The Origin of Naturally Occurring Perchlorate: The Role of Atmospheric Processes

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Perchlorate, an iodide uptake inhibitor, is increasingly being detected in new places and new matrices. Perchlorate contamination has been attributed largely to the manufacture and use of ammonium perchlorate (the oxidizer in solid fuel rockets) and/or the earlier use of Chilean nitrate as fertilizer ($\sim$0.1% perchlorate). However, there are regions such as the southern high plains (Texas Panhandle) where there is no clear historical or current evidence of the extensive presence of rocket fuel or Chilean fertilizer sources. The occurrence of easily measurable concentrations of perchlorate in such places is difficult to understand. In the southern high plains groundwater, perchlorate is better correlated with iodate, known to be of atmospheric origin, compared to any other species. We show that perchlorate is readily formed by a variety of simulated atmospheric processes. For example, it is formed from chloride aerosol by electrical discharge and by exposing aqueous chloride to high concentrations of ozone. We report that perchlorate is present in many rain and snow samples. This strongly suggests that some perchlorate is formed in the atmosphere and a natural perchlorate background of atmospheric origin should exist.

Introduction

Presently there is great concern that the lower Colorado River is contaminated with $4-16$ μg/L levels of perchlorate (*1*). The source of this contamination is believed to be ammonium perchlorate, made in millions of tons during the cold war as the preferred missile propellant. In March 2004, California became the first state to set a drinking water public health goal (*2*, *3*) of 6 μg/L. At least seven other states (AZ, MA, MD, NM, NV, NY, TX) have advisory levels (*4*, *5*) that range from 1 to 18 μg/L. The U.S. Environmental Protection Agency has recommended a regulatory level of 1 μg/L in drinking water;

this is considered unrealistic and unwarranted by three other U.S. federal agencies. An advisory opinion from the National Academy of Sciences is expected to settle this controversy. With the ability to detect sub-μg/L levels, perchlorate is increasingly being found in a variety of places and a variety of matrices.

Concern about Perchlorate. Broadleaf vegetables such as lettuce irrigated with Colorado River water in Arizona and the central valley of California have been reported to accumulate perchlorate (*6*). A recent study by Food and Drug Administration (FDA) scientists show median concentrations in lettuce (CA and AZ), as well as in edible portions of cantaloupe (AZ) to be 10 μg/kg; whole cantaloupe registered much higher (*7*). These findings suggest that human exposure to perchlorate may come from sources beyond drinking water. The concern about perchlorate stems from the fact that it displaces iodide from the thyroid gland. This particular property of perchlorate is utilized in the "perchlorate challenge" test, which has long been used to assess the efficiency of iodide uptake by the thyroid gland (*8*). The problem is that even at much lower dosages than those used in the perchlorate challenge test, perchlorate competitively inhibits iodide transport. Iodine-containing thyroid hormones are essential for proper neural development from the fetal stage through the first years of life (*9*−*11*). This concern is therefore particularly relevant to pregnant and lactating mothers and young children. In a study (*12*) of randomly bought dairy milk samples in Lubbock, a small Texas city, all 7 samples were found to contain perchlorate by ion chromatography − mass spectrometry, in the range of $1-6$ μg/L. Since that time, milk samples from across California have also been reported to contain perchlorate at comparable or higher levels (*13*, *14*). Initial measurements by the FDA in milk from various states by ion-chromatography-tandem mass spectrometry show a median value of 6.5 μg/L (*7*).

Perchlorate in Southern High Plains Groundwater. The first discovery of perchlorate in groundwater in the U.S. came from a sampling of wells in San Gabriel Valley, CA, in early 1985 (*15*). Since a large rocket engine test facility in the area utilized leach pits for disposal and gravel pits for burning of leftover fuel, it was easy to attribute a source. More recently, "rocket fuel" has become a synonym of perchlorate in the popular press. However, perchlorate has been found in readily measurable concentrations in places where no anthropogenic sources can be readily ascertained. For example, the groundwater in a 775 km^2 area straddling Gaines and Dawson Counties in the Southern part of the Texas panhandle consistently measures over 20 μg/L perchlorate, some samples approach 60 μg/L perchlorate (*16*). This original 9-county study (*16*) has now been extended to 56 counties, 54 in Texas (137,000 km^2) and 2 in NM (17,600 km^2) (*17*). Perchlorate was found (limit of detection (LOD) 0.1 μg/L, with >22% of the sample measuring 4 μg/L) in groundwater in 51 of these 56 counties. At least in this region, perchlorate is commonly present in groundwater.

