

Perchlorate Behavior in a Municipal Lake Following Fireworks Displays

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Perchlorate salts of potassium and ammonium are the primary oxidants in pyrotechnic mixtures, yet insufficient information is available regarding the relationship between fireworks displays and the environmental occurrence of perchlorate. Here we document changes in perchlorate concentrations in surface water adjacent to a site of fireworks displays from 2004 to 2006. Preceding fireworks displays, perchlorate concentrations in surface water ranged from 0.005 to 0.081 $\mu\text{g/L}$, with a mean value of 0.043 $\mu\text{g/L}$. Within 14 h after the fireworks, perchlorate concentrations spiked to values ranging from 24 to 1028 \times the mean baseline value. A maximum perchlorate concentration of 44.2 $\mu\text{g/L}$ was determined following the July 4th event in 2006. After the fireworks displays, perchlorate concentrations decreased toward the background level within 20 to 80 days, with the rate of attenuation correlating to surface water temperature. Adsorption tests indicate that sediments underlying the water column have limited (<100 nmol/g) capacity to remove perchlorate via chemical adsorption. Microcosms showed comparatively rapid intrinsic perchlorate degradation in the absence of nitrate consistent with the observed disappearance of perchlorate from the study site. This suggests that at sites with appropriate biogeochemical conditions, natural attenuation may be an important factor affecting the fate of perchlorate following fireworks displays.

Introduction

Detection of perchlorate in groundwater and surface water around the United States has fueled recent evaluations of the source, distribution, and biogeochemical processes governing perchlorate behavior in aquatic environments. Much of the current concern over this anion stems from the fact that perchlorate ingestion may pose an adverse human health risk because perchlorate interferes with the production of thyroid hormones required for normal metabolism and the development of mental function (1, 2). Elevated perchlorate concentrations may also pose a risk to aquatic ecosystems. Fish from contaminated sites have been found

to contain several thousands of parts per billion (ppb) of perchlorate in the head area and hundreds of ppb in the fillets (3). In addition, recent histological assessments show that fish from perchlorate-contaminated sites have increased thyroid follicular hyperplasia, hypertrophy, and colloid depletion at perchlorate concentrations as low as 100 $\mu\text{g/L}$ and exposure times of 30 d (4, 5).

The potential impact of perchlorate on human and ecosystem health is directly tied to its mobility and attenuation in the environment. Perchlorate salts are highly soluble in water and perchlorate ions weakly adhere to mineral and organic surfaces (6–9); thus, abiotic attenuation pathways of perchlorate are frequently considered to be unimportant. Attenuation of perchlorate in the environment, however, can be effectively mediated by microaerophilic or anaerobic microorganisms that transform ClO_4^- to Cl^- following the pathway $\text{ClO}_4^- \rightarrow \text{ClO}_3^- \rightarrow \text{ClO}_2^- \rightarrow \text{Cl}^- + \text{O}_2$ (10–13). Perchlorate-reducing organisms can use a variety of organic carbon substrates as electron donors, such as glucose, acetate, vegetable oils, and natural organic carbon compounds present in soils and sediments (6, 8, 14, 15). Biological transformation of perchlorate has been successfully utilized for drinking water treatment (16–17) and for in situ groundwater remediation (18–21).

Occurrences of perchlorate in groundwater and surface water stem from both anthropogenic and natural sources. Anthropogenic sources of perchlorate include ammonium perchlorate, a major ingredient of rocket fuel that powers the space shuttle and the U.S. nuclear missile arsenal. In addition, potassium perchlorate is a key ingredient in the production of fireworks, explosives, road flares, and other minor uses (22). Natural sources of perchlorate were generally thought to be restricted to fertilizers mined from Chilean caliche deposits (23). However, recent studies suggest a possible atmospheric origin for background levels of perchlorate, formed from chloride or hypochlorite during atmospheric lightning discharges or from reactions involving ozone, solar energy, and chloride (24–26). Other work proposes multiple possible sources of perchlorate to subsurface and surface environments such as mineralogical impurities, agricultural fertilizers, or in situ formation via electrochemical processes (27). Although fireworks are commonly referred to as a source of perchlorate to the environment (28–29), few data are available to evaluate impacts to groundwater or surface water resources (30). For example, Dasgupta et al. (29) note, in their recent examination of sources of perchlorate to the environment, that a knowledge gap exists regarding the relationship between fireworks displays and the environmental occurrence of perchlorate. This paper documents the time-dependent concentrations of perchlorate observed in a municipal lake following four fireworks displays from 2004 to 2006.

