

# Mobilization of Naturally Occurring Perchlorate Related to Land-Use Change in the Southern High Plains, Texas

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Perchlorate ( $\text{ClO}_4^-$ ) reservoirs that accumulated in semiarid unsaturated zones, similar to chloride ( $\text{Cl}^-$ ), can contaminate underlying aquifers if they are mobilized. The purpose of this study was to evaluate  $\text{ClO}_4^-$  mobilization related to land-use change from natural to agricultural ecosystems in the southern High Plains (SHP, USA), where large  $\text{ClO}_4^-$  concentrations ( $\leq 60 \mu\text{g/L}$ ) are found in the underlying Ogallala aquifer. Boreholes were drilled and sampled beneath natural ecosystems (3 boreholes) and beneath nonirrigated (rainfed, 7 boreholes) agricultural ecosystems. Large  $\text{ClO}_4^-$  reservoirs (361–934 g  $\text{ClO}_4^-/\text{ha}$ ; peaks 47–111  $\mu\text{g ClO}_4^-/\text{L}$  pore water), that accumulated for up to  $\sim 30,000$  yr under natural ecosystems, are being displaced to depths of 2.2 to  $>9.2$  m in sampled boreholes under rainfed agriculture by increased drainage/recharge. High correlations between  $\text{ClO}_4^-$  and  $\text{Cl}^-$  under natural areas ( $r = 0.81$ ) and rainfed agricultural areas ( $r = 0.88$ ) indicate that accumulation and mobilization of  $\text{ClO}_4^-$  can be predicted from  $\text{Cl}^-$  data. Minimal analysis of  $\text{ClO}_4^-$  (e.g., two points, minimum and maximum  $\text{Cl}^-$  concentrations in each profile) can be used to predict  $\text{ClO}_4^-$  inventories to within 9% of estimates based on detailed sampling. A pooled linear regression model based on all data in this study (99 points) predicts  $\text{ClO}_4^-$  inventories to within 19% of measured inventories. Continued mobilization of pre-existing unsaturated zone  $\text{ClO}_4^-$  reservoirs (361–934 g/ha) could increase the current groundwater  $\text{ClO}_4^-$  values by a further 8–21  $\mu\text{g/L}$  in the SHP.

## Introduction

Perchlorate ( $\text{ClO}_4^-$ ) is an oxyanion consisting of four O atoms bound to a single Cl atom and is commonly associated with salts of sodium, potassium, and ammonium. Perchlorate is an emerging contaminant in drinking water and food from natural and anthropogenic sources. The health impacts result from  $\text{ClO}_4^-$  competitively inhibiting iodide uptake by the sodium ( $\text{Na}^+$ ) iodide ( $\text{I}^-$ ) symporter (NIS) into the thyroid; therefore, effects of  $\text{ClO}_4^-$  on thyroid function are similar to those of iodide deficiency (1). These effects include decreased

thyroid hormone production which is required for normal development of the central nervous system of fetuses and infants, normal skeletal development and growth, and metabolic activity of infants and adults (1). Perchlorate is currently on the Contaminant Candidate List by the U.S. Environmental Protection Agency (EPA), which includes chemicals being considered for regulation with drinking water standards. The EPA interim guidance in 2003 suggested a reference dose of 0.03  $\mu\text{g ClO}_4^-$  per kg of body weight (bw) per day with a corresponding Drinking Water Equivalent Level (DWEL) of 1  $\mu\text{g/L}$ . However, a National Research Council (NRC) panel in 2005 indicated that a more appropriate reference dose would be 0.7  $\mu\text{g/kg bw/d}$ , which translates to a DWEL of 24.5  $\mu\text{g/L}$  (2). The NRC standard was adopted by EPA in 2005. A DWEL assumes that all of the contaminant is derived from drinking water; however,  $\text{ClO}_4^-$  has also been found in other liquids and foods, e.g., milk (1.9–11.3  $\mu\text{g/g}$ ), various types of lettuce (mean 8.06–11.8  $\mu\text{g/g}$ ), spinach (mean 115  $\mu\text{g/g}$ ), cantaloupe (mean 28.6  $\mu\text{g/g}$ ), and tomatoes (mean 13.7  $\mu\text{g/g}$ ) (3). While no Federal Maximum Contaminant Level (MCL) for  $\text{ClO}_4^-$  currently exists, it is possible that if one were adopted it would be lower than the DWEL of 24.5  $\mu\text{g/L}$  based on source apportionment. Various states have set different advisory levels for  $\text{ClO}_4^-$ : Arizona, 14  $\mu\text{g/L}$ ; California, 6  $\mu\text{g/L}$ ; Maryland, 1  $\mu\text{g/L}$ ; Massachusetts, 2  $\mu\text{g/L}$ ; Nevada, 18  $\mu\text{g/L}$ ; New Mexico, 1  $\mu\text{g/L}$ ; New York, 5  $\mu\text{g/L}$  drinking water planning level and 18  $\mu\text{g/L}$  drinking water notification level; and Texas, 17  $\mu\text{g/L}$  residential protective cleanup level (PCL) and 51  $\mu\text{g/L}$  industrial/commercial PCL. Widespread  $\text{ClO}_4^-$  contamination in water was first determined in the United States in 1997 following the development of an analytical method that provided a 4  $\mu\text{g/L}$  detection level. An estimated 11 million people have  $\text{ClO}_4^-$  at concentrations  $>4 \mu\text{g/L}$  in their drinking water (2).

