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Natural Chlorate in the Environment: Application of a New IC-ESI/MS/MS Method with a $Cl^{18}O_3^-$ Internal Standard

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A new ion chromatography electrospray tandem mass spectrometry (IC-ESI/MS/MS) method has been developed for quantification and confirmation of chlorate (ClO_3^-) in environmental samples. The method involves the electrochemical generation of isotopically labeled chlorate internal standard ($Cl^{18}O_3^-$) using ^{18}O water ($H_2^{18}O$). The standard was added to all samples prior to analysis thereby minimizing the matrix effects that are associated with common ions without the need for expensive sample pretreatments. The method detection limit (MDL) for ClO_3^- was 2 ng L^{-1} for a 1 mL volume sample injection. The proposed method was successfully applied to analyze ClO_3^- in difficult environmental samples including soil and plant leachates. The IC-ESI/MS/MS method described here was also compared to established EPA method 317.0 for ClO_3^- analysis. Samples collected from a variety of environments previously shown to contain natural perchlorate (ClO_4^-) occurrence were analyzed using the proposed method and ClO_3^- was found to co-occur with ClO_4^- at concentrations ranging from <2 ng L^{-1} in precipitation from Texas and Puerto Rico to >500 mg kg^{-1} in caliche salt deposits from the Atacama Desert in Chile. Relatively low concentrations of ClO_3^- in some natural groundwater samples (<0.1 μg L^{-1}) analyzed in this work may indicate lower stability when compared to ClO_4^- in the subsurface. The high concentrations of ClO_3^- in caliches and soils (3–6 orders of magnitude greater) as compared to precipitation samples indicate that ClO_3^-, like ClO_4^-, may be atmospherically produced and deposited, then concentrated in dry soils, and is possibly a minor component in the biogeochemical cycle of chlorine.

Introduction

Chlorate is produced artificially for a wide range of applications including the production of chlorine dioxide and application as a defoliant and herbicide (*1*). It is also present as an undesirable byproduct in the wastewater of pulp and paper mills, in discharges from disinfection units that use chlorine and chlorine dioxide, and in commercial hypochlorite solutions that are used for household and industrial applications (*2, 3*). Chlorate is currently not regulated in drinking water, although the state of California has set a notification level of 800 μg L^{-1} (*4*). Chlorate is known to be formed by thermal and photodecomposition of aqueous hypochlorite ($HOCl/OCl^-$) (*5, 6*). Previous laboratory experiments have also shown that ClO_3^- can be produced by ozone (O_3) oxidation of aqueous chlorine and oxy-chlorine compounds (e.g., chlorine dioxide (ClO_2) and chlorite (ClO_2^-)) (*7*). More recently, ClO_3^- has been detected as a major product in studies evaluating perchlorate (ClO_4^-) formation during UV and O_3 mediated oxidation of aqueous and dry Cl precursors (e.g., chloride (Cl^-), OCl^-, and ClO_2) (*8–11*). If similar processes involving aqueous and/or dry Cl species are involved in natural ClO_4^- formation, then ClO_3^- should co-occur with ClO_4^- at concentrations similar to or exceeding those of the latter species. However, few studies have attempted to quantify ClO_3^- in environmental samples, or to correlate its occurrence with other anions, including ClO_4^-.

The Atacama Desert in Chile has long been known to contain large natural deposits of both common (e.g., nitrate (NO_3^-), sulfate (SO_4^{2-}) and Cl^-) and uncommon anions including ClO_4^- (*12*). Atacama ClO_4^- was exported in NO_3^- fertilizer products and thereby entered soils and groundwater in the US (*13, 14*). Recent studies indicate natural ClO_4^- not attributable to imported Atacama-derived fertilizers is also widespread in the US. For example, natural "indigenous" ClO_4^- has been detected in groundwater within Texas and New Mexico (*15, 16*), subsoils of the expansive southwestern deserts (*17*), caliche-type deposits in the Mojave Desert (*18*) and wet atmospheric deposition throughout the US (*19*). Although ClO_3^- has been detected in surface and bottled waters in the U.S (*20*), and ice cores obtained from the Arctic region (*21*), information regarding its origins and distribution in the environment is extremely limited.

