

Probability of Detecting Perchlorate under Natural Conditions in Deep Groundwater in California and the Southwestern United States

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S Supporting Information

ABSTRACT: We use data from 1626 groundwater samples collected in California, primarily from public drinking water supply wells, to investigate the distribution of perchlorate in deep groundwater under natural conditions. The wells were sampled for the California Groundwater Ambient Monitoring and Assessment Priority Basin Project. We develop a logistic regression model for predicting probabilities of detecting perchlorate at concentrations greater than multiple threshold concentrations as a function of climate (represented by an aridity index) and potential anthropogenic contributions of perchlorate (quantified as an anthropogenic score, AS). AS is a composite categorical variable including terms for nitrate, pesticides, and volatile organic compounds. Incorporating water-quality parameters in AS permits identification of perturbation of natural occurrence patterns by flushing of natural perchlorate salts from unsaturated zones by irrigation recharge as well as addition of perchlorate from industrial and agricultural sources. The data and model results indicate low concentrations (0.1–0.5 $\mu\text{g/L}$) of perchlorate occur under natural conditions in groundwater across a wide range of climates, beyond the arid to semiarid climates in which they mostly have been previously reported. The probability of detecting perchlorate at concentrations greater than 0.1 $\mu\text{g/L}$ under natural conditions ranges from 50–70% in semiarid to arid regions of California and the Southwestern United States to 5–15% in the wettest regions sampled (the Northern California coast). The probability of concentrations above 1 $\mu\text{g/L}$ under natural conditions is low (generally <3%).

INTRODUCTION

Recent advances in analytical methods have resulted in widespread detection of perchlorate in groundwater in the United States.^{1,2} Perchlorate disrupts formation of thyroid hormones by interfering with iodide uptake, and infants and fetuses may be most at risk because of the role of thyroid hormones in early brain development.³ California has a maximum contaminant level (MCL) of 6 $\mu\text{g/L}$ for perchlorate in drinking water, and the U.S. Environmental Protection Agency is evaluating possible regulation. Given the potential deleterious health effects of perchlorate ingestion, an understanding of the natural and anthropogenic contributions of perchlorate to groundwater is needed. The goal of this study is to identify the probability of detecting perchlorate in deep groundwater under natural conditions. These conditions are as follows: the source of the perchlorate is natural and the abundance and distribution in the groundwater is controlled by natural processes.

Perchlorate from natural sources was first documented in the sodium nitrate deposits of Chile's Atacama desert⁴ and has since been detected in a number of other arid environments including salts accumulated in thick unsaturated zones in the southwestern United States.⁵ Correlations between perchlorate and other anions and stable isotopic data suggest an atmospheric origin for the perchlorate in these arid environments,^{5–8} and perchlorate is present in precipitation.^{1,9,10} Perchlorate inferred to be natural in origin has been detected in groundwater in semiarid areas of the Southwest¹¹ and in many locations across the United States with climate ranging from arid to humid.¹

A primary uncertainty in this apparent widespread distribution of natural perchlorate in groundwater is the lack of direct

evidence for the pristine character of the samples. Contamination of groundwater by anthropogenic sources of perchlorate would likely result in other effects on water quality, in particular, addition of anthropogenic organic constituents and nitrate. Perchlorate in groundwater containing no modern water, such as the Pleistocene groundwater in New Mexico, is unambiguously from a natural source and present in natural abundance;¹² however, limiting investigation of perchlorate distribution under natural conditions to old groundwater precludes investigation of most groundwater used for drinking water supply. Data for stable isotopic ratios of perchlorate, in combination with other data, have been used to identify perchlorate of industrial origin and from Chilean Atacama nitrate^{6,13} and to detect perturbation by irrigation recharge of occurrence patterns of perchlorate from natural sources.⁸ Unfortunately, the large amount of perchlorate required for isotopic analysis makes it impractical to collect samples from a large number of sites with low perchlorate concentrations.

