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Atacama Perchlorate as an Agricultural Contaminant in Groundwater: Isotopic and Chronologic Evidence from Long Island, New York

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Perchlorate (ClO_4^-) is a common groundwater constituent with both synthetic and natural sources. A potentially important source of ClO_4^- is past agricultural application of ClO_4^- -bearing natural NO_3^- fertilizer imported from the Atacama Desert, Chile, but evidence for this has been largely circumstantial. Here we report ClO_4^- stable isotope data ($\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$), along with other supporting chemical and isotopic environmental tracer data, to document groundwater ClO_4^- contamination sources and history in parts of Long Island, New York. Sampled groundwaters were oxic and ClO_4^- apparently was not affected by biodegradation within the aquifers. Synthetic ClO_4^- was indicated by the isotopic method in groundwater near a fireworks disposal site at a former missile base. Atacama ClO_4^- was indicated in agricultural and urbanizing areas in groundwaters with apparent ages >20 years. In an agricultural area, ClO_4^- concentrations and $\text{ClO}_4^-/\text{NO}_3^-$ ratios increased with groundwater age, possibly because of decreasing application rates of Atacama NO_3^- fertilizers and/or decreasing ClO_4^- concentrations in Atacama NO_3^- fertilizers in recent years. Because $\text{ClO}_4^-/\text{NO}_3^-$ ratios of Atacama NO_3^- fertilizers imported in the past ($\sim 2 \times 10^{-3} \text{ mol mol}^{-1}$) were much higher than the $\text{ClO}_4^-/\text{NO}_3^-$ ratio of recommended drinking-water limits ($7 \times 10^{-5} \text{ mol mol}^{-1}$ in New York), ClO_4^- could exceed drinking-water limits even where NO_3^- does not, and where Atacama NO_3^- was only a minor source of N. Groundwater ClO_4^- with distinctive isotopic composition was a sensitive indicator of past Atacama NO_3^- fertilizer use on Long Island and may be common in other areas that received NO_3^- fertilizers from the late 19th century through the 20th century.

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Introduction

Perchlorate (ClO_4^-) in drinking water or food can cause health problems by interfering with iodide uptake and hormone production in the thyroid gland (1). Recommended limits for ClO_4^- concentrations in drinking water in the USA range from about 1 to 25 $\mu\text{g L}^{-1}$ (10–250 nmol L^{-1}), reflecting uncertainty about the harmful exposure level. Perchlorate is a component of solid rocket fuels and explosives, and these products and their manufacturing facilities are well-known sources of local ClO_4^- contamination. Other synthetic sources of ClO_4^- include fireworks, road flares, chlorate herbicides, and bleach products, but the extent of their influence on groundwater is largely unknown. In addition, ClO_4^- is a minor component of natural NO_3^- -rich salt deposits in the Atacama Desert in Chile, which have been refined and distributed worldwide as NO_3^- fertilizer products (mostly NaNO_3). Atacama NO_3^- fertilizer has been imported to the USA since the late 1800s. Although manufactured sources of N fertilizer have been more important globally since the middle 1900s, Atacama NO_3^- is still used locally on some crops, including tobacco, cotton, vegetables, and fruit trees including citrus (2), and it is a common component of “organic” fertilizers. ClO_4^- also is present in atmospheric deposition (3), and natural accumulations of ClO_4^- presumed to be of atmospheric origin are common in desert soils of the southwestern USA (4). Groundwater concentrations of nonsynthetic ClO_4^- of the order of 10–1000 nmol L^{-1} or more could result from historical Atacama NO_3^- fertilizer use or from evaporative enrichment of atmospheric deposition in arid regions (2, 5, 6), but it may be difficult to distinguish these and other sources of ClO_4^- on the basis of chemical and hydrologic evidence alone. Recent studies indicate ClO_4^- from different natural and synthetic sources has distinctive Cl and O isotopic compositions (7–9), but field studies of these differences are just beginning and they have not been explored systematically in diverse groundwater settings.

The objectives of the current study were to test the applicability of Cl and O isotopes as source indicators of groundwater ClO_4^- in the humid eastern USA, and to determine sources of ClO_4^- affecting groundwater usability in Suffolk County, eastern Long Island, New York. Groundwater is the sole source of public water supply and a carefully protected resource in Suffolk County. Perchlorate is present in groundwater in many locations on Long Island (10) and some important public water supplies are being treated to remove ClO_4^- at substantial cost, based on a New York State drinking-water guidance level of 5 $\mu\text{g L}^{-1}$ (50 nmol L^{-1}). Various potential sources of ClO_4^- are present, including agriculture (past or present), fireworks manufacture and use, military bases including missile storage and launch facilities, road-flare runoff, and lawn fertilizer, among others.