Perchlorate compounds readily dissolve in water, resulting in the  $\text{ClO}_4^-$  anion, which is similar to  $\text{Cl}^-$  in its high solubility ( $>200 \text{ g/L}$ ) and mobility because of poor sorption onto clays. However,  $\text{ClO}_4^-$  can be reduced microbially under anaerobic conditions to  $\text{Cl}^-$  and water, which is one of the treatment technologies for  $\text{ClO}_4^-$  (2). Sources of  $\text{ClO}_4^-$  are both natural and anthropogenic. In addition, natural sources can be distributed anthropogenically, such as through application of Chilean nitrate fertilizers (4). The +7 oxidation state of Cl in  $\text{ClO}_4^-$  resulted in its widespread use in solid propellants in rockets and missiles, in explosives and fireworks, and in automobile air bags. Early studies focused on point source contamination of groundwater from U.S. Department of Defense and industrial facilities (1). Natural salts of  $\text{ClO}_4^-$  accumulate in arid regions from atmospheric sources, e.g., hyperarid conditions in the Atacama Desert, Chile, over 6–10 million years (5). Similar processes have occurred in semiarid regions over much shorter timescales ( $\sim 10,000$ – $15,000$  yr) in the southwestern United States resulting in large  $\text{ClO}_4^-$  reservoirs (up to 1 kg/ha) in unsaturated zones (6). Previous studies have shown that there are large  $\text{ClO}_4^-$  concentrations ( $\leq 60 \mu\text{g/L}$ ) in the underlying aquifers in some regions, e.g., the Ogallala aquifer in the southern High Plains (7).

It is important to understand the linkage between  $\text{ClO}_4^-$  in unsaturated zone reservoirs and in underlying aquifers. High  $\text{ClO}_4^-$  concentrations in the Ogallala aquifer are not derived from the reservoirs beneath natural ecosystems, because there is no groundwater recharge beneath natural ecosystems in interplaya settings in the SHP (8). Bulge-shaped accumulations of  $\text{Cl}^-$  and upward matric potential gradients in these regions indicate that water has been moving upward

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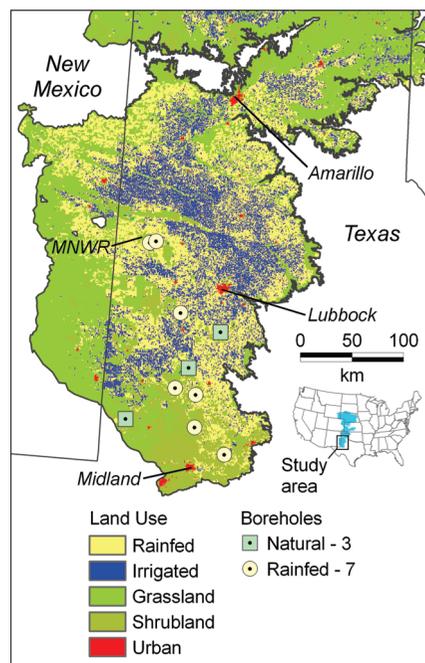
and soils have been drying out since the Pleistocene (10,000–15,000 yr) (9). Conversion of natural ecosystems to rainfed agriculture has changed water partitioning at the land surface. Although natural ecosystems and rainfed agricultural ecosystems ultimately only receive water from precipitation, partitioning of precipitation at the land surface differs between these two settings. In contrast to perennial grasslands and shrublands with deep roots ( $\geq 3$  m), crops have shallow roots ( $\sim 1$  m) and long fallow periods without vegetation ( $\sim 7$  months in the SHP) that allow water to drain below the root zone and recharge the aquifer (9). Therefore, increased drainage/recharge beneath cropland (median 24 mm/yr in the SHP) can mobilize salts that accumulated under natural ecosystems into the underlying aquifer, as shown by  $\text{Cl}^-$  concentrations in previous studies (9).

The objective of this study was to evaluate mobilization of naturally occurring  $\text{ClO}_4^-$  related to land use change from natural to rainfed (nonirrigated) agricultural ecosystems in the SHP. Unique aspects of this study include the focus on  $\text{ClO}_4^-$  mobilization rather than distribution, which was evaluated in a previous study (6), focus on unsaturated zone profiles (10 profiles) linking land surface and groundwater  $\text{ClO}_4^-$  concentrations, with emphasis on rainfed agricultural ecosystems (7 profiles) rather than on natural ecosystems and irrigated agricultural ecosystems as in previous studies (6). This study emphasizes relationships between  $\text{ClO}_4^-$  and  $\text{Cl}^-$  to assess the ability of  $\text{Cl}^-$  to predict  $\text{ClO}_4^-$  distribution and mobilization. Evaluation of  $\text{ClO}_4^-$  mobilization is similar to an inverse problem in which the outputs ( $\text{ClO}_4^-$  concentrations in the unsaturated zone and groundwater) are measured and these data are used to estimate inputs and evaluate transport of  $\text{ClO}_4^-$  through the system. This inverse approach is required because there is no information on long-term  $\text{ClO}_4^-$  concentrations in precipitation. The current study should further our understanding of linkages between  $\text{ClO}_4^-$  reservoirs in semiarid unsaturated systems and groundwater  $\text{ClO}_4^-$  contamination by evaluating  $\text{ClO}_4^-$  mobilization under rainfed agricultural areas.

## Experimental Section

**Site Description.** The study area in the SHP (75,000 km<sup>2</sup>) in Texas is underlain by the Ogallala aquifer, the largest aquifer in the United States. Rainfed agriculture refers to nonirrigated agriculture that relies solely on rainfall for water input and is also referred to as dryland agriculture. Land use in the SHP includes natural grasslands (33%) and shrublands (12%) used for grazing, rainfed agriculture (42%) dominated by cotton production, irrigated agriculture (11%), and other (2%) (1992 National Land Cover Data, NLCD, Figure 1). Land use classification from NLCD 1992 is generally consistent with NLCD 2000 (10). The unsaturated zone ranges from 0 to 134 m thick (median 37 m). Clay content in surface soils (upper 1.5–2.0 m) ranges from 1 to 68% (mean 28%) based on the SSURGO database (11). Mean annual precipitation ranges from 376 mm in the south (Midland, 1931–2005) to 501 mm in the north (Amarillo, 1947–2005). Median  $\text{Cl}^-$  concentration in precipitation ranges from 0.06 to 0.19 mg/L (1985–2006; median 0.13 mg/L (National Atmospheric Deposition program (NADP), Muleshoe station, <http://nadp.sws.uiuc.edu/>) (Figure 1).