Three primary sources of anthropogenic perchlorate have potential to reach California groundwater: industrial, agricultural, and disinfection. Most known sites of perchlorate contamination from industrial sources are associated with facilities that manufactured or tested solid rocket fuel; other sites include the following: military munitions storage, use, and disposal and manufacturing and disposal of pyrotechnics, safety flares, and

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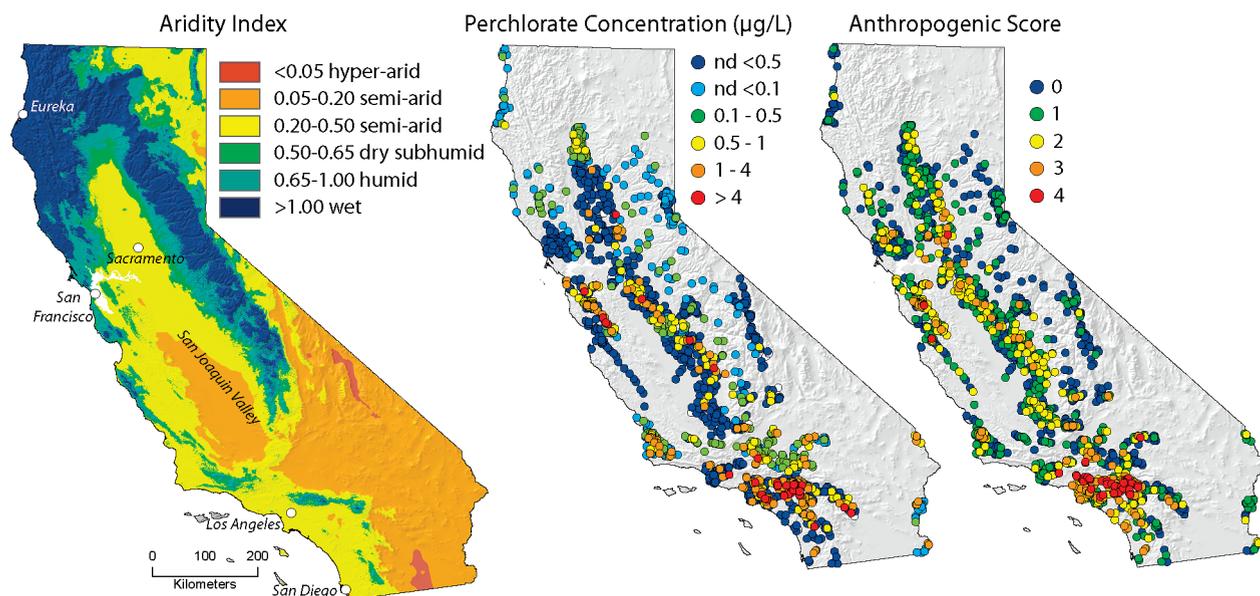


Figure 1. (A) Aridity index classification for California. (B) Perchlorate concentrations and (C) anthropogenic scores for groundwater samples collected for the California Groundwater Ambient Monitoring and Assessment Priority Basin Project, May 2004 through October 2009 (ref 21; Supporting Information Table SI-3).

explosives.^{14–16} Colorado River water imported to southern California is contaminated with perchlorate downstream of perchlorate manufacturing facilities in Nevada.¹⁷ Agricultural sources include the Chilean nitrate fertilizer applied extensively in the early to mid 1900s.^{13,18,19} We consider irrigation an agricultural source if it redistributes perchlorate salts originally naturally present in the unsaturated zone. Redistribution likely results in higher concentrations and greater detection frequencies of perchlorate in deep groundwater than would be present under natural conditions. Finally, perchlorate is a degradation product of hypochlorite solutions that are widely used for drinking water disinfection.²⁰

The objective of the current study was to develop a model for predicting the probability of detecting perchlorate, at various concentration thresholds, under natural conditions in deep groundwater in the southwestern United States. The model was developed using data from 1626 wells, primarily public drinking water supply wells, sampled for the California Groundwater Ambient Monitoring and Assessment Priority Basin Project (GAMA-PBP) (ref 21; Supporting Information Table SI-1). These wells sample deeper groundwater than the domestic wells sampled in many other large studies.^{1,22}