Experimental Section

Sample Locations. Groundwater containing ClO_4^- was collected from three different areas in Suffolk County (Figure 1a), each representing a different land use and/or water use. The DL transect (North Fork area, near Cutchogue) consisted of three clusters of three observation wells (5.1 cm diameter, 1.5 m screened interval) in a northwest-southeast array across the middle of the North Fork Peninsula (Figure 1b). Land use in this area in 2006–2007 was largely agricultural, with turf grass, corn, grapes, and potatoes as important crops. The DL wells were screened within the surficial upper glacial aquifer, which consists of Pleistocene moraine and outwash sediments dominated by brownish sand and gravel with local

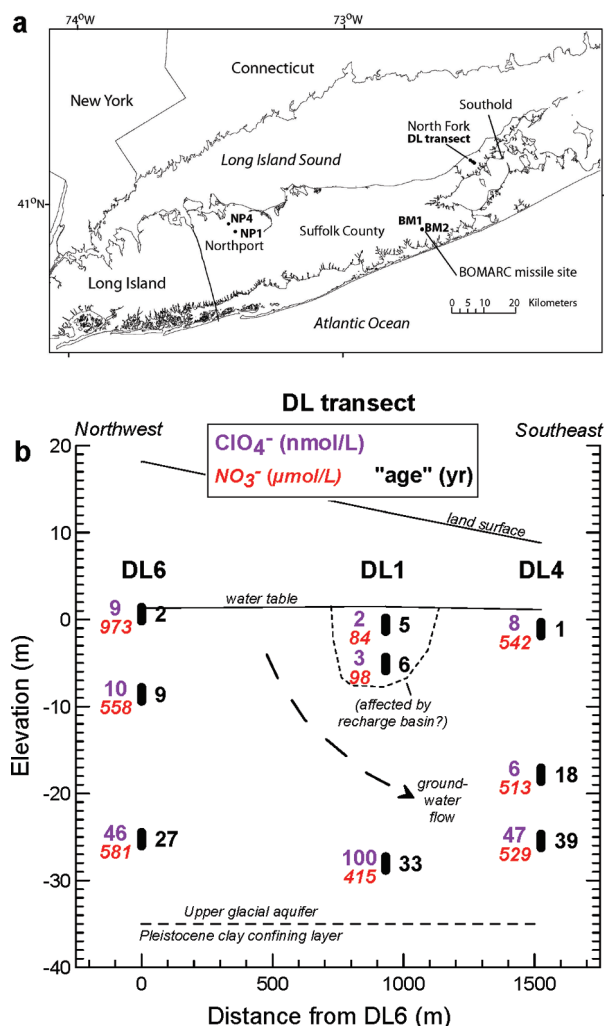


FIGURE 1. (a) Map of Long Island, New York, showing locations of samples. (b) Vertical profile of the DL groundwater transect in 2007 showing well screens (vertical bars), ClO_4^- and NO_3^- concentrations, and composite mean apparent groundwater ages.

silt and clay (11). The deepest well screens were a short distance above a lower confining unit, which begins at approximately -35 to -31 m elevation (12) and consists of Pleistocene glacial-lake clay, silt, and sand.

Two samples were obtained from observation wells (BM1, BM2) at a former BOMARC missile site near Westhampton (Figure 1a). The BOMARC (Boeing and Michigan Aerospace Research Center) missile program at this site was active between 1957 and 1969 (http://www.dnma.state.ny.us/forts/fortsQ_S/suffolkBOMARC.htm) and included the first version of the BOMARC missile, the CIM-10A, which was powered in part by liquid-fuel booster rockets; available data do not indicate deployment of the CIM-10B with solid-fuel rockets. At the time of this study (2006–2008), this site was used by Suffolk County as a police training facility and included a weapons firing range and fireworks disposal pit. The general direction of groundwater flow was from north to south. Both sampled wells were upgradient from the former missile silos and downgradient from the firing range and fireworks disposal pit.

Two samples were obtained from large-volume production wells (NP1, NP4) in the Northport area (Figure 1a). This was an important farming region prior to the 1950s, and some vegetable and sod farms still existed in the area in 2007, but the majority of the land was residential at the time of this study. The screened intervals of these wells (NP1 =

117 ± 9 m, NP4 = 92 ± 9 m below the water table) were in the Magothy aquifer, which underlies the upper glacial aquifer.

Sample Collection and Analyses. Samples were collected for isotopic analysis of ClO_4^- , NO_3^- , and SO_4^{2-} , along with major and minor element chemistry, major dissolved gases (Ar , N_2 , O_2 , and CH_4), and atmospheric environmental tracers (^3H , ^3He , SF_6 , and chlorofluorocarbons (CFCs)) to determine the timing of ClO_4^- infiltration and its relation to other natural and anthropogenic constituents, as illustrated previously in studies of agricultural NO_3^- (13–15). Samples were collected mainly between December 2006 and January 2007. DL transect wells were resampled in December 2007 to April 2008 for dissolved gases, including SF_6 and CFCs. ClO_4^- was analyzed by IC/MS/MS at Texas Tech University (3). ClO_4^- for isotopic analysis was collected on Purolite A530E selective ion-exchange resin columns and then recovered, purified, and analyzed as described previously (7–9, 16). Shallow DL wells were not analyzed for ClO_4^- isotopes because of low concentrations. Analytical methods and results for most constituents are summarized in the Supporting Information.

