW2	MW3	BW2	JYT1	GW2	KJ1
Well Type	PSW ¹	PSW	Monitor	Monitor	Monitor	Irrigation	Monitor	PSW
County, State	Sandoval, NM	Sandoval, NM	Martin, TX	Martin, TX	Bailey, TX	Kent, TX	Gaines, TX	Roosevelt NM
Latitude (N)	35.274	35.292	32.417	32.416	33.966	33.246	32.667	33.643
Longitude (W)	-106.732	-106.693	-102.155	-102.155	-102.765	-100.622	-102.376	-103.34
Land Surface Elevation (m)	1776	1686	881	881	1170	612	954	1285
Mid-Screen Elevation (m)	1383	1257	843	830	1147	594	943	
Screen Elevation ± (m)	94	178	1.2	3	3	1.2	3	
Water-Table Elevation (m)	1468	1488	846	846	1150	604	945	1250
Unsaturated-Zone Thickness (m)	308	198	35	35	21	8	9.0	35
Sample Date	9/12/2007	9/13/2007	11/8/2005	11/7/2005	11/9/2005	1/10/2006	6/1/2006	3/1/2007
Field parameters								
T (°C)			22.6	21.5	20.4	25.9	20.1	16.1
Specific Conductivity (µs/cm)			4709	4508	731	1818	6935	2411
Field O ₂ (µmol/L)			213	174	236	190	91	230
Field pH			6.95	8.25	7.47		6.45	6.64
Water Chemistry								
TDS (g/l)			3.06	2.97	0.52	1.8	4.96	1.89
F (µmol/L)	38	58	215	192	128		190	66
Cl (µmol/L)	255	598	25000	37000	1600	5300	29000	12000
Br (µmol/L)	2	2	68	111	5	8	98	27
NO ₃ (µmol/L)	187	137	577	209	120	437	129	370
SO ₄ (µmol/L)	669	1039	13000	9500	1100	8100	26000	7400
ClO ₄ (µmol/L)	0.0067	0.0085	0.20	0.11	0.02	0.04	2.05	0.15
Alkalinity (µmol/L as HCO ₃)			4200	4000	4500	3200	6600	2800
Isotopes								
H ₂ O δ ² H (‰)	-85.4	-96.8	-42.6	-46.6	-39.0	-32.1	-39.0	-42.8
H ₂ O δ ¹⁸ O (‰)	-11.66	-12.90	-5.75	-6.54	-5.71	-5.22	-5.43	-5.96
H ₂ O δ ³ H (TU) (±)	-0.22 (0.27)	0.32(0.22)	2.54(0.2)	0.34(0.17)	0.14(0.16)	3.68(0.22)	1.15(0.19)	0.15(0.23)
DIC δ ¹³ C (‰)	-7.7	-6.4	-6.4	-6.4	-3.9	-11.2	-9.9	-7.7
DIC δ ¹⁴ C (pmc ²)(±)	11.6(0.2)	5.9(0.1)	38.4(0.3)	33.6(0.3)	83.5(0.5)	99.7(0.4)	98.1(0.4)	91.5(0.4)
DIC pmc Age (years) ³	17300	22700	7700	8700	1450	25	151	710
SO ₄ ²⁻ δ ³⁴ S (‰)	1.1(0.2)	4.8(0.2)	7.3(0.2)	7.7(0.2)	7.4(0.2)	10.2(0.2)	8.7(0.2)	10.1(0.2)
SO ₄ ²⁻ δ ¹⁸ O (‰)	3.0(0.2)	4.5(0.1)	7.7(0.1)	8.4(0.1)	4.6(0.2)	8.8(0.2)	3.7(0.1)	2.9(0.1)
Dissolved Gases								
CH ₄ (µmol/L) (±)	0.000	0.000	0.000	0.000	0.000	0.055 (0.007)	0.000	0.000
Ar (µmol/L) (±)	12.35 (0.02)	13. (0.03)	13.91 (0.03)	13.9 (0.08)	13.91 (0.09)	13.52 (0.08)	15.22	13.21 (0.01)
N ₂ (µmol/L) (±)	497(2)	534(1)	606(2)	581(4)	557(2)	589(8)	615	547(2)
Ar-N ₂ equilibration T (°C)	19.2	16.3	20.5	18.6	15.2	23.2	12.8	18.3
Ar-N ₂ excess air (ccSTP/L)	1.4	1.7	3.7	2.5	1.4	3.4	2.0	2.2

¹PSW=public supply well; ²pmc not normalized for δ¹³C; ³Conventional age from Libby half-life (8033 yr), not normalized for δ¹³C

Figure S1. Sample Locations

Figure S2. Comparison of $\text{NO}_3^-/\text{ClO}_4^-$ and $\text{Cl}^-/\text{ClO}_4^-$ molar ratios in new samples with previously published values for wet deposition across the contiguous United States (excluding coastal sites)[13] and vadose-zone salt accumulations in the southwestern United States[14]. The reported average $\text{Cl}^-/\text{ClO}_4^-$ ratio is shown for groundwater (GW) in the SHP [15].

Figure S3. Distribution of ClO₄⁻ and other anions with depth below land surface at a rangeland site in the southern High Plains, western Texas. The water table was more than 15 m below land surface. Concentrations are given as mass of leachable anions per mass of solid material that was leached. Sample SHP-V was taken from 200-400 cm below land surface at this site.

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