We use logistic regression^{22–24} to quantify the relation between the probability of perchlorate detection and water quality indicators and other proxies of natural and anthropogenic perchlorate sources and processes. Because perchlorate forms naturally in the atmosphere, we hypothesize that the distribution of perchlorate under natural conditions in groundwater is correlated with climate and use an aridity index that incorporates precipitation and evapotranspiration as the proxy for natural sources and processes. The extent of evaporative concentration of precipitation in the hydrologic cycle is likely to increase with increasing aridity. Groundwater quality characteristics (occurrence of volatile organic compounds, pesticides, and nitrate) and proximity to known sites of groundwater contamination with point sources of anthropogenic perchlorate are used as proxies for potential industrial, agricultural, and disinfection byproduct sources of perchlorate or for anthropogenic processes redistributing

perchlorate originally from a natural source. A predicted probability of perchlorate occurrence as a function of climate is then obtained by setting the anthropogenic proxies to zero. Separate models are developed for probability of occurrence relative to perchlorate thresholds between 0.1 and 4 $\mu\text{g/L}$ to estimate the concentration ranges of perchlorate under natural conditions in California groundwater. We extrapolate the models to predict the distribution of perchlorate under natural conditions in deep groundwater across the southwestern United States.

METHODS

Groundwater samples for this study were collected from 1626 sites in California between May 2004 and October 2009 and analyzed for a broad suite of water quality constituents, including perchlorate (Figure 1). Each site was sampled once. The sites were located in study units that represent a reasonably complete sampling of the range of hydrogeologic conditions encountered in California (Supporting Information Figure SI-1). Brief descriptions of site selection, sample collection, and quality control procedures are given in the Supporting Information. Detailed descriptions of methods and compilations of all data collected can be found in USGS Data Series Reports for the study units (Supporting Information Table SI-1).

Groundwater samples were analyzed for perchlorate by two laboratories. Montgomery Watson Harza (MWH) Laboratory (Monrovia, CA) analyzed the first 1125 samples, using a modified version of USEPA Method 314.0 with a minimum reporting limit (RL) of 0.5 $\mu\text{g/L}$.²⁵ Ten percent of the samples analyzed by MWH were reported as nondetections with raised RLs ranging from 1 to 50 $\mu\text{g/L}$. Weck Laboratory (City of Industry, CA) analyzed the last 501 samples, using USEPA Method 331.0 with a minimum RL of 0.1 $\mu\text{g/L}$.²⁶

Given the potential sources of perchlorate, the following potential explanatory variables were examined: climate, well construction, land use parameters, and chemical constituents that might be correlated with sources. The climate at each sampling site was summarized

Table 1. Potential Explanatory Variables Tested As Proxies for Natural and Anthropogenic Contributions of Perchlorate to Groundwater

variable	potential source			form of variable tested in models	
	agricultural	industrial	natural	continuous	categorical ^c
aridity index (AI)	—	—	X	continuous values	no categorical form
nitrate (N) ^a	X	X	—	concentration	1 = nitrate > 3 mg/L; 0 = nitrate ≤ 3 mg/L
pesticides and fumigants (PF) ^a	X	—	—	total concentration	1 = at least 1 compound detected; 0 = no detections
solvents and fuel components (SF) ^a	—	X	—	total concentration	1 = at least 1 compound detected; 0 = no detections
trihalomethanes	—	—	—	total concentration	1 = chloroform > 1 μg/L; 0 = chloroform ≤ 1 μg/L
proximity to known sites (KS) ^a	—	X	—	number within 10 km	1 = at least 1 site within 10 km or at least 2 sites within 25 km; 0 = no sites within 10 km and no more than 1 site within 25 km
urban land use	—	X	—	percent	1 = urban land use > 75%; 0 = urban land use ≤ 75%
agricultural land use	X	—	—	percent	1 = agricultural land use > 75% or orchard/vineyard > 50%; 0 = agricultural land use ≤ 75% and orchard/vineyard ≤ 50%
orchard/vineyard land use	X	—	—	percent	

^a Component of Anthropogenic Score (AS) used in final model. Data listed in Supporting Information Table SI-3.