Results and Discussion

Distribution and Isotopic Composition of Perchlorate.

Perchlorate was present in all samples (>1 nmol L^{-1}) and some concentrations exceeded the New York drinking-water guidance level of 50 nmol L^{-1} ($5 \mu\text{g} \text{L}^{-1}$) (Table 1). The highest concentrations by far were from the BOMARC site (BM1 = $43\,400$ nmol L^{-1} , BM2 = 3550 nmol L^{-1}), where fireworks disposal and military activities were potential sources. In the DL transect, ClO_4^- concentrations were relatively high in the deepest wells (46 – 100 nmol L^{-1}) and lower in the shallower wells (2 – 10 nmol L^{-1}). Production wells in the Northport area (NP1, NP4) had relatively high ClO_4^- concentrations (84 – 112 nmol L^{-1}).

Previous studies indicate $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values of ClO_4^- (defined in Table 1) are related to the environment and process of ClO_4^- formation (7–9). Distinctive isotopic signatures have been documented for (1) synthetic ClO_4^- formed commercially by electrolytic oxidation of NaCl brine, (2) natural ClO_4^- accumulated with NO_3^- in the Atacama Desert and distributed as a component of natural NO_3^- fertilizer, and (3) other natural sources in the southwestern USA (Figure 2). The $\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values of Long Island ClO_4^- fall into 2 distinct groups (Table 1, Figure 2): the BOMARC wells plot within the synthetic ClO_4^- ranges, whereas the NP production wells and the deep DL transect wells plot within the Atacama ClO_4^- ranges. There is no clear isotopic evidence for ClO_4^- biodegradation, which is consistent with other data indicating the sampled groundwaters were oxic and not denitrified (see below).

At the BOMARC site, the synthetic ClO_4^- isotopic signature was associated with unusually high ClO_4^- concentrations, relatively low NO_3^- concentrations, and young apparent groundwater ages (1–2 years; see below). Sample BM1 (adjacent to a fireworks disposal pit) had anomalously high concentrations of K, Sr, and Sb, which are common constituents of fireworks, used for color and brightness (17). Although various local sources of synthetic ClO_4^- may be present at this former missile site, leaching of unexploded fireworks is supported by proximity of the upgradient well (BM1) to a fireworks disposal pit and association of ClO_4^- with trace elements that are common constituents of fireworks.

At the DL and NP sites, the Atacama ClO_4^- isotopic signature was associated with relatively high concentrations of NO_3^- and locally with other constituents including Ca, Mg, Cl $^-$, and SO_4^{2-} , indicating recharge beneath agricultural (or horticultural) land receiving various types of fertilizers (see below). No other ClO_4^- sources reported to date have

TABLE 1. Selected Data for Groundwater Samples (Extracted from Table S1 in the Supporting Information)^a

well	depth BWT (m)	GW age (years)	NO ₃ ⁻ (μM)	ClO ₄ ⁻ (nM)	ClO ₄ ⁻ δ ³⁷ Cl (‰)	ClO ₄ ⁻ δ ¹⁸ O (‰)	ClO ₄ ⁻ Δ ¹⁷ O (‰)
BM1	11.6	2	97	43400	0.2	-16.7	0.1
BM2	2.1	1	72	3550	0.2	-17.7	-0.1
NP1	117.0	35	792	112.1	-12.5	-3.0	9.4
NP4	92.0	41 ± 4	336	84.3	-13.2	-8.2	7.9
DL6s	0.6	2 ± 2	973	8.7	na	na	na
DL6m	9.8	9 ± 3	558	10.2	na	na	na
DL6d	26.5	27 ± 5	581	45.8	-12.6	-6.0	8.4
DL1s	2.1	5 ± 8	84	1.5	na	na	na
DL1m	6.7	6 ± 3	98	3.4	na	na	na
DL1d	29.5	33 ± 3	415	99.6	-14.0	-6.1	8.2
DL4s	2.2	1 ± 4	542	7.7	na	na	na
DL4m	19.0	18 ± 3	513	5.8	na	na	na
DL4d	26.6	39 ± 1	529	46.6	-12.9	-1.6	10.2

^a DL well clusters are designated shallow (s), medium (m), and deep (d). Depth BWT = depth below water table, middle of well screen. Mean and standard deviation of composite apparent groundwater (GW) ages are from various combinations of techniques (no ± if single technique, see Table S1 and Figure S4 in the Supporting Information). μM = μmol L⁻¹; nM = nmol L⁻¹ = 10⁻³ μmol L⁻¹. Stable isotope data are reported as follows (see the Supporting Information for calibration data) (8, 42): δ³⁷Cl = [n(³⁷Cl)/n(³⁵Cl)]_{sample}/[n(³⁷Cl)/n(³⁵Cl)]_{SMOC} - 1; δ¹⁸O = [n(¹⁸O)/n(¹⁶O)]_{sample}/[n(¹⁸O)/n(¹⁶O)]_{VSMOW} - 1; Δ¹⁷O = [(1 + δ¹⁷O)/(1 + δ¹⁸O)^{0.525}] - 1; values given in parts per thousand (‰).