Materials and Methods

Sample Collection, Handling, and Analysis. Surface water samples were collected along the shoreline of a small lake (62 000 m^2) located in Ada, OK. The site is a park with no known source of perchlorate contamination. Sample collection times were centered on fireworks displays in July 2004, July 2005, November 2005, and July 2006. Figure 1 shows an aerial photograph of the lake, locations of sampling sites, and the location of the fireworks ignition site. Samples for perchlorate analyses were syringe-filtered (0.2 μm pore size) in the field into plastic bottles and kept refrigerated at 4 $^\circ\text{C}$ until analysis. Measurements in the field were made for pH,

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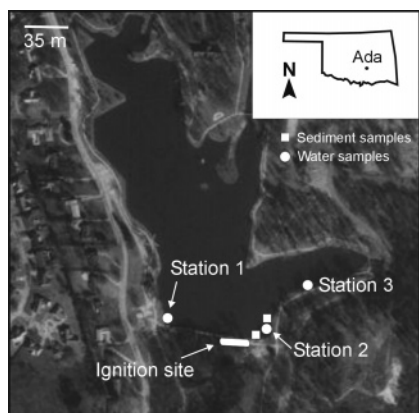


FIGURE 1. Study area, sampling locations, and fireworks ignition site.

specific conductance, and temperature. Samples for stable hydrogen and oxygen isotopic compositions were collected into 20-mL glass vials and sealed to prevent evaporation that can potentially alter $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ ratios. Oxygen- and hydrogen-isotopic ratios of H_2O were analyzed using a high-temperature conversion elemental analyzer linked to a continuous flow isotope ratio mass spectrometer (IRMS, Finnigan Delta plus XP). Filtered samples were also collected for element analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer Optima 3300DV) and anion analysis by capillary electrophoresis (CE, Waters). Sediment samples were collected from the top 10 cm of the bottom sediments at locations near the surface water sampling sites. Sediments were stored at 4 °C in nitrogen-gas purged containers. Sample splits were used for solid-phase characterization, adsorption tests, and microcosm experiments.

Reagents and Standards. Water and acetonitrile (both LC/MS grade manufactured by Riedel-de Haen, Seelze, Germany), sodium perchlorate (minimum 99% purity), and 40% w/w methylamine in water were purchased from Sigma-Aldrich (Milwaukee, WI). Oxygen-18-enriched sodium perchlorate, $\text{NaCl}^{18}\text{O}_4$, was obtained from Isotec (Miamisburg, OH) and was diluted with reagent water to a concentration of 40 $\mu\text{g}/\text{L}$ Cl^{18}O_4 . The liquid chromatography (LC) mobile phase (200 mM methylamine) was prepared by adding 10 mL of 40% w/w methylamine to 490 mL of LC/MS water. Certified second source standards of perchlorate were purchased from Environmental Resource Associates (Arvada, CO).

Perchlorate Analysis. The determination of perchlorate in water was done using a liquid chromatography tandem mass spectrometry (LC/MS/MS) method based on EPA method 331.0 (31, 32). An Agilent 1100 liquid chromatograph and a Finnigan TSQ Quantum Ultra triple-quadrupole mass spectrometer were used for the analysis. Sample volumes of 40 μL were injected, via an Agilent autosampler, onto a Dionex IonPac AS21 column (250 mm \times 2 mm) (Dionex, Millford, MA). The flow rate of the mobile phase, 200 mM methylamine, was 350 $\mu\text{L}/\text{min}$. This allowed the perchlorate anion to elute from the column in ~ 8 min. All PEEK coated fused silica connecting tubing in the liquid chromatograph was replaced with PEEK tubing. Similarly, all Vespel graphite rotor seals in valves and the Vespel graphite injector seat in the LC injector were replaced with parts made of PEEK material. A postcolumn flow of 300 $\mu\text{L}/\text{min}$ acetonitrile was added via a tee before the column flow entered the electrospray source. Optimization of the MS parameters was done using infusion of perchlorate into the mobile phase (further details are provided in the Supporting Information).

A value for the lowest concentration minimum reporting level (LCMRL) for this method, 0.011 $\mu\text{g}/\text{L}$, was calculated using the procedure described elsewhere (33). The method detection limit (MDL) was determined by analyzing seven samples prepared separately at the 0.010 $\mu\text{g}/\text{L}$ level, calculating the standard deviation of the determined concentration, and multiplying the standard deviation by 3.15 (the 97% Student *t* value) (32). The MDL for the method was determined to be 0.003 $\mu\text{g}/\text{L}$ (0.03 nmol/L). The quality control data for this study were collated from sample queues run between July 2004 and August 2006. Over this period, continuing calibration check standards of 0.025 and 0.100 $\mu\text{g}/\text{L}$ had average recoveries of 109% (RSD = 9.2%, $n = 4$) and 103% (RSD = 5%, $n = 13$), respectively. Secondary source standards with certified concentrations at 0.151 and 1.51 $\mu\text{g}/\text{L}$ had average recoveries of 99% (RSD 3.6%, $n = 6$) and 101% (RSD 2.6%, $n = 11$), respectively. During this study fifteen samples were spiked with perchlorate at concentrations between 0.100 and 10 $\mu\text{g}/\text{L}$. The average matrix spike recovery for these samples was 101% (RSD = 11%). The concentration of perchlorate in the samples that were spiked ranged from 0.017 to 11.9 $\mu\text{g}/\text{L}$.

Adsorption and Microcosm Experiments. Precautions were taken to minimize the alteration of sediment samples prior to use in batch adsorption and microcosm experiments. Fresh sediments (wet) were added to 50 mL bottles along with oxygen-saturated deionized water, and aliquots of a stock sodium perchlorate solution. Oxygen-saturated water was used in batch adsorption tests to inhibit potential microbial degradation of perchlorate. The bottles were sealed with screw caps and their contents were mixed on a mechanical shaker for 2 d. All samples were filtered through 0.2- μm syringe filters and analyzed for perchlorate by LC/MS/MS.