**Sample Collection and Analyses.** To evaluate mobilization of  $\text{ClO}_4^-$ , 100 unsaturated soil samples from 10 sites in the SHP were analyzed for  $\text{ClO}_4^-$ . Three sites are in natural grassland/shrubland ecosystems and are farther south than boreholes in the same setting from a previous study (Table 1, Figure 1) (6). The remaining 7 boreholes are in rainfed agricultural settings. Samples from these boreholes had previously been analyzed for water content, matric potential, and  $\text{Cl}^-$  concentrations (10, 11). A detailed description of methods is provided in refs 10, 11 and only a brief description



**FIGURE 1.** Location of sampled boreholes in natural ecosystems (3 boreholes) and rainfed agricultural ecosystems (7 boreholes). Inset shows location of southern High Plains in the United States. Generalized land use is based on National Land Cover Data (NLCD), 1992 (13). Agricultural categories (rainfed and irrigated) represent a combination of NLCD classifications (row crops, 38%; small grains, 12%; pasture/hay, 2%; fallow and orchards, 1%). Irrigation coverage is based on Qi et al. (14).

is provided in this section. Approximately 40 mL of double deionized water was added to about 25 g of air-dried soil. The mixture was placed in a reciprocal shaker for 4 h, centrifuged at 7000 rpm for 20 min, and the supernatant was filtered to 0.2  $\mu\text{m}$ . Soil samples were then oven-dried at 105 °C for 48 h to determine gravimetric water content. Water-extractable  $\text{Cl}^-$  concentrations were measured using ion chromatography (Dionex ICS 2000; EPA Method 300.0, detection limit 0.01 mg/L). Water samples for  $\text{ClO}_4^-$  analyses were filtered through 0.1  $\mu\text{m}$  Supor (PES) membrane IC certified Acrodisc syringe filters. Analysis of  $\text{ClO}_4^-$  was conducted using a sequential ion chromatography–mass spectroscopy (IC–MS/MS) technique with a detection limit of 0.05  $\mu\text{g/L}$  in the supernatant and an analytical uncertainty of  $\sim \pm 20\%$  (Supporting Information).

Water-extractable ion concentrations are expressed on a mass basis as mg or  $\mu\text{g}$  ion per kg of dry soil and were calculated by multiplying the ion concentration in the supernatant by the extraction ratio (g water/g soil). Ion concentrations are also expressed as mg or  $\mu\text{g}$  ion per L of soil pore water and were calculated by dividing concentrations in mg/kg or  $\mu\text{g/kg}$  by gravimetric water content and multiplying by water density. Concentrations on a mass basis are useful for interprofile comparisons to reduce impacts of variations in soil–water contents related to textural variations. Inventories of ions (kg/ha or g/ha) were calculated by multiplying depth-weighted ion concentrations (mg/kg or  $\mu\text{g/kg}$ ) by interval thickness (m), soil bulk density (kg/m<sup>3</sup>), and 10<sup>4</sup> (m<sup>2</sup>/ha) for units conversion.

The time (yr) required to accumulate  $\text{Cl}^-$  in profiles was calculated as follows:

$$t = \frac{\sum \text{Cl}_{uz}^- \rho_v dz}{P \text{Cl}_p} \quad (1)$$

where  $\text{Cl}_{uz}^-$  and  $\text{Cl}_p$  are  $\text{Cl}^-$  concentrations in unsaturated zone (uz) pore water (mg/kg) and in precipitation (mg/L),

**TABLE 1. Concentrations and Inventories of Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> in Sampled Profiles<sup>a</sup>**