Can the Historical Use of Chilean Nitrate Account for the Perchlorate in the Southern High Plains Groundwater? If anthropogenic perchlorate made for use as oxidizer is not obviously responsible, perchlorate originating from Chilean nitrate is usually assumed to be the source. Historically, Chilean nitrate has been used as fertilizer in the U.S. and throughout the world. The presence of perchlorate in naturally occurring Chilean saltpeter was reported by Beckurts (*18*) as early as 1886. The average Chilean caliche ore reportedly contains 6.3% nitrate and 0.03% perchlorate by weight (*19*, *20*). The nitrate fertilizer is produced by solution

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processing of the deposit. Official reviews state that a typical bag of such a "natural" nitrate fertilizer is labeled 98 wt % $NaNO_3$ and 0.09 wt % $KClO_4$ or 0.065 wt % ClO_4^- (20). While some commonly marketed Chilean nitrate based "natural" fertilizers may actually contain 0.2−0.4 wt % ClO_4^- (21, 22), others suggest a range of 0.05−0.2 wt % ClO_4^-(23) with 0.1 wt % thus being an appropriate median value.

The total production of Peruvian and Chilean $NaNO_3$ from 1830 to 1980 (peak production was in 1930) for worldwide distribution was ∼23 million metric tons (Mton, 1000 kg) in terms of N. Chilean nitrate was a major source of nitrogen fertilizer only until the 1930s. Commercial production of synthetic nitrogen fertilizers began by 1915 and surpassed Chilean nitrate use in ∼15 years. By 1950 and 1980, Chilean nitrate respectively accounted for 15% and 0.14% of the world market for fixed nitrogen (24). The U.S. was significantly ahead of the world as a whole in commercializing synthetic N fertilizers; it would be reasonable to believe that the Chilean nitrate share of the total N fertilizer market was lower in the U.S. than in the globe as a whole. Renner (25) anecdotally quotes a 1999 annual U.S. use figure of 68,000 Mtons Chilean nitrate. However, according to other sources (26), the total use of $NaNO_3$ (Chilean and synthetic) in the U.S. had already dropped to 31,500 Mtons by 1994; this is ∼0.3% of the total of 11.4 million Mton N fertilizer used in the same year. It is not known how much of this $NaNO_3$ used is actually Chilean nitrate. One of the marketing strategies for Chilean nitrate is that it is a natural, low-chloride fertilizer. It is often used in "organic" cultivation. Ironically for health conscious consumers, of the lettuce samples we had tested (27), the "organically grown" sample had by far the largest perchlorate content.

There is no historical record of how much Chilean nitrate has been used as fertilizer in specific geographical regions, including the 56-county area in TX and NM referred to above. According to Beaton (26), in the early 1900s, 90% of the N fertilizer consumed in the U.S. was organic N fertilizers, to which cottonseed meal and animal manure were major contributors. Given the current agricultural practice in the southern high plains where growing cotton and farming cattle play dominant roles, it is highly unlikely that Chilean saltpeter was ever the dominant N fertilizer in this region. Irrigated agriculture here largely started after the 1950s, and many of the counties in this semi-arid region still practice only dryland farming. Jackson et al. (16) estimated that the mass of perchlorate under the 9-county area is 974 Mtons. At 0.1% perchlorate content, it will require 974,000 Mtons (156,000 Mtons N) of Chilean nitrate, ∼0.7% of the total ever produced, just to serve this area. Calculations involving (a) best estimates of irrigated cultivated acreage in our study area averaged over the period since the production of Chilean nitrate began and (b) regional N fertilizer recommended application rate of 50 kg/acre-year (28) for cotton, the principal crop in this region show that for many counties it will require well over 100 years of exclusive Chilean nitrate use to account for the perchlorate observed. Further, this assumes that perchlorate is completely conserved. While we do not claim that no Chilean nitrate was ever used in this area, any reasonable projected use of Chilean nitrate (as well as other currently known sources of perchlorate, e.g., fireworks, matches, roadside flares, explosive disposal etc.) falls far short of accounting for the observed perchlorate levels.

Naturally Occurring Perchlorate. Early reports that large concentrations of perchlorate exist in seawater or in a number of Australian natural brine and saline deposits (29) were discredited by subsequent work (30, 31). However, one of these studies (31) showed the presence of perchlorate in natural products e.g., cabbages and beets (6.5−8.5 $\mu g\ kg^{-1}$) suggesting that it is bioaccumulated from the environment. It is noteworthy that these analyses, carried out more than

4 decades ago show the same order of perchlorate content that is presently being reported in lettuce, cantaloupe etc. (7). It is not possible, of course, to ascertain either the reliability of this analysis or to determine the source, if it can be considered reliable. The possibility that rocket fuel perchlorate was present as a contaminant in the early 1960s in Black Mountain, Canberra, Australia where the cabbage and beet specimens were grown (31) is moot (Haddad, P. R.; University of Tasmania, Hobart, Australia, personal communication, 2004). While possible application of Chilean nitrate fertilizer cannot be excluded, the presence of perchlorate in the natural environment at low levels is an equally plausible explanation. Of interest is that it has been reported that some batches of fertilizers *not* derived from Chilean nitrate also contain traces of perchlorate (32, 33).