by the UNESCO Aridity Index (AI),²⁷ the ratio of average annual precipitation²⁸ to average annual potential evapotranspiration.²⁹ Climate is classified as hyperarid (AI < 0.05), arid (0.05 < AI < 0.2), semiarid (0.2 < AI < 0.5), dry subhumid (0.5 < AI < 0.65), humid (0.65 < AI < 1), or wet (AI > 1).²⁷ AI for individual sampling sites ranged from 0.05 to 2.17 (Supporting Information Table SI-3). Well depths and depth to top of screened interval were obtained primarily from drillers' logs. Median well depth and depth to the top of the screened interval in the wells were 122 and 58 m, respectively. Land use within a 500-m radius of each well site was represented as percentages of urban, agricultural, and undeveloped uses.³⁰ The proximity of well sites to known sites of groundwater contamination by industrial sources was determined from the locations of 70 known sites of perchlorate contamination from aerospace, military, manufacturing, and disposal sources.^{14–16} Many of the groundwater sites contaminated with industrial sources of perchlorate also are contaminated with solvents or fuel components; therefore, the sum of solvents and fuel components was used as a chemical marker potentially indicative of industrial sources of perchlorate. The sum of pesticides and fumigants was used as a chemical marker potentially indicative of agricultural sources of perchlorate. All samples were analyzed for VOCs and pesticides at the USGS National Water Quality Laboratory (NWQL; Denver, CO). Nitrate may be a marker of either anthropogenic or natural sources of perchlorate. Most samples were analyzed for nitrate by the NWQL; data for other samples were obtained from the California Department of Public Health (CDPH) database. Perchlorate reduction and nitrate reduction occur at similar oxidation–reduction potentials;³¹ thus, 219 samples classified as manganese reducing or iron reducing and samples with insufficient data to preclude these classifications were not included in statistical analyses. VOC and pesticide analyses, comparison of CDPH and NWQL nitrate data, and oxidation–reduction classification are discussed in the Supporting Information. Possible disinfection sources of perchlorate were represented by chloroform. Free chlorine was not detected in any groundwater samples in this study; however, the presence of chloroform indicates contact with disinfectants at some time by recharge of chlorinated water or by use of hypochlorite solutions in the well. Samples were collected upstream of disinfection systems where present.

Logistic regression models the probability of the dependent variable being in a category, in this case, a detection or non-detection of perchlorate relative to a specified threshold concentration, and is therefore suitable for data sets with many nondetections.^{22–24} Models were tested with the variables representing potential anthropogenic sources treated as both continuous or categorical variables (Table 1), and categorical

variables were treated as both single or composite variables. Comprehensive model tests were done for four threshold perchlorate concentrations, 0.1, 0.5, 1, and 4 μg/L. Model tests for the 0.1 μg/L threshold concentration only included the samples that were analyzed by the Weck laboratory (*n* = 446 for model). Model tests for the higher threshold concentrations included all samples (*n* = 1336, 1397, and 1405 for the 0.5, 1, and 4 μg/L models, respectively). Samples with nondetections relative to raised RLs greater than the thresholds were not included in the models. Once parameters were identified for those four models, we also generated models for additional threshold concentrations. All data used in the final model are listed in Supporting Information Table SI-3.

All regressions were done in S-Plus using the StepAIC procedure.³² The procedure is based on Akaike's Information Criterion as the indicator of goodness-of-fit and is designed to choose simpler models (fewer independent variables) unless a more complex model substantially improves the model fit. The models selected by the StepAIC procedure for each starting variable set and threshold were then evaluated for significance of coefficients and overall goodness of fit.^{22–24} Coefficients with Wald statistic *p* values less than 0.05 were considered significant. Overall goodness of fit was evaluated using the Hosmer–Lemeshow (H–L) statistic and *r*² values for linear regressions comparing the observed detection frequencies and average predicted probabilities associated with deciles of risk.²⁴ The null hypothesis for the H–L statistic is that the observed and predicted values are not different; models with higher *p* values have better fits. The model form with *p* > 0.05 for the H–L statistic for all four thresholds was selected as the final model; however, the final model may not be the best model form for each individual threshold. The fit of the final model was further evaluated using areas under the receiver operating characteristic curves and Pearson residuals (ref 24; Supporting Information).

RESULTS AND DISCUSSION

Calibration of Logistic Regression Model. Logistic regression models were constructed to determine the relationship between the probability of detecting perchlorate at concentrations above four thresholds (0.1, 0.5, 1, and 4 μg/L) and potential explanatory variables representing natural and anthropogenic contributions of perchlorate to groundwater (Table 1). Models were evaluated with continuous and categorical explanatory variables, and similar results were obtained concerning which were the most significant variables. Model fits were improved by