| borehole                        | depth     |             |        | inventory               |                                      | concentration          |                                      |                             | ClO <sub>4</sub> <sup>-</sup> |           | flushed                |                                      | deep                   |                                      |
|---------------------------------|-----------|-------------|--------|-------------------------|--------------------------------------|------------------------|--------------------------------------|-----------------------------|-------------------------------|-----------|------------------------|--------------------------------------|------------------------|--------------------------------------|
|                                 | total (m) | flushed (m) | WT (m) | Cl <sup>-</sup> (kg/ha) | ClO <sub>4</sub> <sup>-</sup> (g/ha) | Cl <sup>-</sup> (mg/L) | ClO <sub>4</sub> <sup>-</sup> (μg/L) | molar (× 10 <sup>-3</sup> ) | peak (μg/L)                   | depth (m) | Cl <sup>-</sup> (mg/L) | ClO <sub>4</sub> <sup>-</sup> (μg/L) | Cl <sup>-</sup> (mg/L) | ClO <sub>4</sub> <sup>-</sup> (μg/L) |
| Natural Ecosystems              |           |             |        |                         |                                      |                        |                                      |                             |                               |           |                        |                                      |                        |                                      |
| And05-02                        | 8.5       | 1.6         | 28     | 5,381                   | 361                                  | 470                    | 33                                   | 49                          | 62                            | 8.3       |                        |                                      |                        |                                      |
| Daw06-01                        | 8.4       | 1.9         | 30     | 25,643                  | 613                                  | 2303                   | 56                                   | 121                         | 111                           | 8.3       |                        |                                      |                        |                                      |
| Lyn06-01                        | 28.2      | 3.1         |        | 41,064                  | 934                                  | 860                    | 19                                   | 123                         | 47                            | 5.5       |                        |                                      |                        |                                      |
| Rainfed Agricultural Ecosystems |           |             |        |                         |                                      |                        |                                      |                             |                               |           |                        |                                      |                        |                                      |
| Bai05-01                        | 11.4      | 7.7         | 28     | 4,665                   | 186                                  | 281                    | 10                                   | 71                          | 59                            | 11.4      | 7.6                    | 2.7                                  | 785                    | 30                                   |
| Daw06-02                        | 9.2       | >9.2        | 10     | 55                      | 22                                   | 3.7                    | 1.4                                  | 7                           | 4.0                           | 5.9       | 3.7                    | 1.4                                  |                        |                                      |
| Gai05-02                        | 10.7      | 8.9         | 21     | 3,210                   | 141                                  | 107                    | 6.1                                  | 64                          | 37                            | 10.7      | 7.9                    | 3.0                                  | 550                    | 21                                   |
| Lam05-01                        | 8.5       | 3.4         | 36     | 10,257                  | 147                                  | 737                    | 10                                   | 196                         | 29                            | 8.5       | 17                     | 2.3                                  | 1,220                  | 17                                   |
| Mar05-02                        | 8.3       | 2.2         | 34     | 6,836                   | 76                                   | 548                    | 6.6                                  | 234                         | 21                            | 8.3       | 24                     | 3.0                                  | 755                    | 10                                   |
| Mar05-04                        | 4.6       | 3.4         | 32     | 576                     | 44                                   | 80                     | 6.7                                  | 37                          | 21                            | 2.8       | 18                     | 5.2                                  | 385                    | 10                                   |
| Ter05-01                        | 7.1       | 5.9         | 28     | 449                     | 29                                   | 38                     | 2.0                                  | 43                          | 6.0                           | 7.1       | 10                     | 1.6                                  | 155                    | 4.5                                  |

<sup>a</sup> Borehole settings include natural ecosystems and rainfed agricultural ecosystems, profile names include county location (And, Anderson; Bai, Bailey; Daw, Dawson; Gai, Gaines; Lam, Lamb; Lyn, Lynn; Mar, Martin; Ter, Terry), yr of drilling, 05 = 2005, etc.; and borehole no.. Total, total depth drilled; Flushed, refers to the zone under rainfed agriculture where the Cl<sup>-</sup> bulge that accumulated under natural ecosystems has been displaced downward to the specified depth (9); profile Daw06-02 was flushed throughout the sampled depth; WT, water table depth; Inventory for Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> throughout total profile depth; Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup>, depth-weighted mean concentration; Molar ratio, Cl<sup>-</sup>/ClO<sub>4</sub><sup>-</sup> molar ratio; Flushed, Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> depth-weighted mean concentrations in Cl<sup>-</sup> flushed zone; Deep, Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> depth-weighted mean concentrations below Cl<sup>-</sup> flushed depth. Flushed and Deep apply only to profiles under rainfed agriculture.

respectively;  $\rho_b$  is bulk density (1600 kg/m<sup>3</sup>),  $dz$  is depth interval, and  $P$  is precipitation (mm/yr). Equation 1 assumes that chloride input ( $PCI_p$ ) has remained uniform over time. Previous studies in the Chihuahuan Desert of Texas have shown that this assumption is reasonable based on similarity of accumulation times from chloride and radioactive decay of <sup>36</sup>Cl on time scale of ~50,000 yr (12).

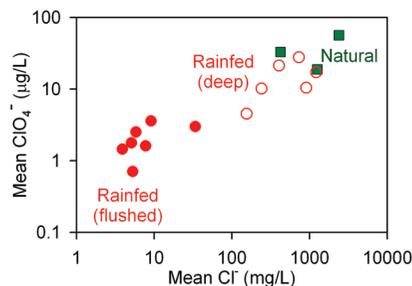
**Linear Regression Analysis.** Relationships between molar concentrations (mM ion/kg soil) of Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> within and between boreholes and ecosystems were examined using standard linear regression analysis methods. Population distributions of Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> are highly skewed toward large values and the data were log-log transformed for regression analysis. Regression models were developed using the general form

$$(\log \text{ClO}_4^-)_i = \beta_0 + \beta_1(\log \text{Cl}^-)_i + \beta_{2j}(x_{ij}) + \beta_{3j}(x_{ij})(\log \text{Cl}^-)_i + \varepsilon_i \quad (3)$$

where  $i = 1, 2, \dots, n$  observations,  $\beta_0$  is the main intercept term,  $\beta_1$  is the main slope term, and  $\varepsilon_i$  is the error. Second-order interactions were quantified by including the indicator variable  $x$ , with  $\beta_{2j}$  and  $\beta_{3j}$  representing the intercept and slope interaction terms, respectively, for  $j = 1, 2, \dots, m-1$  indicator variables where  $m$  is the total number of potential interactions (i.e.,  $m = 2$  ecosystems or  $m = 3$  or 7 boreholes). Simple (minimum) regression models ( $\beta_2, \beta_3 = 0$ ) were developed separately for each borehole to assess within-borehole variability of the Cl<sup>-</sup>-ClO<sub>4</sub><sup>-</sup> relationship and for the data pooled by ecosystem to assess within-ecosystem variability. Interaction regression models ( $\beta_2, \beta_3 \neq 0$ ) were also developed for (a) ecosystem and (b) borehole location from the respective pooled data sets to separately assess the significance of second-order effects. Finally, an overall simple (minimum) regression model was developed from the entire pooled data. The statistical significances of the various main and interaction terms were quantified using  $F$ -test statistics and associated  $p$  values, and predictive power was assessed using the standard error of prediction ( $SE_p$ ), which represents a percentage when using log-log transformed variables.