The Chilean deposits are the largest known natural reservoir of perchlorate. The exact origin of these deposits has represented a considerable puzzle. During most of his career Ericksen, who spent a lifetime on these deposits (24), ascribed a biological origin to Chilean nitrate. However, a posthumous paper coauthored by Ericksen concluded that the nitrogen and oxygen isotopic analysis data were consistent with virtually all the nitrate being of atmospheric origin (34). A recent study (35) suggests that these deposits originated primarily from atmospheric deposition of particles produced by gas to particle conversion over a period of 0.2 to 2.0 million years.

While average concentration data for a large number of samples are not available, in one of the samples of Chilean nitrate from a nitrate-rich vein, Bohlke et al. (34) found iodate, perchlorate and chromate in the range of 100−1000 $mg\ kg^{-1}$. Mechanisms of tropospheric production of iodate are well established (36, 37). In aerosol samples from the tropical Atlantic, iodate was the dominant iodine species (38). This would suggest that perchlorate in the Chilean nitrate may also be of atmospheric origin. Although the presence of chromate in the Chilean deposits is more difficult to rationalize, the pathway may involve gaseous chromyl chloride (CrO_2Cl_2) that is formed under highly acidic and oxidizing conditions. It has recently been suggested that over geologic periods of time, soluble ions such as nitrate can accumulate in subsoil zones beneath deserts and warm shrublands (39). If produced in nature from atmospheric sources, perchlorate may also accumulate in a similar manner. Recent studies on oxygen isotope signatures show that the perchlorate in Chilean saltpeter differs distinctly from synthesized perchlorate (40). Orris et al. (41) have reported the presence of perchlorate in evaporite deposits from many parts of the world. They found potash ores from our neighboring deserts near Carlsbad, NM, believed to be 240−250 million years old (42, 43), to contain 25−3700 mg ClO_4^-/kg.

If perchlorate is naturally formed, there should be detectable background levels in a variety of samples. Evidence toward this has become more recently available, as detection limits have been pushed below the parts per billion levels through IC-MS and LC/IC-MS/MS methods. Roefer et al. (44) have reported detectable levels of perchlorate in the upper Colorado river nearly to the headwaters.

Perchlorate Formation Pathways. Simonaitis and Heicklen (45) proposed in 1975 that $HClO_4$, not as subject to photodecomposition and radical attack as HCl, may be an important sink for stratospheric chlorine. Chlorate radical (•ClO_3) may be formed as an intermediate via reaction 1 (Table 1) and may then be acted on by •OH to produce stable $HClO_4$. Table 1 represents an expanded version of the Simonaitis-Heicklen view, and some of these reactions (reactions 4 and 8) are part of the well-known chlorine-ozone reaction chain (46).

TABLE 1. Atmospheric Reactions that May Lead to Perchlorate

reaction number	reactions
(1)	$Cl\bullet + O_3 + M \rightarrow ClO_3\bullet + M$
(2)	$Cl\bullet + O_2 + M \rightarrow ClO_2$
(3)	$Cl\bullet + O_3 \rightarrow ClO_2 + \bullet O$
(4)	$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
(5)	$ClO\bullet + \bullet O + M \rightarrow ClO_2$
(6)	$ClO\bullet + O_2 \rightarrow ClO_2 + \bullet O$
(7)	$ClO\bullet + O_3 + M \rightarrow ClO_2 + O_2$
(8)	$ClO\bullet + ClO\bullet + M \rightarrow Cl_2O_2$
(9)	$Cl_2O_2 \rightarrow Cl\bullet + ClO_2$
(10)	$ClO\bullet + O_2 + M \rightarrow ClO_3\bullet$
(11)	$Cl_2O_2 + O_3 \rightarrow ClO_3\bullet + ClO_2$

Using balloon-borne interferometric measurements, Jaegle et al. (47) reported that at altitudes between 15 and 20 km, up to 60% of the inorganic chlorine could not be accounted for by the sum of measured HCl, ClONO$_2$, and HOCl. Based on laboratory measurements of the reaction of •ClO with sulfuric acid to form small amounts of HClO$_4$, they suggested that HClO$_4$ may account for the balance of the stratospheric chlorine.