One of the main reasons that there is little information concerning ClO_3^- occurrence in natural samples is that there is no sufficiently sensitive and selective technique available for analyzing ClO_3^- in typical environmental matrices. Tritrimetry, colorimetry and iodometric techniques all suffer from various interferences, whereas capillary electrophoresis and pulsed electrochemical detection are not sensitive enough to determine ClO_3^- at concentrations typical of environmental samples (*22*). Currently, ion chromatography with conductivity detection (IC-CD) is the most common technique for determination of ClO_3^- in water samples and can achieve quantification limits of 10 μg L^{-1} (*23*). Even for environmental samples with relatively high ClO_3^- concentrations, the use of IC may not be useful as background ions (e.g., Cl^- and NO_3^-) can mask the relatively smaller ClO_3^- peaks. Further, the chromatographic retention time is not always considered to be a unique identifier for a specific

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compound. Liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) has been used to increase both the sensitivity and selectivity for ClO_3^- (*3, 20, 22*). However, such methods still require pretreatment for most environmental samples other than relatively low ionic strength water samples (e.g., ice cores). Moreover, the possibility of suppression by specific background ions can reduce the reliability of even the IC-MS/MS method. The problems of ion-suppression can often be avoided by using an isotopically enriched internal standard in conjunction with IC-MS/MS as recently described for ClO_4^- analysis (*17, 24, 25*), but similar methods have not been reported for ClO_3^-.

In this work, we report the development and application of an isotopically enriched internal standard ($Cl^{18}O_3^-$) for use with IC-MS/MS to significantly improve selectivity and sensitivity in the measurement of ClO_3^-. Further, we report preliminary data demonstrating the occurrence of ClO_3^- in groundwater, precipitation, plants, soils, fertilizers, and caliche-type salt deposits. We show for the first time that ClO_3^-, like ClO_4^-, is present in atmospheric deposition, it can accumulate in arid settings, and it can occur at concentrations comparable to that of ClO_4^-.

Experimental Section

Preparation of $Cl^{18}O_3^-$ Internal Standard. The behavior of an isotopically labeled internal standard (IS) and the non-labeled analyte are affected in the same way by chemical and instrumental variations thereby making the IS an accepted methodology for accurate and selective quantification in IC-MS methods. The internal standard ($Cl^{18}O_3^-$) was produced by electrolysis of Cl^- in ^{18}O enriched water ($H_2^{18}O$). Chloride (6 ± 0.1 mg) as potassium chloride (99.6% pure KCl; Fisher, Fairlawn, NJ) was dissolved in 1 g of ^{18}O-enriched water ($H_2^{18}O$; ISOTEC™, Sigma-Aldrich) with a purity of 97 atom % ^{18}O. The electrolysis was performed in a 1.2 mL vial that was sealed with two layers of PARAFILM "M" laboratory film (American National Can, Chicago, IL) to minimize contamination and evaporation of the brine. The electrodes from an anion suppressor (Anion Atlas Electrolytic Suppressor; Dionex Corporation) were used for Cl^- electrolysis in conjunction with a DC power supply (Hewlett-Packard, Model No. 6212C) equipped with a voltage and current regulator. The current and voltage conditions of the electrolysis were set at 20 mA and 3 V, respectively, and the total electrolysis time was 2 days. The generated $Cl^{18}O_3^-$ solution was exposed to UV light (Blak Ray Lamp, λ_{max} = 365 nm) for about 12 h to convert any residual chlorine species (HOCl/OCl$^-$) produced during electrolysis to ClO_3^- and Cl^-. The amount of ClO_3^- produced by electrolysis was determined to be ~0.28 mg as ClO_3^- (287 ± 0.1 mg L^{-1} in the solution) based on analysis by ion chromatography coupled with conductivity detection (IC-CD) following EPA method 317.0 (*23*). The presence of residual Cl^- (~3000 mg L^{-1}) in the generated $Cl^{18}O_3^-$ solution is unlikely to cause any interference in the ClO_3^- analysis as it was diluted by several orders of magnitude, before use resulting in negligible Cl^- contribution (<0.5 mg L^{-1}) from the internal standard. Using the IC-MS/MS in multiple reaction monitoring (MRM) mode, the intensities of the $^{35}Cl^{16}O_3^- \rightarrow {}^{35}Cl^{16}O_2^-$ and $^{37}Cl^{16}O_3^- \rightarrow {}^{37}Cl^{16}O_2^-$ transitions were determined to be less than 0.3% of the intensities of the $^{35}Cl^{18}O_3^- \rightarrow {}^{35}Cl^{18}O_2^-$ and $^{37}Cl^{18}O_3^- \rightarrow {}^{37}Cl^{18}O_2^-$ transitions, thereby ensuring negligible interference of $Cl^{16}O_3^-$ during sample analysis. Although the presence of ClO_4^- would not affect ClO_3^- analysis, it was found that the concentration of $Cl^{18}O_4^-$ and $Cl^{16}O_4^-$ in the generated isotope standard was less than 1% relative to $Cl^{18}O_3^-$.