**Results and Discussion**

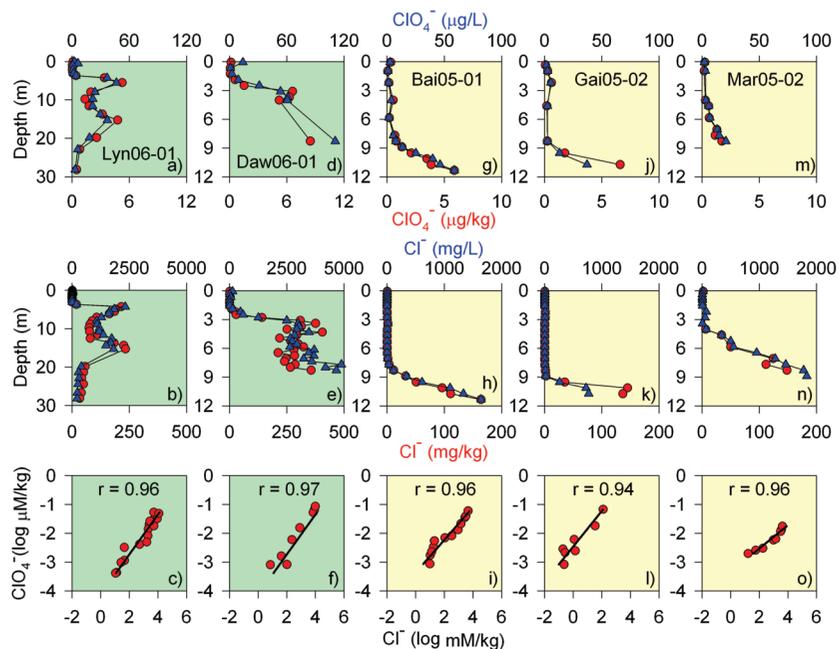
Profile mean concentrations of Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> are high in natural ecosystems and lower in rainfed agricultural eco-



**FIGURE 2. Mean ClO<sub>4</sub><sup>-</sup> versus mean Cl<sup>-</sup> concentrations for boreholes located in different land use settings. Rainfed (flushed) represents the shallower, Cl<sup>-</sup>-flushed zones having young soil-water. Rainfed (deep) represents the deeper, high-Cl<sup>-</sup> zones having old water representative of pre-cultivation (natural) conditions.**

systems (Figure 2, Table 1). Information on water content, matric potential, and Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> concentrations are provided for all measured profiles in Supporting Information Figure S1.

**Perchlorate Reservoirs beneath Natural Ecosystems.** The three boreholes drilled beneath natural shrubland and grassland ecosystems confirm the occurrence of large reservoirs of ClO<sub>4</sub><sup>-</sup> in this setting, similar to the bulge-shaped Cl<sup>-</sup> reservoirs in these regions (10, 11). Peak ClO<sub>4</sub><sup>-</sup> pore water concentrations are 47, 62, and 111 μg/L at depths of 5.5, 8.3, and 8.3 m in each of the profiles, respectively (Table 1, Figure 3a and d, and Supporting Information Figure S1a). Inventories of ClO<sub>4</sub><sup>-</sup> are 361, 613, and 934 g ClO<sub>4</sub><sup>-</sup>/ha. The inventory for the Lyn06-01 profile (934 g ClO<sub>4</sub><sup>-</sup>/ha) is the most complete because entire ClO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup> bulges were sampled whereas only the upper portion of the bulges was sampled in the other two profiles. The ClO<sub>4</sub><sup>-</sup> inventories are within the range of those found in other profiles in the central and southern High Plains (234–1050 g ClO<sub>4</sub><sup>-</sup>/ha (6)). The Cl<sup>-</sup> bulges in the different profiles have been accumulating for 4200 yr (And05-02), 17,300 yr (Daw06-01) (9), and 29,100 yr (Lyn06-01). Concentrations of Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> are highly correlated within profiles ( $r = 0.92, 0.96,$  and  $0.97$ ) (Figure 3c and f, Table 2) and ClO<sub>4</sub><sup>-</sup> concentrations can be estimated from Cl<sup>-</sup> concentrations to within 13–23% in different profiles (Table 2). Correlations are also provided for untransformed data for



**FIGURE 3.** Representative  $\text{Cl}^-$  and  $\text{ClO}_4^-$  profiles in natural grassland/shrubland ecosystems (green) and rainfed agriculture (yellow). Correlations between  $\text{Cl}^-$  and  $\text{ClO}_4^-$  molar concentrations are also shown.