More recently, in flights on the WB-57 aircraft that extended to altitudes up to 19 km, Murphy and Thomson (48) used single particle mass spectrometry for chemical characterization and reported the presence of small amounts of perchlorate in stratospheric sulfate aerosols. Although the presence of chlorine containing species was more abundant in the tropospheric aerosol, the presence of perchlorate was not noted. Interestingly, peaks due to the ions ClO$^-$, ClO$_2^-$, and ClO$_3^-$ were also observed in these experiments but were believed to have originated from the fragmentation of ClO$_4^-$.

If the present stratospheric chlorine burden is dominated by chlorofluorocarbon precursors, large deposits of perchlorate cannot be accounted for by stratospheric perchlorate production over geologic history unless volcanic injection of chlorine into the stratosphere was much higher over that period. Before one enters that speculative domain, it may be useful to look at the possible production of perchlorate in the troposphere where precursor chlorine compounds are much more abundant.

Tropospheric Perchlorate Production. Of all chlorine containing anions, Cl$^-$ ($\Delta G_f^\circ = -137$ kJ/mol) is the most stable. Hypochlorite (OCl$^-$ $\Delta G_f^\circ = -37$ kJ/mol) is routinely formed when molecular Cl$_2$ dissolves in water. It is industrially sold in large quantities as one of the products from chlor-alkali cells. Hypochlorite spontaneously disproportionates to chlorate (ClO$_3^-$, $\Delta G_f^\circ = -3$ kJ/mol) and chloride. This process is slow at room temperature but accelerates rapidly when heated. Chlorate is industrially produced by electrosynthesis of OCl$^-$ from NaCl and then thermally processed to produce chlorate (49), which is used as an oxidizer in a multitude of products. Perchlorate ($\Delta G_f^\circ = -9$ kJ/mol) is not only kinetically stable, its formation from hypothetical processes such as the disproportionation of OCl$^-$ into Cl$^-$ and ClO$_4^-$ or by addition of oxygen to ClO$_3^-$ would be thermodynamically favored. Perchlorate is made by electrooxidation of chlorate (50). The reason that ClO$_4^-$ is not formed in appreciable amounts from the disproportionation of OCl$^-$ or during the electrosynthesis of OCl$^-$ may be kinetic.

Given the precursor ingredients and sufficiently energetic conditions, it should thus be possible to induce the formation of perchlorate. As to OCl$^-$ as a precursor, based on experimental evidence, Winkler et al. first suggested that active chlorine (including molecular or atomic Cl$_2$ and its aqueous dissolution product HOCl) can be formed from sea-salt–NO$_x$ reactions via the production of NOCl and its subsequent photolysis (51). In the marine troposphere, oxidation of organics by atomic chlorine may rival or even exceed that by •OH under some conditions (52). Experimental evidence for the presence of Cl$_2$/HOCl in the marine atmosphere in the range of 0.025−0.25 ppbv is now a decade old (53). Oum et al. (54) have since suggested that an important global source of molecular chlorine (and hence aqueous hypochlorite) is the photolysis of ozone in the presence of sea-salt. Recent model calculations confirm that HOCl should be present in sea-salt aerosols as well as cloudwater (55). Very recently, Cl$_2$ and HOCl were found in measurable levels in both super- and submicron marine aerosol in Oahu, HI (56).

Either ClO$_2$ or •ClO$_3$ may be plausibly formed in the troposphere in a number of pathways (Table 1). Either ClO$_2$ or ClO$_3$• can then be converted to HClO$_4$ by respective reactions with •OOH and •OH. Electrooxidation of ClO$^-$ is known to produce ClO•, ClO$_2$, ClO$_2^-$ and ClO$_3^-$ (57).

Experimental Section

Analysis of Rain and Snow Samples by Large Volume Preconcentration. Rain and snow samples were mostly local with a few samples from other regions as noted. Between 5 and 20 mL samples were preconcentrated directly from the collection containers to avoid possible contamination, Filtered nitrogen pressurization (∼15 psi) of the container was used to achieve sample loading (0.9−1 mL/min) for PC− PE IC (58) coupled to MS analysis (12).

Sonication and High Energy Electrical Discharge. Approximately ∼20 mL of the sample was sonicated for 4 h in a thermostated vessel (25 °C) at 20 kHz. The power density at the transducer face (0.5 cm dia.) was 17 W/cm^2 (Sonics & Materials, Vibra-cell VC 505, 500 W direct immersion sonicator). Synthetic seawater in this and other experiments utilized "Instant Ocean" (www.aquariumsystems.com/salts.htm); the composition has been reported (59).