Ion Chromatographic Conditions. A modification of the IC-MS/MS technique for ClO_4^- (*24*) was used for ClO_3^- analysis. A Dionex LC 20 ion chromatography system

consisting of a gradient pump (GP50), CD25 conductivity detector, AS40 automated sampler and Dionex IonPac AS20 (250 × 2 mm) analytical column were used for all analyses. A binary gradient consisting of 45 mM sodium hydroxide (NaOH) (A) and distilled deionized (DDI) water (B) was used as eluent with a combined flow of 0.3 mL min^{-1}. The gradient was as follows: 25% A held for 10.5 min (includes injection time), followed by a step-up to 100% A, held for 8 min, and finally a step-down to initial conditions at 18.5 min. A 4 min equilibration step at 25% A was used before the beginning of the next sample in the sequence. The IC liquid stream was switched to the inlet of the electrospray ion source (ESI) of the MS/MS from 5.5 to 8.0 min as the residence time of ClO_3^- was ~6.5 min. A 25 μL loop was used for analysis of water, soil, caliche, and plant samples and a 1 mL loop was used for atmospheric deposition samples. Both the gradient time steps and the IC switch to MS were extended by 3 min for the 1 mL loop in accordance with the associated change in residence time of ClO_3^-, which resulted in a total runtime of 25.5 min per sample. The IC flow was combined in a static mixer with 90% acetonitrile (0.3 mL min^{-1}) before injection into the source of the MS/MS as a post column solvent.

Mass Spectrometry. Mass spectrometry was performed using an Applied Biosystems-MDS SCIEX API 2000™ (Applied Biosystems, Foster City, CA) triple quadrupole system equipped with a TurboIonSpray source. The source dependent parameters are as listed in Table S1. Multiple reaction monitoring (MRM) mode was used to quantify ClO_3^- in the samples. The transitions of $^{35}Cl^{16}O_3^-$ (*m/z* 83.01) into $^{35}Cl^{16}O_2^-$ (*m/z* 66.95) and $^{35}Cl^{18}O_3^-$ (*m/z* 89.00) into $^{35}Cl^{18}O_2^-$ (*m/z* 71.00) were used for quantifying the main analyte and the internal standard (IS), respectively; and transitions of $^{37}Cl^{16}O_3^-$ (*m/z* 85.01) into $^{37}Cl^{16}O_2^-$ (*m/z* 68.95) were monitored to ensure that the abundance ratio of $^{35}Cl/^{37}Cl$ was within an acceptable range (2.31 to 3.85) (*26*). Analyst 1.4.1 software was used to acquire data.

Analysis Protocol. A modified extraction procedure for the determination of ClO_4^- in soils and plants (*17, 27*) was used for ClO_3^- analysis. The details of the procedure are provided in the Supporting Information (SI). Water samples including extraction leachates from caliches, soils, and plants were measured without further purification or treatment (e.g., no silver or barium cartridges to remove Cl^-, SO_4^{2-}, etc.) by spiking with 0.2 μg L^{-1} and 0.02 μg L^{-1} of $Cl^{18}O_3^-$ for 0.025 and 1 mL volume loops respectively. The samples were analyzed in batches of eight followed by an analytical duplicate, spike, blank and a continuing calibration check (CCC). The tolerance for deviation in the duplicate samples and CCC was ±20%, and for recovery of sample spike was 80 to 120%. If any one of the above conditions was not met, or if ClO_3^- in the laboratory reagent blank was greater than 0.3 times the method reporting level, then the results of the particular batch were discarded and the samples were reanalyzed (*26*). The CCC and the analytical spike concentration were, in general, 10 ng L^{-1} and 1 μg L^{-1} for the 1 mL and 25 μL loop, respectively. The average CCC recovery was 106 ± 6% (*n* = 17) and the average analytical spike recovery was 96.0 ± 11% (*n* = 17) with the absolute recovery of $Cl^{18}O_3^-$ ranging from 70 to 110%. The deviation between the analytical replicates was 1.9 ± 11% (*n* = 17).