**TABLE 2.** Linear Regression Results for Individual Profile Data and Combined Ecosystem Data<sup>a</sup>

| borehole                        | <i>N</i> | <i>r</i> | $\beta_1$ | $\beta_0$ | $\text{SE}_p$ | $\text{SE}_s$ | $\text{SE}_i$ | <i>F</i> | <i>p</i> |
|---------------------------------|----------|----------|-----------|-----------|---------------|---------------|---------------|----------|----------|
| Natural Ecosystems              |          |          |           |           |               |               |               |          |          |
| And05-02                        | 16       | 0.92     | 0.33      | -2.51     | 0.13          | 0.10          | 0.04          | 73       | <0.0001  |
| Daw06-01                        | 9        | 0.97     | 0.70      | -3.95     | 0.23          | 0.07          | 0.21          | 99       | <0.0001  |
| Lyn06-01                        | 16       | 0.96     | 0.64      | -3.97     | 0.21          | 0.05          | 0.15          | 161      | <0.0001  |
| Rainfed Agricultural Ecosystems |          |          |           |           |               |               |               |          |          |
| Bai05-01                        | 12       | 0.96     | 0.52      | -3.27     | 0.17          | 0.05          | 0.12          | 118      | <0.0001  |
| Daw06-02                        | 7        | 0.04     | 0.07      | -3.03     | 0.31          | 0.79          | 0.77          | 0.01     | 0.9366   |
| Gai05-02                        | 7        | 0.94     | 0.54      | -3.23     | 0.25          | 0.09          | 0.18          | 36       | 0.0019   |
| Lam05-01                        | 8        | 0.91     | 0.55      | -3.66     | 0.26          | 0.10          | 0.28          | 29       | 0.0017   |
| Mar05-02                        | 8        | 0.96     | 0.37      | -3.26     | 0.11          | 0.04          | 0.13          | 71       | 0.0002   |
| Mar05-04*                       | 7        | 0.93     | 0.60      | -3.68     | 0.21          | 0.11          | 0.22          | 33       | 0.0023   |
| Ter05-01                        | 9        | 0.79     | 0.31      | -3.14     | 0.16          | 0.09          | 0.16          | 12       | 0.0112   |
| Combined Ecosystems             |          |          |           |           |               |               |               |          |          |
| natural                         | 41       | 0.81     | 0.51      | -3.31     | 0.39          | 0.06          | 0.17          | 72       | <0.0001  |
| rainfed                         | 58       | 0.88     | 0.48      | -3.36     | 0.25          | 0.03          | 0.08          | 199      | <0.0001  |
| overall                         | 99       | 0.86     | 0.51      | -3.38     | 0.32          | 0.03          | 0.08          | 277      | <0.0001  |

<sup>a</sup> Results of regressing  $\log \text{ClO}_4^-$  on  $\log \text{Cl}^-$  molar concentrations. *N*, number of samples; *r*, correlation coefficient;  $\beta_1$ , slope;  $\beta_0$ , intercept;  $\text{SE}_p$ , prediction standard error;  $\text{SE}_s$ , slope standard error;  $\text{SE}_i$ , intercept standard error; *F*, regression *F*-test statistic; *p*, regression *F*-test statistic *p*-value. Combined results represent pooled minimum models. \* indicates parameters for profile after removing one outlying point that had undue influence on the results.

comparison with previous correlations (6) and are similar to those based on log-transformed data (Supporting Information Table S1 and Figure S2). Mean  $\text{Cl}^-$  to  $\text{ClO}_4^-$  molar ratios are 49,000, 121,000, and 123,000, slightly lower than those found in a previous study (151,000–572,000 (6)). The lower values may result from less complete profile sampling. Similarities in shape of the  $\text{Cl}^-$  and  $\text{ClO}_4^-$  profiles and molar ratios are attributed to a common source from precipitation and dry fallout and a similar evapotranspirative concentration process at the base of the root zone attributed to the semiarid climate and lack of recharge (8).

Wet and dry deposition rates of  $\text{ClO}_4^-$  (32, 35, and 86 mg/ha/yr) were calculated by dividing  $\text{ClO}_4^-$  inventories (361, 613, and 934 g/ha) by the times required to accumulate  $\text{Cl}^-$  in the profiles (4,200, 17,300, and 29,100 yr) (eq 1). Average  $\text{ClO}_4^-$  concentrations in precipitation were estimated by dividing  $\text{ClO}_4^-$  deposition rates by precipitation rates (390, 444, and 514 mm/yr) and are 22, 8, and 6  $\mu\text{g}/\text{m}^3$  (0.022, 0.008,

0.006  $\mu\text{g}/\text{L}$ ). Such estimates assume  $\text{ClO}_4^-$  is conservative (no sources or sinks) and all  $\text{ClO}_4^-$  results from precipitation (no dry deposition). These estimates of  $\text{ClO}_4^-$  in precipitation are similar to or slightly higher than those found previously in this region from unsaturated zone  $\text{ClO}_4^-$  data (2–6  $\mu\text{g}/\text{m}^3$ ) and much lower than those measured in precipitation in Lubbock, in the SHP (mean  $193 \pm 351 \mu\text{g}/\text{m}^3$ ; range: 10–1600  $\mu\text{g}/\text{m}^3$  (6)). A number of possible reasons may exist for the discrepancy between estimated  $\text{ClO}_4^-$  concentrations in precipitation from this study and those measured in precipitation in Lubbock. It is certainly possible that some  $\text{ClO}_4^-$  was reduced by microorganisms. However, the  $\text{ClO}_4^-$  concentrations reported for precipitation (6) may not accurately reflect the long-term average  $\text{ClO}_4^-$  precipitation value, given the large range of reported values and very limited data. More recent evaluations of  $\text{ClO}_4^-$  in wet deposition using controlled samples from the National Atmospheric Deposi-

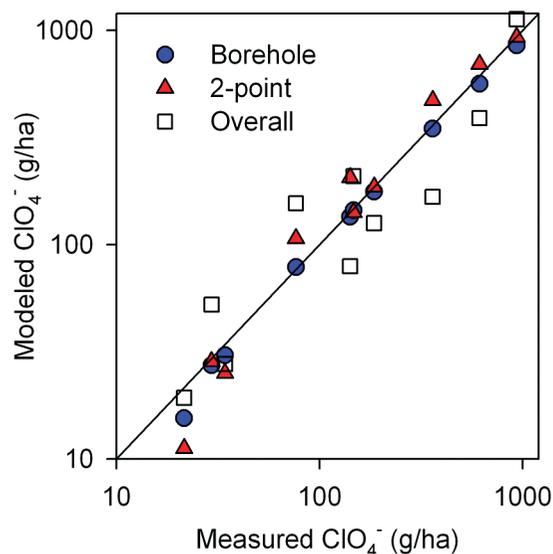
tion Program indicate much lower concentrations similar to those reported from this study (13).