In high energy electrical discharge experiments (conducted in the TTU pulsed power research laboratory, http://www.ee.ttu.edu/ee/faculty/pppr.htm), 7 kJ were discharged in a 100 ns pulse across a 7 mm gap between two stainless steel electrodes submerged in the water sample. Because of the high level of the instantaneous power (70 GW) safety constraints required that the electrodes be immersed in a large volume (∼15-L) of the water sample. Unfortunately, this caused large dilution of any perchlorate that may have been produced.

Aerosol Generation and Characterization. Sodium chloride and NaCl/NaOCl aerosols were generated by a pneumatic concentric nebulizer. The aerosol size was measured by a laser optical particle counter (A2212, Met-One Inc.) The aerosol had a mass median aerodynamic diameter of 0.66 μm with a geometric standard deviation (σ_g) of 2.55. Aerosol mass concentration was measured by filter collection, extraction, and IC analysis to be 0.5−1.0 μg m^{-3}. Commercial NaOCl contains measurable amounts of perchlorate. Addition of commercial NaOCl to the NaCl nebulizer feed raised perchlorate level in the control aerosol to levels that were deemed too high to permit ready detection of additional perchlorate. For this reason, we generated NaOCl in-situ by passing an electrical current (20 mA) through 500 mL of 500 mM NaCl between a platinum anode and a stainless steel cathode (5 × 6 cm active area each) placed 6 cm apart. The total coulombs passed would have converted 0.7% of the NaCl present to NaOCl if NaOCl production was 100% current efficient. However, some of the anodic product is O$_2$ rather than OCl$^-$, resulting in 0.5% conversion of the NaCl to NaOCl. This solution was diluted 10-fold to generate the nebulizer feed. The concentration of the NaOCl in this feed was measured by iodometric titration and found to be 0.25 mM.

Generation of Sustained Electrical Discharge and Analysis of Aerosol. Electrical discharge was created between two automotive spark plugs placed 0.3 cm apart and sealed in two opposing arms of a 2.5 cm bore cross-fitting. The

experiment utilized a square wave generator (760 Hz) and an automotive ignition coil that produced a high voltage (15−20 kV). The primary energy input was 15 W. The aerosol passed through the perpendicular arms of the cross @ 0.14−0.2 standard liters/min and was collected on thoroughly prewashed and dried polycarbonate membrane filters (0.22 μm pore size). The duration of each experiment was 24 h. The filter was then extracted in deionized water and analyzed respectively by IC and IC-MS for Cl^- and ClO_4^-.

Simulated Desertification Conditions with UV/UV−High Level O_3 Exposure. Experiments were conducted in sealed acrylic chambers (0.02 m³). Each chamber contained 2 glass dishes in each of which 500 g of triple-washed Ottawa sand was spread in an even layer. Regimens included (a) control (room light, house air 300 mL/min), (b) UV exposed (house air, 300 mL/min) and (c) ozone exposed conditions (vide infra). UV exposure was produced by 4 UV lights (Spectroline) at a height of 15 cm above the base of the chamber. Of the 4 lights, two emitted at 254 nm (model EF180C, 1180 610 μW/cm² at 15 cm) and two emitted at 312 nm (model EB160C, 610 μW/cm² at 15 cm). For ozone exposures, three separate chambers were exposed to different ozone concentrations by flowing house air through ozone generators (Enaly, EOZ-300Y, http://stores.ebay.ca/ENALYOZONE_W0QQsspagenameZl2QQtZkm) at flow rates of 75, 120, and 300 mL/min (respectively corresponding to measured ozone concentrations of 1300, 1100 and 880 ppmv). Each glass dish initially received 100 mL of a ~650 mg/L solution of Cl^- as NaCl made up in Milli-Q (MQ) water. At the beginning of the experiment, 10 mL of solution was removed from each dish. The dish was then weighed. After 2 days, the dishes were weighed and sufficient MQ water was added to reattain the preexposue weight. The dish was then resampled (10 mL), weighed again and exposure continued. After 4 days, sufficient MQ water was again added to the dishes to reattain the last weight. The dishes were resampled. All samples were analyzed by IC as well as IC-MS.

Parameters Measured in Table 4. Alkalinity was measured by standard established methods. All anions except iodate were measured by suppressed conductometric IC. All metals were measured by Induction Coupled Plasma − Optical Emission Spectrometry on a Leeman Labs DRE-D instrument. Fully validated methods do not exist for iodate in ground-water. We used an ion pair chromatography approach using a cationic ion pairing agent (Waters, Pic-A), a 10 mM KH_2PO_4 eluent at pH 6.0 and a C-18 reverse phase column) on an Agilent 1100 HPLC system with UV detection at 214 nm (Agilent G1314A); very similar approaches are in the literature (60).