Microcosm experiments were conducted in 45 mL glass serum bottles. Duplicate experiments were established containing 1 g of wet sediment, plus solution containing 5 mg/L NO_3^- -N, 1 mg/L ClO_4^- , or a mixture of 1 mg/L ClO_4^- and 5 mg/L NO_3^- -N. All solutions were purged with nitrogen gas to remove dissolved oxygen. Sterile control experiments were set up with HgCl_2 and container controls were prepared by spiking sterile water in serum bottles with the stock nitrate and perchlorate solutions. At selected time intervals, samples were collected from the serum bottles and filtered through 0.2 μm syringe filters prior to sample storage and analysis. An analysis of holding times indicated that perchlorate concentrations were stable for time periods of at least 6 months in filtered solutions (see Supporting Information, Figure S1).

Results and Discussion

Method Improvement. One important modification to the reported LC/MS/MS method (31) that increased the overall method sensitivity of perchlorate determinations was to add acetonitrile postcolumn before the aqueous LC solvent entered the electrospray source. The addition of organic solvents to an aqueous mobile phase can help reduce the effects of surface tension, viscosity, and heat of vaporation (34). An increase in perchlorate response of 170% occurred immediately with as little as 50 $\mu\text{L}/\text{min}$ addition of acetonitrile and continued with acetonitrile flows of up to 500 $\mu\text{L}/\text{min}$ (Figure 2). For this analysis, a postcolumn flow of 350 $\mu\text{L}/\text{min}$ of acetonitrile was used. This resulted in an 8-fold increase in the response of perchlorate and isotopically labeled perchlorate.

Perchlorate Background, Spiking, and Attenuation. Temporal trends in perchlorate concentrations show significant variations centered on the timing of fireworks displays (Figure 3). Perchlorate concentrations preceding fireworks displays, by up to 6 days in July 2005, November 2005, and

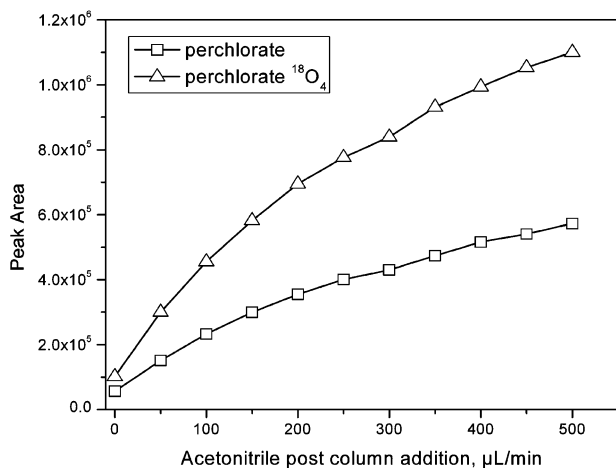


FIGURE 2. Increase in LC/MS/MS peak area response for replicate injections of 0.50 µg/L perchlorate and 1.0 µg/L labeled perchlorate as the flow rate of postcolumn acetonitrile increases.

July 2006, ranged from 0.005 to 0.081 µg/L (0.05 to 0.81 nmol/L), with a mean value of 0.043 µg/L (0.43 nmol/L; $n = 15$). Prior to fireworks displays, the $\text{ClO}_4^-/\text{Cl}^-$ mole ratio in Wintersmith Park surface water was 5.4×10^{-7} . This baseline $\text{ClO}_4^-/\text{Cl}^-$ mole ratio is lower by a factor of $256 \times$ compared to the ratio estimated for modern bulk atmospheric deposition, approximately $1.4 \pm 0.1 \times 10^{-4}$ in New Mexico (26), suggesting perchlorate depletion in Wintersmith Lake surface water relative to chloride due to biological processes or chloride enrichment from other sources.

Sampling events within 14 h after the fireworks showed spikes in perchlorate values ranging from 24 to 1028 \times the mean baseline value. A maximum perchlorate concentration of 44.2 µg/L (444 nmol/L) was determined following the July 2006 display (Figure 3). These trends show significant increases in perchlorate levels that can be reasonably attributed to fireworks sources. Rainfall events do not obviously correlate with perchlorate concentrations which would indicate perchlorate inputs from surface runoff (Figure 3). Various factors potentially impact the absolute increase of perchlorate levels in surface water bodies adjacent to fireworks displays, such as the overall amount of ignited fireworks and efficiency of perchlorate oxidation which controls the mass of perchlorate introduced to the environment, wind direction and velocity which controls the dispersion and fallout of perchlorate-enriched particles, and sampling locations relative to the site of fireworks detonation. About 2–3 \times more fireworks were ignited during the July 2005 display as compared to the November 2005 display (city of Ada, personal communication), which is generally consistent with the observed perchlorate response in surface water (Figure 3).

In a previous study, Canadian surface waters in the Great Lakes Basin were analyzed for the presence of perchlorate (35). Sampling sites included Hamilton Harbor, Niagara River, Lake Huron, and Lake Erie. Surface water samples were analyzed by HPLC/MS/MS using isotopically labeled perchlorate. Perchlorate was detected at several sites at concentrations close to the reported method detection limit of 0.2 µg/L (2.0 nmol/L). Interestingly, perchlorate was detected in Hamilton Harbor, the location of Canada Day fireworks (July 2004). Perchlorate was detected 4 days after the event; a week later perchlorate was undetected at the same site (35).