Table 2. Coefficients and Statistic Measures of Goodness-of-Fit for Final Logistic Regression Model^a

	perchlorate threshold concentration for model			
	0.1 $\mu\text{g/L}$	0.5 $\mu\text{g/L}$	1 $\mu\text{g/L}$	4 $\mu\text{g/L}$
constant ($b_{0,c}$)	0.92	-1.49	-2.76	-5.47
aridity Index (AI) coefficient ($b_{1,c}$)	-1.83	-2.53	-2.27	-3.05
anthropogenic score (AS) coefficient ($b_{2,c}$)	0.81	0.95	1.07	1.38
Hosmer–Lemeshow statistic p value	0.47	0.25	0.14	0.61
r^2 for deciles of risk	0.93	0.97	0.97	0.99

^a Coefficients apply to eq 1. Wald statistic p values were <0.001 for all variables, except for AI in the 4 $\mu\text{g/L}$ threshold concentration model ($p = 0.071$).

combining categorical variables representing anthropogenic contributions of perchlorate into a single ‘anthropogenic score’. A single score yielded better model fits than separate scores representing agricultural and industrial sources because some of the potential explanatory variables may be indicative of both industrial and agricultural influence. The logistic regression model form yielding the best fit simultaneously for models for the four perchlorate threshold concentrations is given in eq 1

$$Pr_c = \frac{e^{(b_{0,c} + b_{1,c}AI + b_{2,c}AS)}}{1 + e^{(b_{0,c} + b_{1,c}AI + b_{2,c}AS)}} \quad (1)$$

where Pr_c is the probability of detecting perchlorate above a concentration, c , AI is the aridity index and represents natural sources of perchlorate to groundwater, AS is the anthropogenic score, and $b_{0,c}$, $b_{1,c}$, and $b_{2,c}$ are the coefficients determined from the regressions (Table 2). AS (eq 2) is the combination of categorical variables and can have integer values of 0–4

$$AS = N + SF + PF + KS \quad (2)$$

where N, SF, PF, and KS are binary categorical variables representing nitrate, solvents, and fuel components, pesticides and fumigants, and known sites of contamination from industrial sources, respectively (Table 1).

Land use characteristics (urban, agricultural, orchard/vineyard) and trihalomethane (THM) concentration greater than or less than 1 $\mu\text{g/L}$ were significant variables for some models tested but were not significant in the model form providing the best fit simultaneously for the four thresholds. The absence of land use in the final model (eq 2) is most probably due to well construction characteristics. Water quality in shallow domestic wells has been found to be closely related to current land use characteristics.²² In contrast, this study generally sampled deep wells with long screened intervals, resulting in samples consisting of mixtures of groundwater of different ages. Although 70% of the samples had tritium activities > 0.2 TU, indicating the presence of some water recharged during the past 60 years, the fraction of groundwater recharged under current land use conditions may be relatively small. Land use patterns in many parts of California have changed substantially in the last 60 years.

This model treats nitrate as a categorical parameter with a threshold of 3 mg/L. Our nitrate variable thus largely reflects anthropogenic rather than natural processes that may cause high nitrate (and perchlorate) concentrations or detection frequencies in

deep groundwater. Nitrate concentrations in shallow groundwater greater than 2³³ or 4 mg/L²² generally correlate with the presence of potential sources of anthropogenic nitrate contamination (fertilizer use, cropland, and population density, likely a proxy for septic and wastewater input). In arid and semiarid regions, where nitrate of natural atmospheric origin accumulates in the unsaturated zone,³⁴ remobilization of nitrate by irrigation recharge can result in nitrate concentrations in groundwater significantly greater than natural background concentrations of approximately 2 mg/L.³⁵ As defined in this study, generation of high nitrate concentrations by remobilization of originally naturally deposited nitrate by irrigation recharge is an anthropogenic process affecting the concentration and detection frequency of nitrate. Stable isotope composition of nitrate and perchlorate in unsaturated zone salts and groundwater from the southwest United States indicate both solutes are natural in origin from atmospheric deposition.⁸

The observed and predicted values from the final model are well-correlated ($r^2 = 0.93$ – 0.99 for the four thresholds individually and $r^2 = 0.98$ for the four together), indicating that the logistic regression model fits the data well (Supporting Information, Figure SI-3). p values for the H–L statistic for the four threshold concentration models ranged from 0.14 to 0.47, indicating that the model is highly significant. p values for the Wald statistic for individual coefficients in the model were <0.001 in all but one case (Table 2). Other measures of model fit are discussed in the Supporting Information.