the distinctive combination of low δ³⁷Cl, low δ¹⁸O, and high Δ¹⁷O that characterize the Atacama ClO₄⁻. High Δ¹⁷O values in both ClO₄⁻ and NO₃⁻ from the Atacama Desert and a few other hyper-arid environments have been interpreted as a result of photochemical reactions involving O₃, leading to the conclusion that those salts represent long-term accumulations of atmospheric deposition (7, 18). Other studies indicate NO₃⁻ and ClO₄⁻ isotopic compositions of Atacama NO₃⁻ fertilizer products typically were similar to those of the natural salt deposits from which they were produced (7–9, 18, 19). The distinctive ClO₄⁻ isotopic signature apparently was not altered substantially by plants, soils, or aquifer interactions during transport from fields to wells in Suffolk County (Figure 2).

Dissolved Gases, Recharge Conditions, and Redox Status of Groundwater. Concentrations of Ne, Ar, N₂, O₂, and CH₄ were used to assess recharge conditions (needed for groundwater dating) and subsequent redox reactions that might have affected ClO₄⁻ stability in the aquifer. Mean concentrations (± 1σ) of Ne, Ar, and N₂ were 0.0106 ± 0.0009 (*n* = 11), 18.0 ± 0.3 (*n* = 22), and 709 ± 23 (*n* = 22) μmol L⁻¹, respectively. These data were compared to hypothetical aqueous concentrations in equilibrium with air at the water table to derive estimates of recharge temperature, concentrations of excess air trapped and dissolved during recharge, and concentrations of excess N₂ that might have been produced in the saturated zone by denitrification (13, 15) (see the Supporting Information). Apparent recharge temperatures and concentrations of excess air were 10.8 ± 0.7 °C and 2.3 ± 0.7 cm³-STP L⁻¹ when calculated from Ne+Ar data (*n* = 10), and 10.0 ± 0.7 °C and 1.8 ± 0.7 cm³-STP L⁻¹ when calculated from Ar+N₂ data (*n* = 22), assuming excess air was dissolved without fractionation. Concentrations of excess N₂ were undetectable (-14 ± 11 μmol L⁻¹) when calculated from all three gases (assuming Ne+Ar recharge conditions). δ¹⁵N values of dissolved N₂ (mean = +0.68 ± 0.07‰, *n* = 22) were consistent with dissolved atmospheric N₂ (i. e., no discernible excess nonatmospheric N₂). Concentrations of O₂ ranged from about 240 to 350 μmol L⁻¹ (mean = 294 ± 32, *n* = 22), about 65–97% of the maximum recharge values (360–370 μmol L⁻¹) based on the Ne, Ar, and N₂ data. All CH₄ concentrations were <0.1 μmol L⁻¹. In summary, combined evidence from dissolved gas data indicates the sampled aquifers were oxic and denitrification within the saturated zone was minimal (e.g., affected <5% of the NO₃⁻ in the DL transect). Because microbial ClO₄⁻ reduction occurs mainly in suboxic conditions and commonly is inhibited by

NO₃⁻ (20, 21), these data indicate that microbial ClO₄⁻ reduction in the sampled parts of the saturated zone was unlikely and ClO₄⁻ concentrations and isotopic signatures likely reflect initial values at the time of recharge.

Groundwater Ages and Fluxes. Groundwater dating provided information needed to evaluate recharge fluxes and possible decade-scale historical changes in recharge chemistry. Apparent recharge dates and ages of groundwater samples (representing time spent in the saturated zone after isolation from air during recharge) were estimated from concentrations of various atmospheric environmental tracers ³H–³He, SF₆, CFC11, CFC12, and CFC113, as summarized previously (22) (see the Supporting Information). Apparent recharge dates and ages derived individually from different tracers were discordant in some cases because (1) apparent CFC recharge dates after 1990 had large uncertainties caused by peaking atmospheric concentrations, (2) apparent SF₆ dates before 1985 may have been affected by low-level background concentrations or contamination, (3) some tracers were contaminated locally (e.g., CFCs in production wells), and (4) some samples probably were mixtures of waters with varying ages. After selection of data based on these criteria (see the Supporting Information), we estimated a composite mean apparent age for each well, with results ranging from 1 to 41 years and typical uncertainties of the order of 2–5 years (Table 1).

At the DL transect, apparent groundwater ages ranged from 1 to 39 years and increased with depth (Figure 1b), consistent with distributed recharge (23). The mean recharge rate was estimated by fitting the DL data with an exponential age-depth model (23) with saturated thickness of 37 m and porosity of 0.30 (24) (see Figure S5 in the Supporting Information). Results of multiple fits with different data subsets yielded a mean recharge rate of 0.50 ± 0.05 m year⁻¹. This is about 44% of the mean annual precipitation (1.14 m year⁻¹) and similar to a previously estimated recharge rate (0.56 ± 0.05 m year⁻¹) based on physical measurements and meteorological data in the North Fork area (24, 25).