Results and Discussion

Method Detection and Reporting Limits. The method detection limit (MDL) was determined by analyzing eight replicate injections of a ClO_3^- solution (4 ng L^{-1}) and calculating the standard deviation of their measurement (*28*). The method reporting limit (MRL) was confirmed by analyzing seven ClO_3^- solutions at the target MRL concentration (4 ng L^{-1}) as outlined in EPA Method 331.0 (*26*). The MDL

TABLE 1. Effect of Common Anions on the Retention Time and Area of the ClO_3^- Isotopic Internal Standard (IS) (as measured for $^{35}Cl^{18}O_3^-$) in the MS/MS Using a 25 μL Loop

compound	concentration (mg L^{-1})	retention[a] time (min)	$Cl^{18}CO_3^-$ retention time (min)	$^{35}Cl^{18}O_3^-$ area (counts)	deviation[b] (%)
F$^-$	100	3.6	6.86	21800	4
Cl$^-$	100	5.0	6.87	18600	−11
NO$_2^-$−N	50	5.9	6.87	4990	−76[c]
Br$^-$	50	7.1	6.88	19900	−5[c]
NO$_3^-$−N	100	7.4	6.84	20400	−2
PO$_4^{3-}$−P	100	15.2	6.88	16600	−20
SO$_4^{2-}$	100	10.0	6.80	19400	−7

[a] The retention times of the individual anions are also provided to compare the effects of the IC conditions on the separation of ClO_3^-. An additional residence time of approximately 0.2 min should be added to determine the adjusted retention times of the common anions in the MS.
[b] Deviation is calculated as, [(Sample)$_{IS}$ − (DDI)$_{IS}$)/(DDI)$_{IS}$] with (Sample)$_{IS}$ and (DDI)$_{IS}$ being values in areas counts of the internal standard as measured by the IC-MS/MS.
[c] NO$_2^-$, Br$^-$, and NO$_3^-$ contribute to most of the ion loading to the MS/MS during the IC switch to MS/MS (5.5 to 8.0 min) of which NO$_2^-$ shows the greatest suppression of the IS peak area ($\sim$80%) based on average IS peak of (DDI)$_{IS}$ = 20 900 ± 1000.

and the MRL using the 1 mL loop using the 1 mL loop were 2 and 4 ng L^{-1} respectively. The lowest calibration standard (0.1 μg L^{-1}) was used as the MRL for the 25 μL volume loop; no MDL was determined in this analytical configuration.

Evaluation of Ionic Interferences. Sodium chlorate (99 + % pure NaClO$_3$; A.C.S Reagent, Sigma-Aldrich, St Louis, MO) reagent salt was used for stock solution preparation and calibration without further purification. All samples were spiked with the Cl^{18}O$_3^-$ internal standard. To determine interference from common ions, the response of the internal standard in the presence of 100 mg L^{-1} of F$^-$ (fluoride), Cl$^-$, SO$_4^{2-}$, PO$_4^{3-}$−P (phosphate) and NO$_3^-$−N and 50 mg L^{-1} of NO$_2^-$−N (nitrite) and Br$^-$ (bromide) was evaluated with respect to DDI water (Table 1). The most significant interference was due to nitrite (NO$_2^-$−N = 50 mg L^{-1}) with an 80% reduction in intensity likely due to suppression effects on ClO$_3^-$ in the MS/MS (Table 1, Figure S1 of the SI). The deviation of the intensity for the other anions was ≤20%. To evaluate the accuracy of ClO$_3^-$ analysis in the presence of background ions, a mixture of anions at the aforementioned concentrations was spiked with 0.1 and 1.0 μg L^{-1} ClO$_3^-$ and the recovery of the spike was found to be 90 ± 1.0% (n = 2), indicating the Cl^{18}O$_3^-$ internal standard was an effective tool for negating matrix effects even in presence of interfering ions, including NO$_2^-$.

Comparison to IC-CD Method. Multiple reaction monitoring was used to quantify ClO$_3^-$ in each of the analyzed samples as described above. The measured isotopic ratio of ^{35}Cl to ^{37}Cl was used for confirmation and was within ±25% of the ^{35}Cl/^{37}Cl ratio of natural samples (Table S2 of the SI). To demonstrate the performance of the proposed IC-ESI-MS/MS method, caliche samples (n = 4) from the Atacama Desert, Chile, that were found to contain sufficient ClO$_3^-$ for IC-CD analysis were measured following EPA standard method 317.0 (23). The comparative results for ClO$_3^-$ analyzed from subsamples of the caliche leachates show good agreement between the methods (deviation not greater than 10%), with the EPA method possibly overpredicting the ClO$_3^-$ concentrations slightly with respect to the method proposed herein (Table S3 of the SI).