Results and Discussion

Rain and Snow Samples. The results are shown in Table 2. The LOD with a 20 mL sample preconcentrated was below 0.01 μg/L. Chloride, nitrate and sulfate were measured in some of the samples. Perchlorate was detectable in 70% of the samples and ranged from below the limit of detection to 1.6 μg/L. There are not enough data at this point to attribute any meaningful correlations. However, one cannot help but note that the highest perchlorate concentration sample also had the highest nitrate concentration. This is likely an indicator of a storm that had considerable amount of electrical activity and hence generated NO_x. For the available data (substituting 0 for "ND" and 0.01 for "trace" in Table 2), nitrate is correlated with perchlorate concentration with an r^2 value >0.6. It is also interesting to note that the hurricane Frances sample had the second highest perchlorate concentration measured. Figure 1 shows the conductivity based ion chromatogram for the rain sample from April 6, 2004 as an illustrative example. The inset of this figure shows the

TABLE 2. Perchlorate Concentrations in Atmospheric Precipitation[a]

date		concentrations, μg/L			
		perchlorate	chloride	nitrate	sulfate
8/8/2003	rain[b]	ND[c]			
9/20/2003	rain	0.1			
2/24/2004	snow	0.08			
2/25/2004	snow	0.4			
4/6/2004	rain	0.2	520	130	390
4/8/2004	rain	0.2	95	300	1000
4/30/2004	rain	ND			
5/8/2004	rain	0.2			
5/10/2004	rain	0.6			
5/11/2004	rain	0.06	170	400	1830
6/3/2004	rain	0.3	310	200	840
6/19/2004	rain	ND	700	780	2900
6/28/2004	rain	ND			
6/29/2004	rain	ND			
7/23/2004	rain	trace[d]	100	170	480
7/23/2004	rain[e]	trace			
7/27/2004	rain	1.6	900	1700	4600
7/30/2004	rain	0.1	220	100	430
8/6/2004	rain	0.02			
8/7/2004	rain	0.02	1300	510	1170
8/23/2004	rain	0.02			
8/30/2004	rain	0.6	14300	280	7450
8/30/2004	rain[e]	0.5			
9/5/2004	rain[f]	0.6			
9/5/2004	blank[f,g]	ND			
11/2/2004	snow	ND			
11/2/2004	snow	ND			

[a] Samples collected in Lubbock, Texas, except as mentioned, all perchlorate data are a minimum of duplicate analyses. At 0.2−0.3 μg/L in real samples, the RSD in replicate in measurements is 14−20%; therefore with the exception of 1 sample, results have one significant figure only. [b] Hingham, MA. [c] Not detectable. [d] Trace, detectable but below the limit of quantitation. [e] Second sequential sample. [f] Cocoa Beach, FL. Hurricane Frances. [g] Field blank.
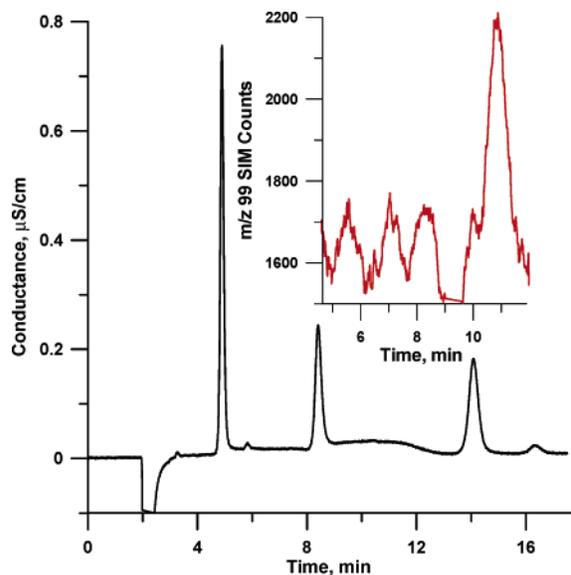

FIGURE 1. Rain chromatogram; April 6, 2004 sample (Table 1). Suppressed conductivity chromatogram, the principal three peaks are from 520, 130 and 390 μg/L chloride, nitrate and sulfate. The inset shows the PC-PE-IC-MS chromatogram of the same sample with selected ion monitoring at m/z 99 ($^{35}ClO_4^-$), the peak at 10.8 min corresponds to 0.24 μg/L ClO_4^-.

PC-PE-IC-MS chromatogram of the same sample in the selected ion monitoring mode at m/z 99, corresponding to $^{35}ClO_4^-$.