At the NP production wells, composite apparent groundwater ages derived from CFCs and ³H–³He were 35 and 41 years, but the well screens were relatively deep below the water table and would imply unrealistic recharge rates if they represented undisturbed aquifer conditions. Low ³H concentration at NP4 (1.6 TU) and high rate of pumping from these and other wells in this area indicate these samples probably were mixtures of young and old water and the age profiles may have been disturbed. Nevertheless, despite

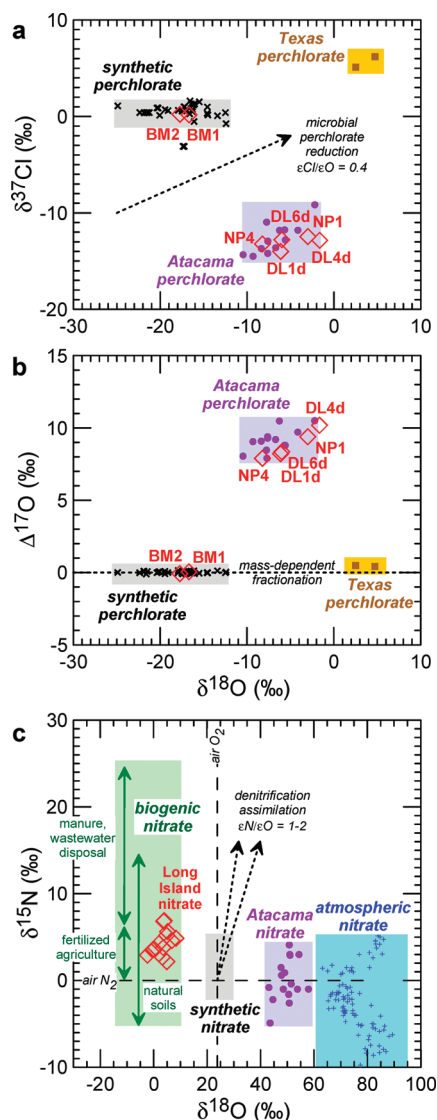


FIGURE 2. Summary of isotope data for ClO_4^- and NO_3^- in groundwater samples (Table 1 and Table S1 in the Supporting Information), compared with major known sources (modified, with additional data, from refs 8, 18, 30) and bioreduction trends (42–44). Texas perchlorate is believed to be natural (6), but with isotopic composition different from Atacama perchlorate (8).

various uncertainties, the combined results of groundwater dating indicate ClO_4^- and other constituents were present in recharge in varying amounts over a period of about 40 years or more.

Agricultural Chemicals in Groundwater. Elevated ClO_4^- concentrations were associated with NO_3^- and other chemicals commonly enriched in agricultural recharge, including Ca, Mg, Cl^- , and SO_4^{2-} (Figure 3 and Figure S6 in the Supporting Information). Two wells (DL1s, DL1m) near a partially wooded recharge basin had low concentrations of ClO_4^- , NO_3^- , and other major solutes and are considered to represent diluted or nonagricultural recharge. Because Long Island is surrounded by ocean, elevated salt concentrations in groundwater could be related to mixing with marine fluids at depth, or to locally high concentrations of marine salts in atmospheric deposition. For comparison with possible recharge values, concentrations of selected constituents in local precipitation were multiplied by 2.3 (= precipitation/recharge) to account for evapotranspiration, and again by 2.0 to represent hypothetical contributions from dry deposi-

tion (see Table S2 in the Supporting Information). Potential concentrations of Cl^- , SO_4^{2-} , and dissolved inorganic N ($\text{NH}_4^+ + \text{NO}_3^-$) for atmospheric recharge components were similar to the lowest values in our groundwater samples, whereas most samples were relatively enriched in Cl^- , SO_4^{2-} , and NO_3^- , along with Ca and Mg, in proportions that were different from those of seawater (Figure 3). Road salts and local deposition of marine aerosols near the coast could be responsible for some elevated Na and Cl^- concentrations. Marine aerosols probably were not a major cause of high Ca and SO_4^{2-} concentrations because of their much larger enrichments and because $\delta^{34}\text{S}[\text{SO}_4^{2-}]$ values (+1 to +8 ‰) were lower than that of seawater (+21 ‰) (see the Supporting Information).