In each of the fireworks events examined in this study, perchlorate concentrations attained a maximum level within 1 d following the display. Subsequently, concentrations decreased and reached the background level after 20–80 d

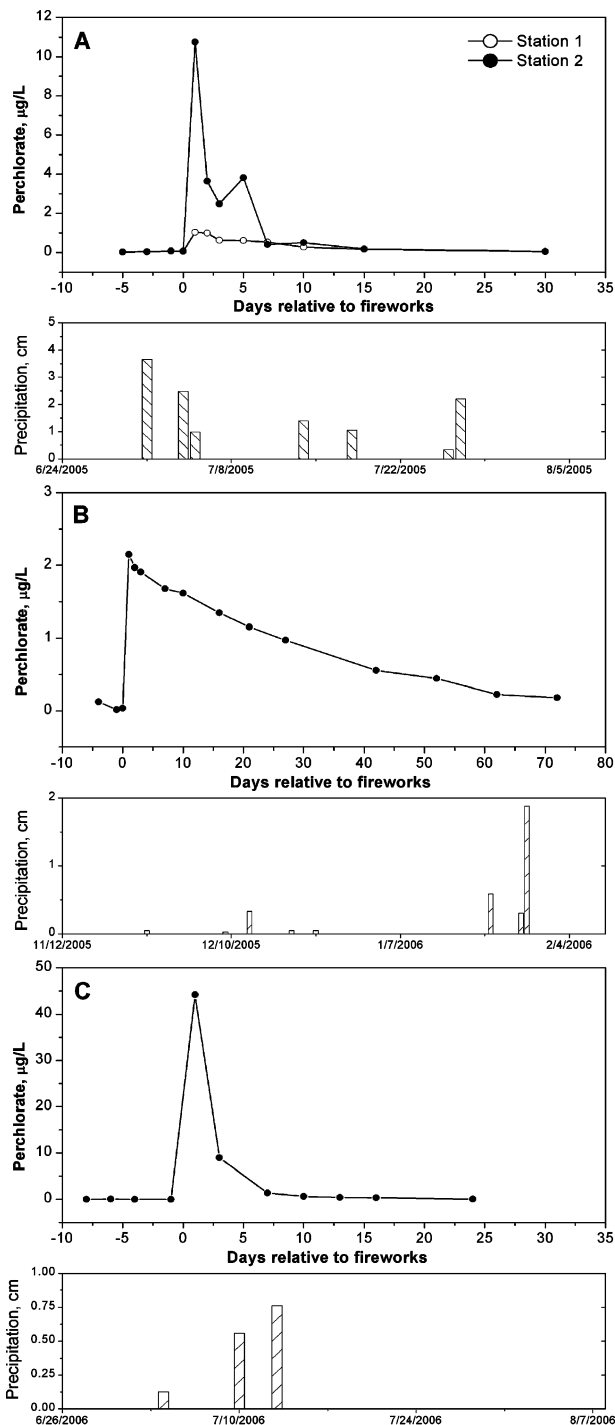


FIGURE 3. Perchlorate concentration trends and precipitation data centered on fireworks displays in (A) July 2005, (B) November 2005, and (C) July 2006. Samples taken from Station 3 before and after the 2004 July 4th display indicated perchlorate concentrations had changed from 0.08 (on July 2, 2004) to 6.42 µg/L (on July 5, 2004). Station 1 was sampled only in July 2005. Data for all sampling events are presented in the Supporting Information (Table S1).

(Figure 3). The reaction kinetics of perchlorate disappearance from the aqueous phase was modeled with a pseudo-first-order rate equation

$$dC/dt = -k_{\text{obs}}C$$

where C is the concentration of perchlorate in the aqueous phase (µg/L), k_{obs} is the observed first-order rate constant (d^{-1}), and t is time (d). Linear regression analysis of plots of

the natural logarithm of perchlorate concentration versus time gave straight-line results with R^2 values ranging from 0.81 to 0.99 (see Supporting Information Figure S2). Values of k_{obs} ranged between 0.03 and 0.28 d^{-1} . Rates of perchlorate removal observed in Wintersmith surface waters are similar to a microbial degradation rate, 0.14 d^{-1} , measured in sediment porewaters from a contaminated site (15). Perchlorate removal rates in Wintersmith Lake correlate with temperature. The fastest rate of perchlorate removal was observed in surface water with a mean temperature of 33.4 °C (July 2006, see Supporting Information Table S1); whereas, the slowest apparent rate occurred in surface water with a mean temperature of 12.4 °C (November 2005). The apparent activation energy (E_a) of the perchlorate removal process was estimated using the equation

$$E_a = -R \frac{d \ln k_{\text{obs}}}{d(1/T)}$$

where E_a is the apparent activation energy (kJ/mol), R is the gas constant (8.314×10^{-3} kJ/mol K), and T is temperature (K). Regression analysis yields an apparent activation energy of 60.5 ± 5.0 kJ/mol (see Supporting Information Figure S3), consistent with cellular and life-related reactions, mineral precipitation–dissolution reactions, but not with adsorption or diffusion processes (36).