Chlorate in Caliches and Soils. As a first application of the proposed method, we analyzed ClO$_3^-$ in environmental samples that were known to contain naturally high concentrations of ClO$_4^-$ (18). This selection was based on the

hypothesis that ClO$_3^-$ should co-occur with ClO$_4^-$, as indicated by studies of natural ClO$_4^-$ formation mechanisms (8−11). The samples include near-surface caliche-type salt deposits from hyper-arid regions of the Atacama Desert, Chile (n = 4), and clay hills in Death Valley, US in the Mojave Desert (n = 4) (18). Additional soil and surface samples were obtained from other arid locations in the Amargosa Desert east of Death Valley (n = 7), southwest African Central Namib Desert, Namibia (n = 1) (29); and the Dry Valleys region of Antarctica (n = 1) (Table 2). The ClO$_3^-$ concentrations in the caliche samples ranged from 0.6 to 530 mg kg^{-1}, with the highest values in the Atacama caliche samples (average ClO$_3^-$ = 300 000 ± 210 000 μg kg^{-1}). The ClO$_3^-$ concentrations in the Death Valley caliches were in general an order of magnitude lower, with an average value of 30 000 ± 21 000 μg kg^{-1}. The average mass ratios of ClO$_3^-$ to ClO$_4^-$ for the caliche samples from Atacama and Death Valley were 1.6 ± 1.7 and 60 ± 70, respectively.

We also analyzed selected historical Atacama NO$_3^-$ fertilizer samples with varying ClO$_4^-$ concentrations (14), to determine if ClO$_3^-$ was present along with ClO$_4^-$ in the finished fertilizer products. Concentrations of ClO$_3^-$ in the fertilizer samples ranged from 53 000 to 520 000 μg kg^{-1}and were 4 to 16× lower than the ClO$_4^-$ concentrations (Table 2). One sample (NCB001−1) representing fertilizer produced since 2002 when the production process was changed to reduce the concentration of ClO$_4^-$ in the fertilizer showed a comparable reduction in ClO$_3^-$ content (Table 2).

Soil samples from two collection areas in the Amargosa Desert had much lower ClO$_3^-$ concentrations (2.0 to 13 μg kg^{-1}) than the Atacama and Death Valley caliches (Table 2, Figure 1). There was considerable variation in the ClO$_4^-$: ClO$_3^-$ ratios among the Amargosa Desert soils, with average mass ratios of 1.0 ± 0.7 and 6.7 ± 3.0 for the G and D sets, respectively. Like ClO$_4^-$, ClO$_3^-$ concentrations typically were relatively high in samples with high Cl$^-$ and NO$_3^-$ concentrations. The coefficients of variation between two colocated (collected 1 m apart) pairs of soil samples from the Amargosa Desert were 37% (D15−16) and 11.5% (D17-D18). Surface samples from Namibia and Antarctica (Dry Valleys) had higher ClO$_3^-$ concentrations (70 and 37 μg kg^{-1}, respectively) than the Amargosa Desert soils, accompanied by higher concentrations of Cl$^-$ and NO$_3^-$ (Table 2).

The low ClO$_3^-$ concentrations measured in the leachate solutions from the aforementioned soil samples could not have been determined accurately by typical IC-CD methods. Further, the use of an IC-MS/MS method without an isotopically labeled internal standard would require sample pretreatment for the removal major anions (e.g., Cl$^-$, Br$^-$, and SO$_4^{2-}$) and still has the potential for analytical inaccuracies due to signal suppression in the presence of NO$_2^-$. The use of Cl^{18}O$_3^-$ as the IS to negate the suppression effects of major and minor anions (e.g., Cl$^-$, NO$_3^-$, and NO$_2^-$), which are present at much higher concentrations in environmental samples, provided simultaneous sensitivity and robustness compared to previous techniques. A comparison of the DV-4 sample chromatograph with continuing calibration check (CCC) chromatographs at similar ClO$_3^-$ levels shows similar characteristics in Cl^{16}O$_3^-$ and IS transition peaks (Figure S2 of the SI), indicating negligible interference in the ClO$_3^-$ signal caused by major anions (see Table 2 for major ions concentration). The average deviation of the soil extraction duplicates was 14 ± 3% (n = 3) and the recovery of the spikes was 117 ± 1% (n = 3).