The same chemicals enriched in some of our samples (NO_3^- , Cl^- , SO_4^{2-} , Ca, and Mg) were interpreted previously to have agricultural sources on Long Island, based on statistical analyses of groundwater chemistry and land use (26–28). Similar enrichments (with the exception of SO_4^{2-}) have been attributed to agricultural effects in other mid-Atlantic aquifers (14, 29). The isotopic composition of NO_3^- was consistent with nitrification in aerated soils (Figure 2c), and similar to those of high- NO_3^- groundwater beneath fertilized agricultural areas elsewhere in the eastern USA (30). Therefore, we interpret these constituents as evidence for agricultural inputs, including N fertilizer in various forms, Ca–Mg–carbonate commonly used to neutralize acidity, possibly some KCl as a source of K, and S or SO_4^{2-} (e. g., CaSO_4 , $[\text{NH}_4]_2\text{SO}_4$) to fertilize potatoes, improve soil texture, combat fungi, or regulate acidity in vineyards. The pesticide aldicarb, applied to control golden nematode and Colorado potato beetle from 1975–1979, was reported in shallow groundwater near the DL transect in the late 1970s and 1980s (12).

Concentrations of NO_3^- in DL wells (excluding DL1s and DL1m) ranged from 415 to 973 $\mu\text{mol L}^{-1}$. Combined with the estimated recharge rate (0.50 m year^{-1}), these data indicate NO_3^- recharge fluxes of 0.21–0.49 $\text{mol m}^{-2} \text{ year}^{-1}$ (2.9–6.8 $\text{g m}^{-2} \text{ year}^{-1}$). Agricultural land-use data (31) combined with N-loading data (32) indicate the mean application rate of fertilizer N on cropland in Suffolk County was approximately $24 \pm 4 \text{ g m}^{-2} \text{ year}^{-1}$ from 1987 to 2001. The fraction of that applied agricultural N load that hypothetically could account for the range of DL recharge NO_3^- fluxes (12–28%) is within range of fractional NO_3^- infiltration losses estimated by similar methods in other well-drained agricultural areas in the eastern USA (14, 33). Thus, although spatial variations are to be expected, and temporal loading variations may not be reflected precisely in recharge history, our estimated NO_3^- recharge fluxes are consistent with agricultural effects in the region.

For ClO_4^- , estimated recharge fluxes indicated by DL wells (excluding DL1s and DL1m) were $0.29\text{--}5.0 \times 10^{-5} \text{ mol m}^{-2} \text{ year}^{-1}$ ($0.29\text{--}5.0 \times 10^{-3} \text{ g m}^{-2} \text{ year}^{-1}$). In arid regions, high evapotranspiration factors and/or redissolution of accumulated salts in the unsaturated zone could yield concentrations of atmospheric anions including ClO_4^- as high as those observed in DL and NP groundwaters (5, 34). However, the low evapotranspiration factors and high recharge rates on Long Island are not consistent with this mechanism for concentrating natural atmospheric deposition, which typically has $\text{ClO}_4^- < 2 \text{ nmol L}^{-1}$ (3, 35). Although correlations between ClO_4^- and other agriculture-related constituents are poor (Figure 3), observed concentrations and fluxes of ClO_4^- , and co-occurrence of ClO_4^- with other agricultural constituents, are consistent with ClO_4^- isotope data indicating an agricultural (or horticultural) source for ClO_4^- in DL and NP samples (see below).

Selected fertilizers used on Long Island around the time of this study had ClO_4^- concentrations ranging from about

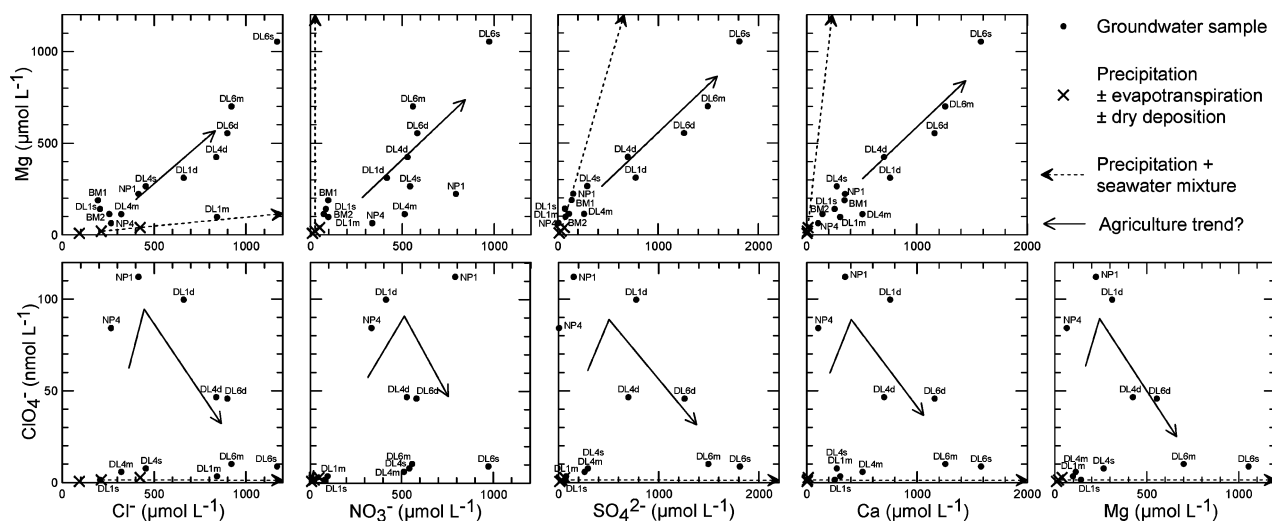


FIGURE 3. Concentrations of ClO_4^- and other selected constituents in groundwater. Dotted arrows indicate hypothetical mixtures of atmospheric deposition and seawater. Solid arrows indicate generalized hypothetical trends related to increasing overall agricultural effects on groundwater chemistry. ClO_4^- concentrations are high in samples with moderate agricultural impacts.