Other Components in Pyrotechnics. White (28) lists over 53 organic and inorganic chemicals important in fireworks as fuels, oxidizers, binding agents, and for various coloration and sound effects. Perchlorate salts of potassium and ammonium are the most common oxidizers in modern fireworks displays, and presumably unreacted perchlorate salts are the compounds that lead to spikes in soluble perchlorate concentrations discussed above. Detonation of fireworks is expected to lead to the quantitative conversion of perchlorate to chloride following, for example, the decomposition reaction for potassium perchlorate:



Thus, complete efficiency in perchlorate oxidation reactions during pyrotechnical displays should result in no remaining perchlorate (37). Not surprisingly, spikes in chloride concentrations were consistently observed after the fireworks displays, but were delayed relative to the timing of perchlorate spikes by 3–5 days (see Supporting Information Figure S4). Chloride concentrations were observed to increase by about 5–7 mg/L compared to pre-fireworks values or by about 25%. Only a small fraction (maximum of 0.3%) of this chloride could have been derived from degrading perchlorate that was present in the lake water; the main source of this chloride is apparently from the dissolution of combustion residues.

Other compounds containing strontium, barium, calcium, sodium, copper, antimony, aluminum, and magnesium are essential color-emitters used in pyrotechnical displays (37). Spikes in the concentrations of these other elements were not detected in Wintersmith Lake. The reasons for this are uncertain but may have to do with the more limited sensitivity of the analytical technique employed for these elements (ICP-OES) coupled in some cases with relatively high background concentrations (Ca, Na, K, Mg) and their lower mass abundance compared to perchlorate in the fireworks. Also the final chemical form, water solubility, and reactivity of metals associated with the remains of detonated fireworks have not been studied in detail.

Oxygen and Hydrogen Isotopes. Stable oxygen and hydrogen isotope ratios are valuable for hydrologic investigations, especially for water-balance evaluations in ground-water and surface water systems. Wintersmith Lake surface water had stable isotope ratios of oxygen and hydrogen that

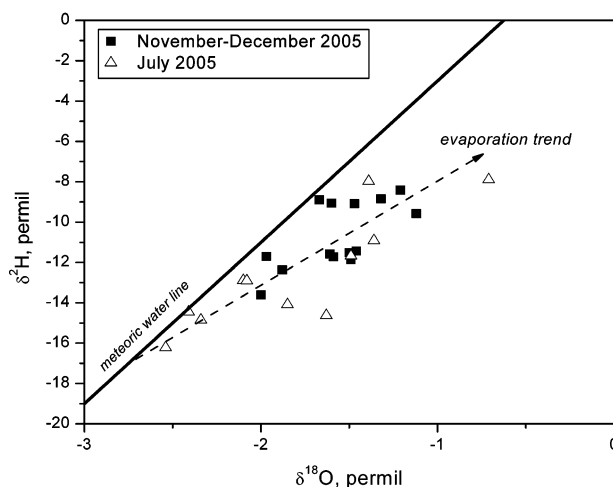


FIGURE 4. Plot of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ of samples collected from Wintersmith Lake.

TABLE 1. Selected Chemical Characteristics for Two Core Sections (0–10 cm Depth) from Wintersmith Lake in Ada, OK

core	% clay	% silt	% sand	sediment pH	TOC, ^a g kg ⁻¹	TIC, ^a g kg ⁻¹	TS, ^b g kg ⁻¹
NBWR	15	12	73	8.46	35.2	4.1	0.16
NBWL	10	8	82	8.03	1.82	0.43	1.2

^a Measured by carbon coulometry. Total carbon (TC) determined by combustion at 950 °C. Total inorganic carbon (TIC) determined by acid extraction using 2 N perchloric acid. Total organic carbon (TOC) is equal to TC – TIC. Total sulfur (TS) measured by sulfur coulometry via combustion at 1100 °C.

showed seasonal variations of about 1.5‰ and 8‰, respectively (Figure 4). Isotopic data show the effects of evaporation in that the meteoric water trend is not observed; rather data follow along a trajectory below the meteoric water trend having a slope of about 5 instead of 8. Ratios of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ are more variable in the summer, because of greater precipitation and generally more intense evaporation compared to the late fall and winter. Considering the limited rainfall that occurred over the period that perchlorate concentrations were decreasing in Wintersmith Lake (Figure 3) and the overall evaporitic trend indicated by the isotopic data (Figure 4), dilution is not expected to be an important factor in lowering perchlorate levels in this system. Dilution of perchlorate concentrations via mixing of the lake water, however, is a possibility that was not assessed during this study.

Adsorption. It is widely accepted that perchlorate does not appreciably sorb to solids and that its mobility and fate in the environment are largely influenced by hydrological and biological factors (9). Core samples retrieved from the bottom of Wintersmith Lake were composed predominately of sand-sized particles and the sediment pH for each core was between 8.0 and 8.5 (Table 1), similar to the mean pH of the overlying water column (8.51 ± 0.44 ; $n = 50$). Core section NBWR was $\sim 20\times$ more enriched in organic matter compared to core section NBWL (Table 1). Also the fraction of clay-sized particles is somewhat higher in the NBWR sample.