**Perchlorate Profiles beneath Rainfed Agriculture.** Perchlorate bulges that accumulated under natural ecosystems have been displaced downward with depth (Figure 3g, j, m) as a result of increased drainage/recharge during the past 33–89 yr (9) in the sampled boreholes beneath rainfed agriculture, similar to the displacement of  $\text{Cl}^-$  bulges (Figure 3h, k, n; Table 1; Supporting Information Figure S1b). Displacement depths of  $\text{ClO}_4^-$  range from 2.2 to 8.9 m below the land surface in 6 of the profiles and  $\text{ClO}_4^-$  was flushed throughout the sampled unsaturated zone (9.2 m depth) in the remaining profile (Daw06-02), similar to  $\text{Cl}^-$ . Concentrations of  $\text{ClO}_4^-$  in the  $\text{Cl}^-$  flushed zone are low (mean 1.4–5.2  $\mu\text{g/L}$ ), similar to low  $\text{Cl}^-$  concentrations in this zone (mean 3.7–24 mg/L) (Table 1). Maximum  $\text{ClO}_4^-$  concentrations are found at or near the base of each of the 6 partially flushed  $\text{Cl}^-$  profiles (6.0–59  $\mu\text{g ClO}_4^-/\text{L}$ ) (Table 1; Supporting Information Figure S1b). Concentrations of  $\text{Cl}^-$  and  $\text{ClO}_4^-$  are highly correlated in each profile ( $r = 0.79$ – $0.96$ ), with the exception of the Daw06-02 profile where  $\text{ClO}_4^-$  concentrations are uniformly low (Supporting Information Table S1, Figure S2). These high correlations between  $\text{ClO}_4^-$  and  $\text{Cl}^-$  indicate that  $\text{Cl}^-$  concentrations can predict  $\text{ClO}_4^-$  concentrations to within 11–31% in different profiles (Table 2). Plant uptake of  $\text{ClO}_4^-$  should have a negligible impact on subsurface  $\text{ClO}_4^-$  distribution at these sites. Accumulation of  $\text{ClO}_4^-$  occurs primarily in the leaves of plants (14), and leaves of the dominant crop in the SHP (cotton) are not harvested.

**Comparison of Chloride–Perchlorate Relationships between Land Use Settings.** Chloride can be used to predict  $\text{ClO}_4^-$  to within 32% ( $r = 0.86$ ) using the overall minimum model that uses the pooled data and omits interaction effects (Table 2). Ecosystem interactions are not significant and the two ecosystem models are coincident with equal slope and intercept. The similarity in slopes between natural and rainfed ecosystems is expected because the deeper portions of incompletely flushed profiles in rainfed agriculture are equivalent to concentrations in natural settings. Borehole location interaction terms for 2 of the boreholes (1 natural, 1 rainfed) are significant within the pooled ecosystem data models, indicating that those boreholes have  $\text{Cl}^-$ – $\text{ClO}_4^-$  relationships that are different from the overall relationship. However, omitting the interaction terms has limited impact on the regressions and generally does not result in an unreasonably large loss of predictive power for the resulting minimum models considering the 2 orders of magnitude range of measured  $\text{ClO}_4^-$  values. The results are detailed in Supporting Information Table S3.

The natural ecosystem minimum model is significant with  $r = 0.81$  and  $\text{SE}_p = 39\%$  (Table 2). Interactions are significant for only one of the natural borehole locations (And05-02), resulting in higher  $r$  (0.95) and lower  $\text{SE}_p$  (20%) relative to the pooled minimum model. The rainfed ecosystem minimum model is also significant with  $r = 0.88$  and  $\text{SE}_p = 25\%$  (Table 2). Interactions are significant also for only one of the rainfed borehole locations (Gai05-02), resulting in marginally higher  $r$  (0.90) and lower  $\text{SE}_p$  (24%). The residuals for all models are normally distributed and variance is uniform for all but one model (the natural ecosystem minimum model, which has greater variance at low  $\text{ClO}_4^-$  concentrations).

Given that  $\text{ClO}_4^-$  analyses are not routinely performed and can be expensive, how much  $\text{ClO}_4^-$  information is required to characterize the  $\text{ClO}_4^-$  inventory? To address this question, the  $\text{ClO}_4^-$  inventory for each borehole was estimated using (1) simple regression models developed for each borehole based on all the data within a profile, (2) simple 2-point models developed for each borehole based on only the  $\text{Cl}^-$  and  $\text{ClO}_4^-$  data pairs representing the minimum and maxi-



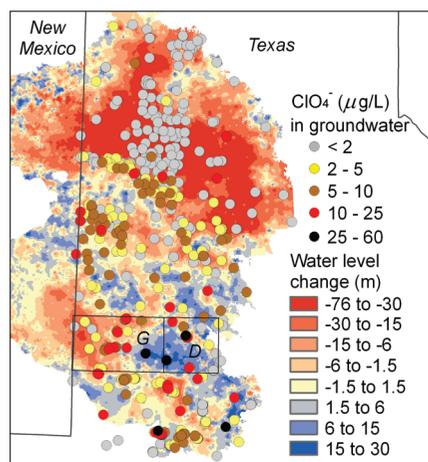
**FIGURE 4. Measured versus estimated  $\text{ClO}_4^-$  inventories. Different estimates use linear regression models based on all samples within each borehole (Borehole), the minimum and maximum  $\text{Cl}^-$  concentration samples in each borehole (2-point), and the overall minimum model (Overall). Line shown represents the 1:1 line.**

mum  $\text{Cl}^-$  values within a profile, and (3) a single overall minimum model that combines all the data.