0.001 to 9 mg kg^{-1} (see Table S3 in the Supporting Information). Relatively high concentrations were in dried plant material (“kelp” product) and some other organic fertilizers, some of which may have included Atacama NO_3^- components. Sources like these could be responsible for some groundwater ClO_4^- , but only if applied at relatively high rates, as their ClO_4^- concentrations are orders of magnitude lower than those of Atacama NaNO_3 imported in the past ($\sim 1400\text{--}4000 \text{ mg kg}^{-1}$; see Table S3 in the Supporting Information). Inconsistent reports of ClO_4^- in natural KCl and other evaporite salts have not been fully resolved, but $\text{ClO}_4^-/\text{Cl}^-$ ratios in some common KCl fertilizer products are too low to account for the ClO_4^- in our samples (36–39) (see Table S3 in the Supporting Information). Our data do not indicate a correlation between ClO_4^- and either K or Cl⁻ in Long Island groundwater.

Relation between Perchlorate and Nitrate in Agricultural Recharge. Although ClO_4^- isotope data indicate an Atacama source for groundwater ClO_4^- in some areas, NO_3^- isotope data do not indicate an Atacama source for the NO_3^- (Figure 2). This apparent discrepancy can be explained by a combination of two factors: (1) Atacama NO_3^- was only a small fraction of total applied N fertilizer, and (2) Atacama NO_3^- may have been largely assimilated and replaced in recharging groundwater with new biogenic NO_3^- formed in agricultural soils, whereas Atacama ClO_4^- may have been recharged without being replaced or lost substantially by processes resulting in isotopic alteration. Replacement of Atacama NO_3^- with biogenic NO_3^- in soils would be consistent with observations elsewhere, indicating the distinctive O isotopic composition of atmospheric NO_3^- is preserved only in hyper-arid environments and lost where more biologically active soils exist (18, 19). In some environments, therefore, the existence and isotopic composition of ClO_4^- may be more reliable indicators of atmospheric deposition or Atacama NO_3^- fertilizer use than the existence or isotopic composition of NO_3^- .

Hypothetical concentrations of Atacama NO_3^- that potentially could be associated with observed groundwater ClO_4^- can be estimated by comparing concentrations and $\text{ClO}_4^-/\text{NO}_3^-$ ratios of groundwaters and Atacama NO_3^- fertilizers. If ClO_4^- in older NP and DL groundwaters (>20 years, $46\text{--}112 \text{ nmol L}^{-1}$) was derived from Atacama NO_3^- fertilizer with a $\text{ClO}_4^-/\text{NO}_3^-$ mole ratio of 2×10^{-3} (see Table S3 in the Supporting Information), then the maximum concentration of NO_3^- from that source would be around $23\text{--}56 \text{ μmol L}^{-1}$, and corresponding maximum Atacama N

recharge fluxes would be around $0.011\text{--}0.028 \text{ mol m}^{-2} \text{ year}^{-1}$. Compared individually by sample, these Atacama NO_3^- fluxes would equal 4–12% of estimated total NO_3^- in recharge. Compared to county-level loading data, the amount of Atacama fertilizer N needed to account for the ClO_4^- would be only about 0.7–1.6% of total N applied per unit area of cropland. Conversely, if all applied fertilizer N was Atacama NO_3^- , then hypothetical ClO_4^- concentrations could have been as high as $670\text{--}1580 \text{ nmol L}^{-1}$ ($67\text{--}157 \text{ μg L}^{-1}$) if based on recharge N data, or 6850 nmol L^{-1} (682 μg L^{-1}) if based on county-level cropland loading data. These comparisons would need to be modified if ClO_4^- was removed permanently by plants or microbial processes in soils. Nevertheless, they are consistent with Atacama NO_3^- N being only a minor source of the total NO_3^- N, and they illustrate the potential for small amounts of Atacama NO_3^- fertilizer to have contaminated large amounts of groundwater with ClO_4^- in the past.