Constant-pH sorption tests were conducted with perchlorate loadings from about 10 to 450 μg perchlorate per g of sediment. Core section NBWL showed no potential to remove perchlorate from solution, as 96–102% of the spiked perchlorate was recovered in the aqueous phase (Figure 5). However, core section NBWR removed up to about 10 μg of perchlorate per g of sediment (100 nmol g^{-1}) (Figure 5). The measurable sorption capacity for this material may be related to a higher abundance of organic carbon and an overall finer

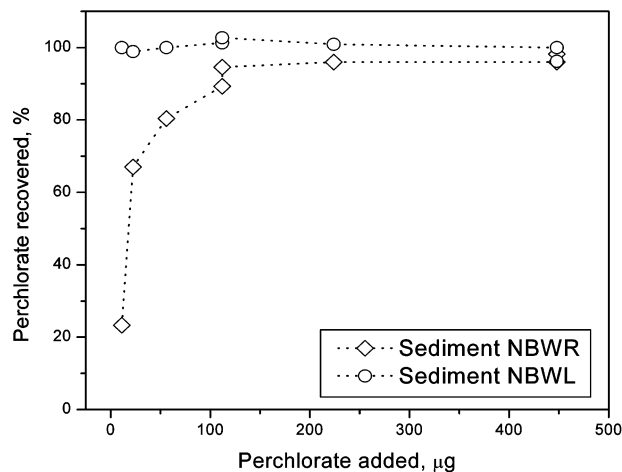


FIGURE 5. Results of sediment adsorption tests. Perchlorate recovered as a function of perchlorate loading to 1 g of sediment, pH 7.5 ± 0.3 , and 2 day exposure time.

grain size (Table 1). As noted in previous studies, it can be difficult to discern between chemical adsorption and microbial degradation in batch experiments with perchlorate (8, 9). The batch adsorption experiments were conducted over 48 h with initial aerobic conditions that should have prevented any microbial perchlorate degradation. The results of the adsorption tests suggest that sediments underlying Wintersmith Lake have only a minor capacity to remove perchlorate via sorption. However, this mechanism of removal cannot be completely discounted. More detailed assessments of the spatial distribution of organic carbon content and perchlorate adsorption capacity may allow for a better estimate of perchlorate adsorption and desorption.

Microcosms. Microcosm experiments show that Wintersmith Lake sediments contain microbial communities capable of reducing both nitrate and perchlorate, with nitrate reduction being favored (Figure 6). In nitrate-free microcosms, perchlorate was degraded from 1 mg/L after 18 d to at or below 0.05 µg/L; whereas, in microcosms with both perchlorate and nitrate present the start of perchlorate reduction lagged several days behind nitrate reduction, and up to 35 d was needed for perchlorate concentrations to decrease below 0.05 µg/L. Note that the mean value of nitrate in Wintersmith Lake was determined to be 40 µg/L. Interestingly, the lowest perchlorate concentrations obtained in the microcosms fall within range of the observed pre-fireworks background levels in Wintersmith Lake (Figure 6a), perhaps suggesting that microbial perchlorate reduction becomes unfavorable at very low concentrations (38). Simultaneous reduction of perchlorate and nitrate was observed. However, perchlorate reduction was clearly favored only after nitrate concentrations were reduced to below 200 µg N/L. Note that a transient period of ammonia production, perhaps due to dissimilatory nitrate reduction to ammonia, occurred prior to denitrification. Pseudo-first-order rate constants were determined by fitting perchlorate data in the initial nonlinear decay period. Rate constants ranged from 0.39 to 0.59 d⁻¹ and are comparable to rates observed in previous microcosm studies on sediments from contaminated sites (15, 39). Additional studies to examine the effects of initial concentrations of perchlorate and nitrate have not been conducted, but the results indicate that microbial perchlorate reduction can occur at initial perchlorate levels much greater than are observed resulting from several fireworks displays.

Implications. Spikes in perchlorate concentrations significantly above background levels were noted after four separate fireworks displays, and in one case concentrations in Wintersmith Lake reached 44 µg/L. Maximum concentra-

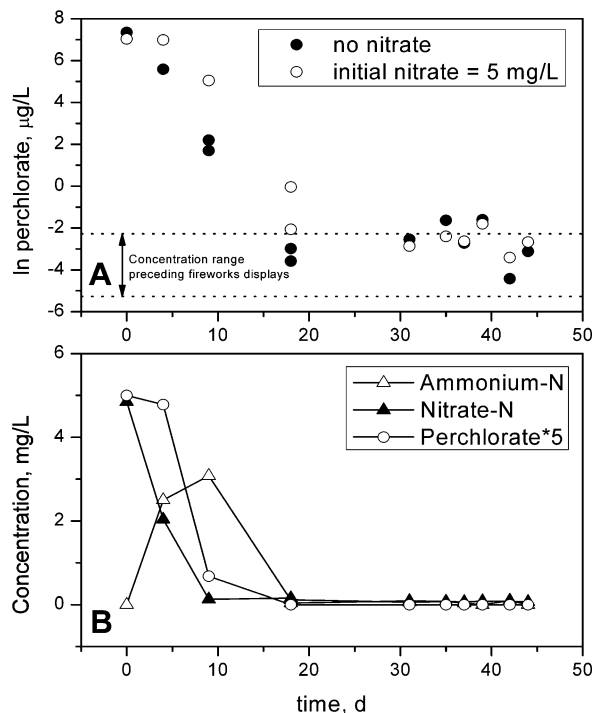


FIGURE 6. Results of microcosm studies showing degradation of perchlorate and nitrate as a function of time (sediment sample NBWR). (A) Perchlorate concentration change with and without nitrate with respect to time. (B) Microcosm concentration of ammonia-N, nitrate-N, and perchlorate with respect to time. Perchlorate concentrations were multiplied by 5 to make trends more apparent.