AI and AS are significantly inversely correlated (Spearman test: $p < 0.001$; $\rho = -0.12$); however, based on the Wald statistic p values, colinearity of the variables is not considered a problem in the models for thresholds 0.1, 0.5, and 1 $\mu\text{g/L}$ (Table 2). The StepAIC procedure eliminated the AI variable in the model for threshold 4 $\mu\text{g/L}$ (Wald statistic not significant), but we retained it for consistency of model form. The inverse correlation between AI and AS reflects the fact that groundwater is used extensively for public drinking water supply in the areas where most Californians live (potential for higher AS); these areas are not generally located in the humid parts of the state (higher AI); for example, the greater Los Angeles area is semiarid (low AI). The sample set used for the 0.1 $\mu\text{g/L}$ model had a significantly higher median AI ($p = 0.028$) and lower median AS ($p < 0.001$) than the sample sets used for the other models.

Probability of Detecting Perchlorate under Natural Conditions. The logistic regression model yields the probability of detecting perchlorate under natural conditions as a function of climate (AI) when the anthropogenic score (AS) is set to zero in eq 1. The range of AI in the California data set used to construct the model (Figure 1) spans much of the range in AI in the entire Southwestern United States; thus, we extrapolate the model to predict occurrence of perchlorate under natural conditions in the entire region. For a threshold concentration of 0.1 $\mu\text{g/L}$, the predicted probability in the arid to semiarid (AI = 0.05–0.5) region encompassing most of Southern California, California’s Central Valley, Nevada, Utah, Arizona, New Mexico, and West Texas is 50–70% (Figure 2a). This high predicted probability of detecting low concentrations of perchlorate agrees with observed detection frequencies in a national study of domestic wells considered unlikely to be affected by anthropogenic sources based on land use characteristics.¹ The observed detection frequency of perchlorate greater than 0.1 $\mu\text{g/L}$ for the 50 samples from Arizona, Utah, and Nevada is 64%;¹ our predicted probability for the same region is 60–70% (Figure 2a). Even in relatively wet areas, such as the Northern California coast (AI = 1.3–1.6), the predicted probability is approximately 15%.

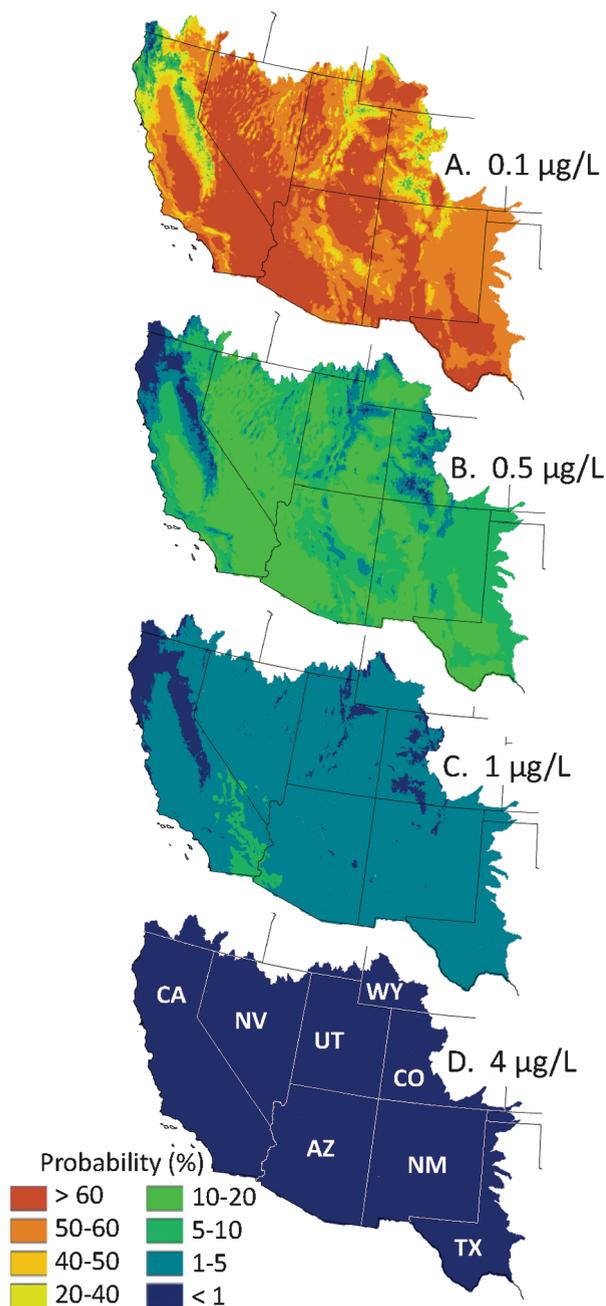


Figure 2. Predicted probabilities of detecting perchlorate under natural conditions in deep groundwater at a concentration greater than four threshold concentrations.