Dated Long Island groundwaters provide a record of decreasing ClO_4^- and relatively constant or slightly increasing NO_3^- in recharge between about 1966 and 2006 (Figure 4). An upward decrease in ClO_4^- concentrations in DL groundwater could indicate either (1) decreasing proportion of Atacama NO_3^- with constant ClO_4^- concentration in applied N fertilizer mixtures, or (2) constant application rates of both Atacama NO_3^- and other N fertilizers during a period when ClO_4^- concentrations in Atacama NO_3^- fertilizer decreased. Compared to the mean molar ratio of $\text{ClO}_4^-/\text{NO}_3^-$ in Atacama NO_3^- ores and fertilizer products imported in the 20th century ($\sim 2 \times 10^{-3}$), some reports indicate the refining process was changed around 2000 to reduce ClO_4^- concentrations in NO_3^- fertilizer product by about 1 order of magnitude (40). A statement from a major manufacturer in 2001 indicates new NaNO_3 product should have $\text{ClO}_4^- < 100 \text{ mg kg}^{-1}$ ($\text{ClO}_4^-/\text{NO}_3^- < 8.5 \times 10^{-5} \text{ mol mol}^{-1}$) (2). The ClO_4^- concentrations and $\text{ClO}_4^-/\text{NO}_3^-$ ratios in recharge represented by our samples apparently decreased around 20–30 years ago (Figure 4), before the announced decrease in Atacama fertilizer ClO_4^- content. Therefore, we interpret our data as indicating a decreasing application rate of Atacama NO_3^- fertilizer with pre-2000 ClO_4^- concentrations, which may or may not have been followed by post-2000 low- ClO_4^- Atacama fertilizer. Continued use of Atacama fertilizer with $\text{ClO}_4^- < 100 \text{ μg kg}^{-1}$ at past application rates presumably would lower the groundwater-recharge concentrations further.

The groundwater recharge trends of decreasing ClO_4^- and relatively constant or slightly increasing NO_3^- concentrations

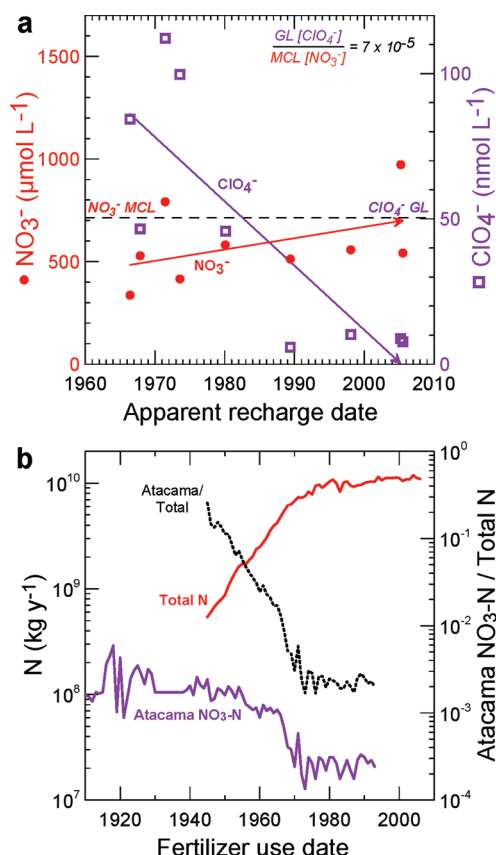


FIGURE 4. Trends related to changing agricultural inputs. (a) ClO_4^- and NO_3^- concentrations in dated groundwaters, compared to EPA NO_3^- maximum contaminant level (MCL) and New York ClO_4^- guidance level (GL). Data are from Northport (NP wells) and North Fork (DL transect, minus DL1s and DL1m). (b) Records of national (USA) Atacama NO_3^- and total N fertilizer use (2, 45, 46).

between 1966 and 2006 (Figure 4A) resemble qualitatively the national trends of Atacama and non-Atacama N fertilizer use in the USA (Figure 4B). Production wells 200–300 m southwest of the DL transect produced water with $\text{ClO}_4^- \approx 20\text{--}60 \text{ nmol L}^{-1}$ from open intervals approximately 26–33 m below the land surface (Suffolk County Water Authority data from 2005–2006), possibly representing the gradient between low and high ClO_4^- in the DL profile. Northport data also indicate relatively high ClO_4^- concentrations in groundwaters several decades old, recharged when land use was more agricultural than at present. Wells screened in high- ClO_4^- zones in areas like these may experience decreasing ClO_4^- concentrations in the future as younger low- ClO_4^- groundwater moves downward, although large and variable pumping rates could disturb these patterns. Atacama ClO_4^- may be common in other oxic aquifers underlying areas with agricultural histories ranging from the late 19th century through the 20th century. Groundwaters in such areas could exhibit varying trends of Atacama ClO_4^- concentrations with depth and groundwater age, in many cases accompanied by decreasing NO_3^- concentrations with age (41).

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Note Added in Proof

In this paper, “solutes introduced into the hydrologic environment as a result of man’s activities are referred to as contaminants, regardless of whether or not the concentrations reach levels that cause significant degradation of water quality” (47).

Supporting Information Available

Brief description of analytical methods, summary of data, interpretation of dissolved gases and atmospheric environmental tracers, description of NO_3^- and SO_4^{2-} isotope results, and additional tables and figures cited in the paper (Tables S1–S3 and Figures S1–S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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