TABLE 3. Perchlorate Formed under Simulated Desertification Conditions and O₃/UV Exposures

	t = 0 days perchlorate formed, µg/L	t = 2 days perchlorate formed, µg/L	t = 4 days		
			perchlorate formed, µg/L	total chloride loss, mg/L	total nitrate formed, mg/L
O₃ low flow	<0.5	1.3 ± 0.3 (n=6)	0.6 ± 0.2 (n=5)	220 ± 80 (n=4)	415 ± 5 (n=4)
O₃ medium flow	<0.5	1.8 ± 1.1 (n=6)	3.0 ± 1.3 (n=5)	340 ± 10 (n=4)	155 ± 15 (n=4)
O₃ high flow	<0.5	2.7 ± 1.7 (n=6)	2.3 ± 1.0 (n=6)	360 ± 90 (n=4)	120 ± 30 (n=4)
UV high flow	<0.5	1.1 ± 0.6 (n=7)	1.1 ± 0.9 (n=7)	20 ± 40 (n=4)	nd
control high flow	<0.5	<0.5	<0.5	Nd[a]	nd

[a] Not detectable within experimental uncertainty.

Sonication and High Energy Electrical Discharge. Sonication of local tap water for 4 h did not enhance the perchlorate content that was discernible over the control. However, under the same conditions, the synthetic seawater sample produced up to 340 µg/L perchlorate.

Ultrasonication causes cavitation that can lead to extremely high local temperatures. We examined another high energy process — electrical discharge through a body of water. With a single discharge, perchlorate formation was not detectable over control in either tap water or synthetic seawater samples, with or without 50 mg/L levels of spiked OCl^- and/or ClO_3^-. But with 10 successive discharges through the same samples, perchlorate formation was detectable at a level of 10±1 µg/L over control in all samples. Energetically the yield of perchlorate was very poor ($\sim$50 GJ/mol). However, this encouraged us to look at another process that routinely occurs in the atmosphere: the passage of lightning through a column of chloride-bearing aerosol.

Electrical Discharge through NaCl Aerosol. There was no detectable perchlorate on the filter ($[ClO_4^-]/[Cl^-] = 0$) in the absence of an electrical discharge. When passed through the discharge, perchlorate was detectable on the filter in 9 out of 10 experiments with the $[ClO_4^-]/[Cl^-]$ ratio ranging from 1.5×10^{-4}–6.9×10^{-2} with aerosol flow rates ranging from 120 to 190 cm³ min⁻¹; this ratio increased with increasing residence time in the discharge.

In a second analogous set of experiments, the 50 mM NaCl feed solution used for generating the aerosol was partially oxidized so that 0.25 mM of the chloride was oxidized to OCl^-; some traces of perchlorate may be formed during this oxidation because the control aerosol in this case exhibited measurable perchlorate levels with $[ClO_4^-]/[Cl^-] = (1.2-3.1) \times 10^{-5}$. Perchlorate was not only detectable in 9 of 9 samples that passed through the discharge, the $[ClO_4^-]/[Cl^-]$ ratio was $(0.30-7.0) \times 10^{-3}$, 2 orders of magnitude greater than that in the control. While any benefit from the prior presence of OCl^- in the aerosol cannot be gleaned from a comparison of these two sets of results, more detailed experiments are being conducted to determine if OCl^- is mechanistically involved in the pathway of perchlorate formation. Nevertheless, these experiments clearly show that perchlorate can be formed from chloride and/or hypochlorite by processes that routinely occur in nature, notably, atmospheric lightning.

Simulated Desertification Conditions. As early as 1949, Yeatts and Taube (61) studied the kinetics of production of molecular chlorine upon reaction of ozone with chloride solutions. Aside from studies already mentioned regarding the atmospheric presence of OCl^-/HOCl, current interest in atmospheric chlorine have led others to reexamine this reaction in solution (62–65) or on the surface of NaCl particles (66). In the latter case, recent experiments show that oxygenated products do form even on the dry salt surface (67). Much of the studies in solution find or assume that OCl^- is formed. Hypochlorite can spontaneously disproportionate into ClO_3^-. It has been reported that chlorate forms

during the ozonation of chloride containing natural waters via a pathway that involves the •OH radical (68). It would be logical to assume that •OH oxidation of ClO_3^- will lead to ClO_4^-, but ClO_4^- was not measured in these experiments. As early as 1874, Fairley (69) reportedly observed the direct production of ClO_4^- from ozonation of OCl^-. Other than this, we are unaware of any work in the intervening two centuries that show that ozone-chloride reactions can form perchlorate.