Low concentrations (0.1–0.5 µg/L) of perchlorate are predicted to occur under natural conditions in groundwater across a wide range of climates, beyond the arid to semiarid climates in which they mostly have been previously reported.

The predicted probability of detecting perchlorate under natural conditions decreases rapidly as the threshold concentration increases. Probabilities across the Southwest United States range from <1% to 18% for a threshold of 0.5 µg/L (Figure 2b) and <1% to 6% for a threshold of 1 µg/L (Figure 2c) and are <1% for a threshold of 4 µg/L (Figure 2d). Perchlorate concentrations in groundwater greater than 1 µg/L are unlikely to be representative of natural conditions.

The model captures the effect of redistribution of originally naturally deposited perchlorate salts in the unsaturated zone by irrigation recharge, an anthropogenic process. Redistribution likely results in increases in perchlorate concentrations and detection frequencies in groundwater. The variable AS includes two possible indicators of agricultural activity, nitrate and pesticide/fumigants, and irrigation may result in transport of these constituents from the surface to groundwater.

Predicted probabilities of detecting perchlorate under natural conditions in West Texas and eastern New Mexico are 5–10% for a threshold of 0.5 µg/L and <1% for a threshold of 4 µg/L (Figure 2b and 2d), substantially lower than measured perchlorate detection frequencies in public-supply wells of approximately 50% for a threshold of 0.5 µg/L and 10% for a threshold of 4 µg/L.¹¹ Rajagopalan et al.¹¹ infer a natural origin for the perchlorate, based on atmospheric anion ratios in the groundwater and the absence of sufficient use of Chilean nitrate fertilizers and crop defoliant or of industrial sources in the area. They observed that perchlorate concentrations were inversely correlated to depth below the water table and concluded that the high concentrations and detection frequencies resulted from flushing of accumulated natural perchlorate from the thick unsaturated zone to deeper groundwater by irrigation recharge. In other words, the source of the perchlorate was natural but the concentrations and detection frequencies were affected by anthropogenic processes.

The only region in California in which perchlorate concentrations were inversely correlated to depth was the San Joaquin Valley, the southern half of California's Central Valley (Figure 1). The San Joaquin Valley is one of the most extensively irrigated regions in the United States, and irrigation has changed groundwater flow patterns, increasing the volumes of recharge and discharge by approximately a factor of 6, and increasing the vertical component of flow.³⁶ The predicted probability of detecting perchlorate with concentration greater than 0.5 µg/L under natural conditions in the San Joaquin Valley is approximately 18% (Figure 2b), and the observed detection frequency is approximately 30% (study units V6 and V7; Supporting Information Table SI-3). Correlations among water quality constituents and between water quality and depth suggest that the increase in detection frequencies is due to irrigation recharge. Perchlorate, nitrate, total concentration of pesticides and fumigants, and uranium concentrations in the San Joaquin Valley groundwater samples were all significantly positively correlated with one another (Spearman test; $p < 0.001$ to $p = 0.004$; $\rho = 0.66$ – 0.25), and all were significantly negatively correlated with depth (Spearman test; $p < 0.001$ to $p = 0.003$; $\rho = -0.58$ to -0.25). Uranium is not associated with anthropogenic sources of perchlorate nor with atmospheric deposition; increasing uranium concentrations in groundwater are associated with leaching of sediments by downward-moving, bicarbonate-bearing irrigation recharge.³⁷ We suggest that the perchlorate and uranium are being leached from sediments in the unsaturated zone by irrigation recharge that carries nitrate, pesticides, and fumigants from agricultural activities on the surface. Two-thirds of the samples from the San Joaquin Valley have detections of pesticides or fumigants and/or nitrate concentrations greater than 3 mg/L and thus have AS values greater than 0, indicating that the presence of irrigation recharge is captured by the components of AS reflective of agricultural sources of perchlorate.