Estimated  $\text{ClO}_4^-$  inventories were compared with measured  $\text{ClO}_4^-$  inventories (Figure 4). Results show that borehole inventories estimated using the individual borehole regression models have an average error of  $\pm 4\%$  relative to measured inventories, which quantifies within-borehole deviation from the borehole regressions and provides a baseline for comparison. Inventory estimates using the 2-point models indicate that analyzing  $\text{ClO}_4^-$  only in samples that correspond to the range of  $\text{Cl}^-$  (minimum and maximum) in each borehole results in an average error of  $\pm 9\%$  relative to measured inventories, reducing the number of samples used in this study by a factor of 5 while resulting in only a marginal loss of accuracy. Finally, borehole inventory estimates based on the single overall minimum model predict  $\text{ClO}_4^-$  inventories with an average error of  $\pm 19\%$  relative to measured inventories, which essentially quantifies the loss of accuracy that results from ignoring borehole location effects.

**Relationship between Unsaturated Zone Profiles and Groundwater Perchlorate Distribution.**

Previous studies have shown that concentrations of  $\text{ClO}_4^-$  in groundwater in the SHP ( $<0.5$ – $59 \mu\text{g/L}$ , median  $2.1 \mu\text{g/L}$ ) are inversely related to water table depth and aquifer saturated thickness, indicating a surface source of  $\text{ClO}_4^-$  because shallow water tables are more vulnerable to surface-based contamination and lower aquifer saturated thicknesses result in less dilution of contaminants (7). The surface source is also supported by high correlations between  $\text{ClO}_4^-$  and  $\text{IO}_3^-$ , known to be of atmospheric origin (15). The current distribution of  $\text{ClO}_4^-$  is attributed to past flushing of  $\text{ClO}_4^-$  from the unsaturated zone into the underlying aquifer. The highest groundwater  $\text{ClO}_4^-$  concentrations ( $\leq 60 \mu\text{g/L}$ ) are in the southern part of the SHP, in Gaines and Dawson counties (Figure 5). High  $\text{ClO}_4^-$  concentrations in Dawson County ( $<0.5$ – $59 \mu\text{g/L}$ , median =  $8.0 \mu\text{g/L}$ , 17 samples) are generally collocated with a zone of water table rises attributed to increased recharge under rainfed agriculture during the past few decades (Figure 5; mean 7.1 m,  $3400 \text{ km}^2$  area (9)) and low unsaturated zone  $\text{Cl}^-$  and high matric potentials also indicative of recharge (9). This region coincides with unsaturated zone  $\text{Cl}^-$  and  $\text{ClO}_4^-$  profiles that are completely flushed (e.g., Daw06-02,



**FIGURE 5.** Groundwater  $\text{ClO}_4^-$  concentrations in the Texas portion of the southern High Plains aquifer (7). The background represents groundwater level changes from predevelopment (earliest data prior to 1980 in a given area, average 1956, 5861 wells) to the present (latest data after 1980 in a given area, average 2001, 3837 wells) based on the Texas Water Development Board groundwater database ([www.twdb.state.tx.us](http://www.twdb.state.tx.us)). Highest  $\text{ClO}_4^-$  values ( $\geq 10 \mu\text{g/L}$ ) generally coincide with regions that are dominated by rainfed agriculture where groundwater levels have risen in Dawson (D) and Gaines (G) counties and with regions of intensive irrigation in Gaines County.

Table 1, Supporting Information Figure S1b). High  $\text{ClO}_4^-$  concentrations in the Gaines county area ( $< 0.5\text{--}30 \mu\text{g/L}$ , median =  $5.2 \mu\text{g/L}$ , 39 samples) coincide with an area of intensive irrigation and may be attributed to  $\text{ClO}_4^-$  mobilization caused by irrigation return flow.

Many of the unsaturated zone profiles from agricultural areas are incompletely flushed of  $\text{Cl}^-$  (10 out of 19 profiles under rainfed agriculture) (9). These profiles are also incompletely flushed of  $\text{ClO}_4^-$ . How will continued flushing of such  $\text{ClO}_4^-$  reservoirs impact future  $\text{ClO}_4^-$  concentrations in the underlying Ogallala aquifer? The impact of flushing  $\text{ClO}_4^-$  through the unsaturated zone can be evaluated by mixing  $\text{ClO}_4^-$  inventories from natural profiles (361–934 g/ha) with groundwater over the median aquifer saturated thickness, which is 15 m in the SHP. This process would increase existing groundwater  $\text{ClO}_4^-$  concentrations (Figure 5) by a further 8–21  $\mu\text{g/L}$  (Supporting Information). Reducing the thickness of the mixing zone in the aquifer would linearly increase the magnitude of the change in  $\text{ClO}_4^-$  concentrations. Multilevel groundwater well data indicate that  $\text{ClO}_4^-$  concentrations are greater in the shallow zone and decrease with depth in the aquifer (6), indicating that these estimated changes in groundwater  $\text{ClO}_4^-$  concentrations may represent a lower bound on actual increases. Estimated time lags to reach the water table from  $\text{Cl}^-$  data in the profiles evaluated in previous studies range from ~120 to 500 yr for various profiles in the SHP (9).

The  $\text{ClO}_4^-$  reservoirs under natural ecosystems are bulge shaped and should ultimately be transported through the aquifer system. High  $\text{ClO}_4^-$  concentrations in groundwater, particularly in Dawson and Gaines counties, are attributed to mobilization of  $\text{ClO}_4^-$  caused by increased recharge following cultivation. Concentrations of  $\text{ClO}_4^-$  in groundwater are predicted to increase in the SHP from continued mobilization of  $\text{ClO}_4^-$  reservoirs beneath agricultural ecosystems. The implications of these  $\text{ClO}_4^-$  concentrations on

drinking water quality will ultimately depend on whether a federal MCL or other state regulatory standard is adopted. However, groundwater from many areas of the SHP currently exceeds both the DWEL calculated based on the EPA reference dose for  $\text{ClO}_4^-$  as well as all state regulatory values that currently exist.

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### Supporting Information Available

Additional figures, tables, and calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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