Our experiments were admittedly conducted at ozone levels that are far higher than ambient. The ozone generators used also produce a significant amount of NO_x which was not measured but is evidenced from the appearance of nitrate in the solutions analyzed. Perchlorate concentrations in all samples were <0.5 µg/L at the beginning of the experiment. During exposure, much of the water evaporated from each exposed dish. The evaporation of water (and loss of chloride for O₃-exposed samples, due presumably to the loss of Cl_2/HOCl) was apparent in all experiments and increased with increasing gas flow rate through the chamber. This experimental design was a crude simulation of desertification. No loss of chloride within experimental error was observed with the UV exposure and control experiments, and no formation of nitrate or chlorate was detected in these experiments either. Although perchlorate was detected in some of the UV exposure runs, the overall levels were lower than the comparable high flow ozone experiments. Since ozone concentrations decrease in these experiments with increased ozone flow rate, it would appear that higher flow conditions that lead to greater evaporation and a more concentrated chloride solution are more conducive to forming perchlorate. So much chloride is lost from the solution in the high flow ozone exposure experiment that there is less accumulated perchlorate at the end of 4 days for the high flow, lower ozone regime than for the medium flow, higher ozone regime. In future experiments, ozone concentration and gas flow rate will be independently varied.

Perchlorate and Iodate in Groundwater. Initially we had monitored perchlorate concentrations in groundwater over a 9-county area of the Texas panhandle (16). More recently, the study area was extended to 56 counties in two states (17). Since iodate is believed to be of atmospheric origin, we determined iodate concentrations in a subset of 46 samples that came mostly from the original 9-county study and were chosen to represent the full range and distribution of perchlorate in those samples. In Table 4, we present correlation coefficients of perchlorate with the other measured parameters for only this 46-sample subset as well as for all available data. To our knowledge, iodate concentrations in groundwater have never been mapped. Iodate shows by far the best correlation with perchlorate than any other measured parameter. The iodate-perchlorate data are shown in Figure 2. A forced fit through the origin gives a iodate-to-perchlorate ratio of $\sim$14; in the only data for mined Chilean caliche that we know of, this ratio is 2 (20). Although the correlation of fluoride with perchlorate in the iodate-measured subset is the next highest, the perchlorate-fluoride

TABLE 4. Correlation of Perchlorate with Other Measured Parameters

| parameter	iodate subset r^2 N = 46	r^2, all available data N = 765
dissolved oxygen	0.0106	0.0800[a]
NO_2^-	0.0212	0.0016
NO_3^-	0.0232	0.0448
total Mn	0.0456	0.0001
total Fe	0.0684	0.0079
Ca^{2+}	0.0755	0.0310
alkalinity as $CaCO_3$	0.1009	0.0109[b]
Cl^-	0.1524	0.1526
K^+	0.153	0.1199
Br^-	0.1534	0.2411
Mg^{2+}	0.1574	0.1668
Na^+	0.2212	0.0443
Sr^{2+}	0.2734	0.2223
TDS	0.2954	0.1580
SO_4^{2-}	0.2988	0.1424
F^-	0.3679	0.0864
IO_3^-	0.4420	

[a] N = 663. [b] N = 736.
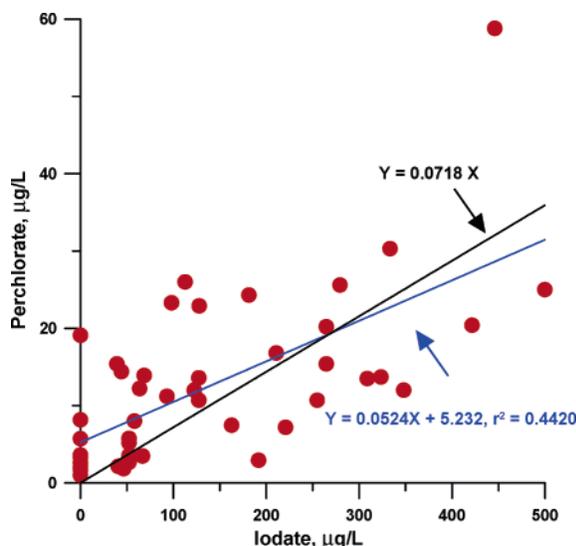
FIGURE 2. Correlation between iodate and perchlorate in Texas panhandle groundwater

correlation coefficient is not nearly as high in the full data set. The high iodate-perchlorate correlation in the Texas Panhandle groundwater is consistent with a hypothesis of atmospheric origin. However, this particular aspect needs to be supported by more extensive determination of iodate by a fully validated procedure. Although perchlorate contamination in some situations is undoubtedly anthropogenic, the presence of perchlorate in many other places would appear to be of natural origin.

Acknowledgments

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