The West Texas and eastern New Mexico groundwater data set contains many samples with nitrate concentrations > 3 mg/L (although nitrate and perchlorate are only weakly positively correlated) but does not include data for pesticides and fumigants.¹¹ Land use in the area is dominantly agricultural and

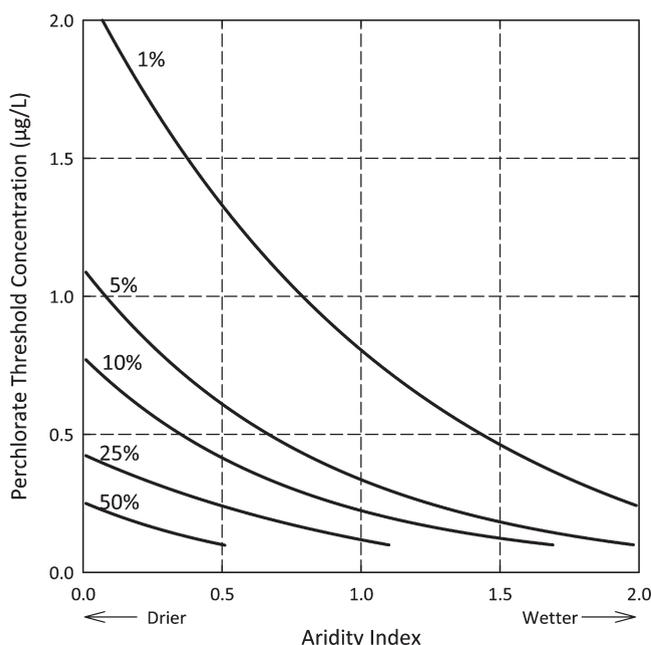


Figure 3. Probability of detecting perchlorate under natural conditions as a function of perchlorate threshold concentration and aridity index.

extensively irrigated.¹¹ It is possible that many of the groundwater samples would have AS greater than zero due to high nitrate concentrations and/or the presence of pesticides or fumigants. Using the logistic regression model (eq 1; Table 2) and an estimated AS value of 1.5 (average value in the San Joaquin Valley), the predicted probability of detecting perchlorate at concentrations greater than $0.5 \mu\text{g/L}$ in West Texas would be 21–36%, significantly greater than the predicted probability of 6–12% under natural conditions ($\text{AS} = 0$) and closer to the observed detection frequency of approximately 50%.¹¹ For an AS value of 2, the predicted probability is 30–50%.

The results in Figure 2 are summarized in graphical form in Figure 3, which shows the predicted probability of detecting perchlorate under natural conditions as a function of aridity index and perchlorate concentration threshold. We constructed models of the form in eq 1 for perchlorate concentration thresholds of $0.1\text{--}2 \mu\text{g/L}$ in $0.1 \mu\text{g/L}$ increments, calculated probabilities with AS set to zero, and then plotted curves of perchlorate concentration versus AI for a range of detection probabilities (Figure 3). The curves terminate at a concentration of $0.1 \mu\text{g/L}$ because that is the lowest reporting limit in the data set used to construct the model. One would predict that 10% of deep groundwater samples collected in a semiarid place like San Diego ($\text{AI} = 0.20$) would contain perchlorate with concentration greater than $0.61 \mu\text{g/L}$ under natural conditions and that 10% of deep groundwater samples collected in a relatively wet place like the Northern California coast ($\text{AI} = 1.3\text{--}1.6$) would contain perchlorate with concentrations greater than approximately $0.13 \mu\text{g/L}$ under natural conditions (Figure 3). In areas with arid, semiarid, humid, or wet climates ($\text{AI} = 0.05$ to $\text{AI} > 1$), perchlorate concentrations in deep groundwater greater than $1 \mu\text{g/L}$ likely reflect the contribution of perchlorate from anthropogenic sources or redistribution of naturally deposited perchlorate by anthropogenic processes. For hyperarid climates ($\text{AI} < 0.05$), the model predicts approximately 6% of deep groundwater samples would contain perchlorate at concentrations greater than $1 \mu\text{g/L}$ under natural conditions.

■ ASSOCIATED CONTENT

S Supporting Information. Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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