Chlorate in Plants. Previous studies have indicated ClO$_4^-$ accumulation in plants with respect to soil concentrations (30, 31). To determine if ClO$_3^-$ is also bioaccumulated, plant-foliage samples were obtained from the Amargosa Desert for comparison with soils from the same site. Creosote bush, (*Larrea tridentata*) specimens had an average ClO$_3^-$ concentration of

TABLE 2. Concentrations of ClO_3^- in Desert Caliche Salt Deposits, Soils, Fertilizers, and Plants

soils[a]	location	description	ClO_3^- ($\mu g\,kg^{-1}$)	ClO_4^- ($\mu g\,kg^{-1}$)	Cl^- ($mg\,kg^{-1}$)	NO_3^--N ($mg\,kg^{-1}$)
P1	Atacama, Chile	6 m depth, caliche	340 000	240 000	80 000	12 000
P2		6 m depth, halite caliche	330 000	330 000	460 000	44 000
P4		50 cm depth, chunk of $NaNO_3$	530 000	130 000	61 000	22 000
UIC 24		Vertical vein (J-470)	20 000	220 000	130 000	66 000
DV3	Death Valley,	Confidence Hills-1 caliche	41 000	250	320 000	1 800
DV4	California	Bully Hill caliche	600	800	80 000	28 000
DV5		Saratoga Hills-1 caliche	32 000	950	63 000	5 900
DV6		Zabriskie caliche	57 000	1 700	140 000	4 400
G25S	Amargosa Desert,	0–30 cm depth, G-sets	3.0	2.5	5.9	1.8
G43S	Nevada		4.7	4.5	7.2	2.2
G73S			2.5	19	3.6	<1.0
D15		0–30 cm depth, D-sets	7.6	2.1	71	24
D16			13.0	2.7	134	51
D17			1.7	0.2	<1.0	<1.0
D18			2.0	0.2	1.9	<1.0
AF1	Namibia, Africa	surface sample from evaporation point near Hosabes spring	70	400	352	1100
AN1	University Valley, Antarctica	surface sample	37	202	540	410
fertilizers[b,c]						
[b]USGS-35	Atacama derived	$NaNO_3$ high purity chips from Chile	53 000	260 000	NA	166 000
[b]RSIL N7791		$NaNO_3$ industial-grade from SQM Industries	150 000	2 375 000	NA	170 000
[b]Chile-375		$NaNO_3$ refined pellets	520 000	2 130 000	NA	166 000
[c]NCB001–1		SQM industries- new process	7 100	22 000	NA	160 000
plants						
G71P	Amargosa Desert,	Creosote bush	380	45 000	NA	NA
G62P	Nevada	(*Larrea tridentata*)	180	37 000	NA	NA
G44P			160	15 000	NA	NA

[a] ClO_4^-, Cl^-, and NO_3^- data for the Atacama (P1, P2, P4 and UIC 24) and Death Valley (DV- 3, 4,5 and 6) caliche samples were obtained from a previous study (*18*). [b] Atacama fertilizer samples as described in a previous study on ClO_4^- occurrence in Long Island groundwater (*14*). [c] Recent Atacama-derived fertilizer sample after processing for ClO_4^- reduction.

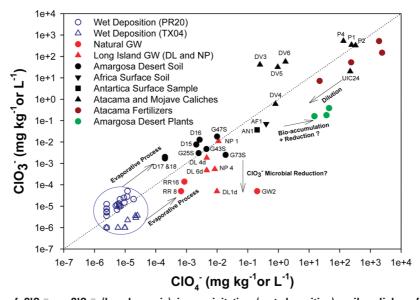**FIGURE 1. Comparison of ClO_3^- vs ClO_4^- (log–log axis) in precipitation (wet deposition), soil, caliches, fertilizers, groundwater (GW), and plant samples from different sites. Concentration units for soil and plant samples are in mg per kg-dry sample whereas for precipitation and groundwater samples, units are mg per L of sample. The arrows represent abiotic and biotic processes that could account for different concentrations and ratios of ClO_3^- and ClO_4^- in the environment, with the hypothesis being that precipitation is the major source of natural ClO_3^-.**

$240 \pm 122\,\mu g\,kg^{-1}$ ($n = 3$), which is about 2 orders of magnitude greater than the soil values (Table 2), indicating possible bioaccumulation in the plants (Figure 1). The corresponding average ClO_4^- concentration in the plant samples was $32\,000 \pm 16\,000\,\mu g\,kg^{-1}$. The average mass ratio of ClO_3^- to ClO_4^- in the plants was 0.008 ± 0.003, considerably lower than in soils (1.0 ± 0.7) from the same site, possibly indicating relative loss of ClO_3^- by microbial reduction in the root zone or after uptake with respect to ClO_4^-. A comparison of a plant sample

chromatograph with a standard similar to the sample concentration and laboratory reagent blank shows identical IS peak characteristics (Figures S3 and S4 of the SI). The deviation in the extraction duplicate was within 6% ($n = 1$) and the recovery of the spike was 108% ($n = 1$).