tions observed in this study following fireworks displays exceed current action levels for drinking water (e.g., 6 µg/L State of California; 4 µg/L State of Texas, and 1 µg/L State of Massachusetts). It is unclear if aquatic organisms are affected at these concentration levels, although previous work indicates thyroid impacts in fish at perchlorate concentrations as low as 100 µg/L and exposure times of 30 d (4). Microcosm tests showed comparatively rapid intrinsic perchlorate degradation in the absence of nitrate consistent with the observed disappearance of perchlorate from Wintersmith Lake, indicating that natural attenuation may be an important factor affecting the fate of perchlorate in the environment following fireworks displays. The availability of organic carbon to provide energy for perchlorate reducing bacteria may be a key factor governing perchlorate attenuation rates in the environment. Results from this study highlight the need for additional studies of perchlorate behavior following fireworks displays in relation to surface water and groundwater quality, particularly in urban areas.

Acknowledgments

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Supporting Information Available

Additional information, data, and figures as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Wolff, J. Perchlorate and the thyroid gland. *Pharmacol. Rev.* **1998**, *50*, 89–105.
- (2) National Research Council. *Health Implications of Perchlorate Ingestion*; National Research Council of the National Academy of Sciences, National Academies Press: Washington, DC, 2005.
- (3) Anderson, T. A.; Wu, T. H. Extraction, cleanup, and analysis of perchlorate anion in tissue. *Bull. Environ. Contam. Toxicol.* **2002**, *68*, 684–691.
- (4) Bradford, C. M.; Rinchar, J.; Carr, J. A.; Theodorakis, C. Perchlorate affects thyroid function in eastern mosquitofish (*Gambusia holbrooki*) at environmentally relevant concentrations. *Environ. Sci. Technol.* **2005**, *39*, 5190–5195.
- (5) Theodorakis, C.; Rinchar, J.; Anderson, T.; Liu, F.; Park, J. W.; Costa, F.; McDaniel, L.; Kendall, R.; Waters, A. Perchlorate in fish from a contaminated site in east-central Texas. *Environ. Pollut.* **2006**, *139*, 59–69.
- (6) Urbansky, E. T. Perchlorate chemistry: Implications for analysis and remediation. *Bioremed. J.* **1998**, *2*, 81–95.
- (7) Logan, B. E. Assessing the outlook for perchlorate remediation. *Environ. Sci. Technol.* **2001**, *12*, 483A–487A.
- (8) Tipton, D. K.; Rolston, D. E.; Scow, K. M. Transport and biodegradation of perchlorate in soils. *J. Environ. Qual.* **2003**, *32*, 40–46.
- (9) Urbansky, E. T.; Brown, S. L. Perchlorate retention and mobility in soils. *J. Environ. Monit.* **2003**, *5*, 455–462.
- (10) Coates, J. D.; Achenbach, L. A. Microbial perchlorate reduction: Rocket-fuelled metabolism. *Nature Rev. Microbiol.* **2004**, *2*, 569–580.
- (11) Logan, B. E. A review of chlorate- and perchlorate-respiring organisms. *Bioremed. J.* **1998**, *2*, 69–79.
- (12) Rikken, G. B.; Kroon, A. G.; Van Ginkel, C. G. Transformation of (per)chlorate into chloride by a newly isolated bacterium: Reduction and dismutation. *Appl. Microbiol. Biotechnol.* **1996**, *45*, 420–426.
- (13) Wu, J.; Unz, R. F.; Zhang, H.; Logan, B. E. Persistence of perchlorate and the relative numbers of perchlorate- and chlorate-respiring microorganisms in natural waters, soils, and wastewater. *Bioremed. J.* **2001**, *5*, 119–130.
- (14) Herman, D. C.; Frankenberger, W. T. Microbial-mediated reduction of perchlorate in groundwater. *J. Environ. Qual.* **1998**, *27*, 750–754.
- (15) Tan, K.; Anderson, T. A.; Jackson, W. A. Degradation kinetics of perchlorate in sediments and soils. *Water, Air Soil Pollut.* **2004**, *151*, 245–259.
- (16) Kim, K.; Logan, B. E. Fixed-bed bioreactor treating perchlorate-contaminated waters. *Environ. Eng. Sci.* **2000**, *17*, 257–265.
- (17) Xu, J.; Song, Y.; Min, B.; Steinberg, L.; Logan, B. E. Microbial degradation of perchlorate: principles and applications. *Environ. Eng. Sci.* **2003**, *20*, 405–422.
- (18) Giblin, T.; Herman, D.; Deshusses, M. A.; Frankenberger, W. T. Removal of perchlorate in ground water with a flow-through bioreactor. *J. Environ. Qual.* **2000**, *29*, 578–583.
- (19) Hunter, W. Bioremediation of chlorate or perchlorate contaminated water using permeable barriers containing vegetable oil. *Curr. Microbiol.* **2002**, *45*, 287–292.
- (20) Logan, B. E.; LaPoint, D. Treatment of perchlorate- and nitrate-contaminated groundwater in an autotrophic, gas phase, packed-bed bioreactor. *Water Res.* **2002**, *36*, 3647–3653.
- (21) Leeson, A.; Borden, R. C.; Lieberman, M. T. Emulsified-oil biobarrier provides long-term treatment of perchlorate/VOC plume. *Technol. News Trends* **2006**, *27*, 1–2.
- (22) Motzer, W. E. Perchlorate: problems, detection, and solutions. *Environ. Forensics* **2001**, *2*, 301–311.
- (23) Ericksen, G. E. The Chilean nitrate deposits. *Am. Sci.* **1983**, *71*, 366–374.
- (24) Dasgupta, P. K.; Martinelango, P. K.; Jackson, W. A.; Anderson, T. A.; Tian, K.; Tock, R. W.; Rajagopalan, S. The origin of naturally occurring perchlorate: The role of atmospheric processes. *Environ. Sci. Technol.* **2005**, *39*, 1569–1575.
- (25) Rajagopalan, S.; Anderson, T. A.; Fahlquist, L.; Rainwater, L.; Ridley, M.; Jackson, W. A. Widespread presence of naturally occurring perchlorate in high plains of Texas and New Mexico. *Environ. Sci. Technol.* **2006**, *40*, 3156–3162.
- (26) Plummer, L. N.; Böhlke, J. K.; Doughten, M. W. Perchlorate in Pleistocene and Holocene groundwater in north-central New Mexico. *Environ. Sci. Technol.* **2006**, *40*, 1757–1763.
- (27) Jackson, W. A.; Anadam, S. K.; Anderson, T.; Lehman, T.; Rainwater, K.; Rajagopalan, S.; Ridley, M.; Tock, R. Perchlorate occurrence in the Texas Southern High Plains aquifer system. *Ground Water Monit. Remed.* **2005**, *25*, 137–149.
- (28) White, D. G. Pollution caused by fireworks. *Am. Environ. Lab.* **1996**, *24*–26.
- (29) Dasgupta, P. K.; Dyke, J. V.; Kirk, A. B.; Jackson, W. A. Perchlorate in the United States. Analysis of relative source contributions to the food chain. *Environ. Sci. Technol.* **2006**, *40*, 6608–6614.
- (30) Evaluation of Perchlorate Contamination at a Fireworks Display Dartmouth, Massachusetts; Massachusetts Department of Environmental Protection: Boston, MA, 2005; <http://mass.gov/dep/cleanup/sites/umdrop.htm>.
- (31) Wendelken, S.; Vanatta, L.; Coleman, D.; Munch, D. Perchlorate in water via US Environmental Protection Agency Method 331: Determination of methods uncertainties, lowest concentration minimum reporting levels, and Hubaux-Vos detection limits in reagent water and simulated drinking water. *J. Chromatogr. A* **2006**, *1118*, 94–99.
- (32) EPA Method 331.0. *Determination of perchlorate in drinking water by liquid chromatography electrospray ionization mass spectrometry*; EPA Document 815-R-05-007; U.S. Environmental Protection Agency: Washington, DC, 2005.
- (33) *Statistical Protocol for the Determination of the Single-Laboratory Lowest Concentration Minimum Reporting Level (LCMRL) and Validation of the Minimum Reporting Level (MRL)*; 815-R-05-006; U.S. Environmental Protection Agency, Office of Ground Water and Drinking Water: Cincinnati, OH; www.epa.gov/OGWDW/methods/sourcalt.html.
- (34) Voyksner, R. Combining Liquid Chromatography with Electrospray Mass Spectrometry. In *Electrospray Ionization Mass Spectrometry*; Cole, R., Ed.; J. Wiley: New York, 1997.
- (35) Backus, S. M.; Klawuun, P.; Brown, S.; D'sa, I.; Sharp, S.; Surette, C.; Williams, D. J. Determination of perchlorate in selected surface waters in the Great Lakes Basin by HPLC/MS/MS. *Chemosphere* **2005**, *61*, 834–843.
- (36) Langmuir, D. *Aqueous Environmental Geochemistry*; Prentice Hall: Upper Saddle River, NJ, 1996.
- (37) Conkling, J. A. *Chemistry of Pyrotechnics. Basic principles and theory*; Marcel Dekker: New York, 1985.
- (38) Nerenberg, R.; Kawagoshi, Y.; Rittmann, B. E. Kinetics of a hydrogen-oxidizing, perchlorate-reducing bacterium. *Water Res.* **2006**, *40*, 3290–3296.
- (39) Tan, K.; Anderson, T. A.; Jackson, W. A. Temporal and spatial variation of perchlorate in streambed sediments: results from in-situ dialysis samplers. *Environ. Pollut.* **2005**, *136*, 283–291.

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