Chlorate in Atmospheric Deposition. The presence of naturally occurring ClO_4^- in the environment has been attributed to atmospheric generation, deposition, and accumulation processes (*15–18*). To investigate possible
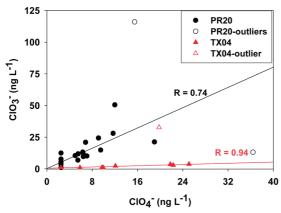
FIGURE 2. Comparison of measured ClO_3^- and ClO_4^- concentrations in precipitation samples from Puerto Rico and Texas. Data for ClO_4^- obtained from ref _19_.

codeposition of ClO_3^-, weekly precipitation samples previously analyzed for ClO_4^- (_19_) were obtained from National Atmospheric Deposition Program (NADP) sites at Big Bend National Park in southwest Texas (TX04, elevation = 1056 m), and El Verde in eastern Puerto Rico (PR20, elevation = 380 m) for the year 2005. The 2005 annual precipitation amounts at the TX04 and PR20 sites were 26.6 and 315.5 cm, respectively (_32_). The sample collection protocol and details of shipping and handling of samples are described elsewhere (_19_). The ClO_3^- concentrations in the precipitation samples ranged from <2 ng L^{-1} to 116 ng L^{-1} (n = 38). Average ClO_3^- concentrations for the PR20 and TX04 sites, after elimination of values below the MDL, were 19 ± 25 (n = 21) and 9.0 ± 13 ng L^{-1} (n = 7), respectively. For comparison, the average ClO_4^- concentrations were 7.1 ± 3.2 and 21 ± 24 ng L^{-1} for the PR20 and TX04 sites, respectively (_19_). A plot of ClO_3^- vs ClO_4^- (Figure 2) indicates a positive but scattered correlation between these ions in the combined data set from both sites ($R \approx 0.38$, $p > 0.05$). When one TX04 and two PR20 extreme values of ClO_3^- and ClO_4^- are removed as outliers, there are significant correlations at both sites (R = 0.74 and 0.94 with $p < 0.001$ for PR20 and TX04, respectively) (Figure 2). The mass ratios of ClO_3^- to ClO_4^- for TX04 and PR20 sample sets (minus the outliers) were 0.12 ± 0.02 and 2.00 ± 0.40, respectively. The ClO_3^- to ClO_4^- mass ratios produced in the laboratory by aqueous O_3 and UV oxidation experiments with various Cl species range from 40 to 5000 (_8, 10, 11_), whereas preliminary experiments involving oxidation of dry Cl^- salts coated on sand and glass resulted in lower ratios of 0.1 to 30 (_9_). Our measured ClO_3^- to ClO_4^- ratios in precipitation samples are more like those of "dry" oxidation experiments, and much lower than those of aqueous O_3 and UV oxidation experiments. Further studies on the heterogeneous oxidation of Cl species may provide a more detailed picture of the inter-relation of natural production of ClO_4^- and ClO_3^-.

Chlorate in Groundwater. Archived groundwater samples containing "indigenous" natural ClO_4^- were obtained from the southern high plains (SHP), Texas (sample GW2) and the Middle Rio Grande Basin (MRGB), New Mexico (samples RR8 and RR16) (_16, 18_). ClO_4^- in the SHP groundwater has been attributed to flushing of subsurface salts accumulated over ∼10 000 years as a result of modern irrigation (_18_). The MRGB groundwaters have apparent ages >15 000 years and are thought to represent mountain-front recharge from low elevations with high dissolved O_2, and major anion concentrations representing atmospheric fluxes with varying amounts of evapotranspiration (_16, 18_). The relatively low ClO_3^- to ClO_4^- mass ratios in the SHP groundwater (<0.0005) and MRGB groundwater (≤0.2) as compared to some of the atmospheric deposition and other terrestrial samples may indicate that ClO_3^- was less stable than ClO_4^- at some point

in the subsurface hydrologic cycle (Table S4 of the SI). The SHP and MRGB samples are from locations with no known anthropogenic ClO_4^- contamination, and therefore with no known cause for artificial bias to lower the ClO_3^- to ClO_4^- mass ratio. Nitrate in GW2 may have been partially denitrified, as indicated by elevated $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios (_18_), in which case ClO_3^- or ClO_4^- also might have been susceptible to reduction in soil or groundwater. As the groundwater samples were filtered and remained oxygenated before analysis, we expect ClO_3^-, like NO_3^- and ClO_4^-, may have been reasonably stable during sample storage, but this was not tested systematically and further study may indicate otherwise.

Archived groundwater samples (n = 7) from a previous study of ClO_4^- sources in Suffolk County, Long Island, New York (_14_), also were analyzed for ClO_3^- (Table S4 of the SI). Three samples (DL1d, DL4d and DL6d) were from observation wells in an agricultural area. Two samples (NP1 and NP4) were from relatively deep production wells in a transitional area that formerly was largely agricultural. All 5 DL and NP samples had ClO_4^- with isotopic compositions indicating it was introduced with NO_3^- fertilizer from the Atacama Desert. Two additional Long Island samples (BM1 and BM2) were from observation wells at a former missile site that was used as a police training facility at the time of sampling. Both BM samples had exceptionally high ClO_4^- concentrations, with isotopic compositions indicating synthetic origin (_14_). The ClO_3^- concentrations were highest in well water from BM1 and BM2 (190 and 20 μg L^{-1}, respectively) (Table S4). The water from the BM1 and BM2 was interpreted to contain salts (including ClO_4^-, K (potassium), Sr (strontium), Sb (antimony)) derived from leaching of unexploded fireworks from a fireworks disposal area upgradient from the wells (_14_). Thus the source of high ClO_3^- in these wells also may be from the fireworks disposal area, which would be consistent with use of ClO_3^- in fireworks (_13, 33_). Concentrations of ClO_3^- were one to several orders of magnitude lower in the NP and DL samples, ranging from <0.1 to 1.84 μg L^{-1} (Table S4 of the SI). The co-occurrence of ClO_3^- in all the sampled Atacama NO_3^- fertilizers (Table 2), and the likely agricultural source of the elevated ions (NO_3^-, ClO_4^-, Ca (calcium), and Mg (magnesium)) in the NP and DL samples (_14_), indicates that ClO_3^- in the NP and DL groundwater samples may have originated from the use of these fertilizers, although some ClO_3^- in production wells could also be derived from well treatment procedures.

Implications. Our proposed method for ClO_3^- analysis by IC-ESI-MS/MS with a $Cl^{18}O_3^-$ isotopic internal standard provides a highly specific and sensitive method, particularly when compared with other currently available techniques. Further, this method requires minimal sample preparation without the use of cleanup cartridges (e.g., silver and barium) for most natural water and soil samples. Limited data from a variety of matrices show that natural ClO_3^- is widespread in the environment, having been detected in precipitation, plants, soils, and desert caliche deposits at magnitudes similar to that of ClO_4^- (Figure 1). Although the comparison of ClO_3^- concentration in different sample matrices is not straightforward, the ratio of ClO_3^- to ClO_4^- can still be used to assess the processes involved in the ClO_3^- geochemical cycle. High concentrations of ClO_3^- in caliches and soils compared to precipitation samples indicates that ClO_3^-, like ClO_4^-, may be atmospherically produced and deposited, then concentrated in dry soils, and is possibly a minor component in the biogeochemical cycle of chlorine (Figure 1). Comparatively lower concentrations of ClO_3^- in natural groundwater samples and plants analyzed to date, though limited in number, may imply relatively low stability of ClO_3^- compared to ClO_4^- in the subsurface or biosphere. The presence of natural ClO_3^- in environments similar to ClO_4^- could potentially explain why there is a variety of micro-organisms capable of specifically

reducing ClO_3^- to Cl^- in the natural environment, as all ClO_4^- reducing bacteria described to date also utilize ClO_3^- as a terminal electron acceptor (*34*). Further, if the current understanding of formation mechanisms of natural ClO_4^- is accurate, then it is possible that ClO_3^- co-occurs with ClO_4^- and even accounts for some of the reported ClO_4^- detected on Mars by the Ion Selective electrode (ISE) since ClO_3^-, like ClO_4^-, has high selectivity for the ISEs as dictated by the Hofmeister series (*35*). Further work on the terrestrial distribution of ClO_3^- may provide useful information about sources and fate of ClO_4^- and other oxy-anions.

Acknowledgments

Supporting Information Available

Details of the extraction procedure for soils and plants, sample chromatograms, and groundwater analysis (Table S1–S4, Figure S1–S4). This information is available free of charge via the Internet at http://pubs.acs.org/.

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