

Vulnerability of Recently Recharged Groundwater in Principle Aquifers of the United States To Nitrate Contamination

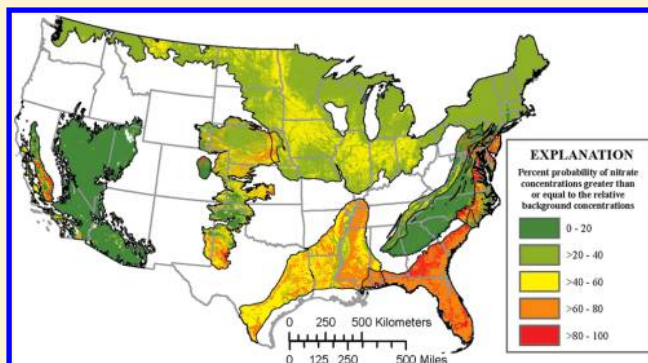
Jason J. Gurdak^{*,†} and Sharon L. Qi[‡]

[†]Department of Geosciences, San Francisco State University, San Francisco, California 94132, United States

[‡]U.S. Geological Survey, Cascades Volcano Observatory, Vancouver, Washington 98683, United States

S Supporting Information

ABSTRACT: Recently recharged water (defined here as <60 years old) is generally the most vulnerable part of a groundwater resource to nonpoint-source nitrate contamination. Understanding at the appropriate scale the interactions of natural and anthropogenic controlling factors that influence nitrate occurrence in recently recharged groundwater is critical to support best management and policy decisions that are often made at the aquifer to subaquifer scale. New logistic regression models were developed using data from the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) program and National Water Information System for 17 principal aquifers of the U.S. to identify important source, transport, and attenuation factors that control nonpoint source nitrate concentrations greater than relative background levels in recently recharged groundwater and were used to predict the probability of detecting elevated nitrate in areas beyond the sampling network. Results indicate that dissolved oxygen, crops and irrigated cropland, fertilizer application, seasonally high water table, and soil properties that affect infiltration and denitrification are among the most important factors in predicting elevated nitrate concentrations. Important differences in controlling factors and spatial predictions were identified in the principal aquifer and national-scale models and support the conclusion that similar spatial scales are needed between informed groundwater management and model development.



INTRODUCTION

Nitrate (NO_3^-) is the most ubiquitous nonpoint-source (NPS) contaminant of groundwater resources worldwide.¹ The reduction of NO_3^- in groundwater can release the greenhouse gas nitrous oxide² and pose well-known ecological and human-health risks.^{3,4} The U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for NO_3^- in drinking water is 10 mg/L (as Nitrogen (N)).⁵ Health concerns, including methemoglobinemia or “blue baby” disorder, spontaneous abortion, and increased risk of non-Hodgkins lymphoma, have been linked to drinking water with NO_3^- concentrations as low as 2.5 to 4 mg/L.^{6–9} The annual cost for U.S. water treatment to meet federal NO_3^- standards has been estimated in the hundreds of millions to billions of dollars.^{10,11}

In the U.S., more than 40 million people, including most rural populations, obtain drinking water from domestic self-supply (private) wells that generally receives no treatment prior to use, and about 40% of the Nation's public water supply is from groundwater in principle aquifers (PAs).¹² PAs are regionally extensive aquifers and aquifer systems of national significance because of their high productivity or use and are critically important sources of potable water.¹³ In 2000, total groundwater withdrawals from PAs were estimated at more than 289 million m^3 per day.¹⁴ A recent (2010) national

assessment of PA groundwater quality reported 50% of the 5,101 wells sampled had $\text{NO}_3^- > 1.0$ mg/L,¹⁵ which has been proposed as a nationwide relative background concentration or threshold indicative of anthropogenic sources.¹⁶ Aquifer-scale studies indicate that the distribution of NO_3^- concentrations in groundwater vary by PA, with many PAs having median $\text{NO}_3^- > 1.0$ mg/L and higher percentiles that exceed the 10 mg/L MCL.^{17,18}

Understanding the governing natural and anthropogenic factors of groundwater vulnerability to NPS NO_3^- contamination within and among PAs is fundamental to developing effective policy and management practices to reduce N inputs and protect groundwater as a safe drinking-water source.¹⁹ Groundwater management is often implemented at the local or aquifer scale. However, prior vulnerability assessments have been conducted at the aquifer or national scales and along various points within the flow system that represent a range of apparent groundwater ages and residence times, including shallow (young) and deep (old) groundwater.^{15,16,20–27} Although NO_3^- concentrations are highly variable at the

Received: February 20, 2012

Revised: May 2, 2012

Accepted: May 14, 2012

Published: May 15, 2012

national scale, shallow (young) and oxic groundwater beneath areas with high N inputs is the most vulnerable component of the flow system.¹⁵ Groundwater from wells that are screened deep in the flow system is generally less vulnerable because apparent groundwater ages often predate anthropogenic activities.^{28,29} As well depth and water residence time increase, oxygen (O_2) is the first electron acceptor removed from solution, resulting in anoxic conditions that promote attenuation of NO_3^- through denitrification.³⁰ No studies have systematically identified the governing factors of NPS NO_3^- contamination for the most vulnerable component of the flow system, recently recharged groundwater (defined here as <60 years old), within or among individual PAs.

In its second decade (2002–2012), a major focus of the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) program is on regional- and national-scale assessments of groundwater-quality status and trends in 19 (of 62) PAs,¹³ which account for about 75% of the total estimated withdrawals of groundwater for drinking-water supply.³¹ NAWQA evaluates water quality at a regional scale within and among PAs and considers the intrinsic susceptibility and vulnerability of groundwater resources to contamination.³¹ Intrinsic susceptibility conceptualizes the inherent hydro-geologic properties of the groundwater-flow system and the sources of water and stresses on the system, including infiltration and recharge rates, hydraulic conductivity, thickness and characteristics of the unsaturated zone, confined/unconfined nature of the aquifer, and well discharge.³² Vulnerability includes the concepts of intrinsic susceptibility, as well as the proximity and characteristics of sources of naturally occurring and anthropogenic contamination, factors that affect contaminant transport from land surface to a specific location within the groundwater-flow system, and the *in situ* geochemical conditions.

The focus of this paper is on quantifying vulnerability to NPS NO_3^- contamination. We present logistic-regression models and corresponding maps that predict the vulnerability of recently recharged groundwater in 17 PAs to NPS NO_3^- contamination. The 17 PAs cover parts of all 48 contiguous States and include the Basin and Range, Biscayne, California Coastal Basins, Cambrian-Ordovician, Central Valley, Coastal Lowlands, Denver Basin, Edwards-Trinity, Floridan, Glacial, High Plains, Mississippi Embayment, New England Crystalline, North Atlantic Coastal Plain, Piedmont and Blue Ridge, Rio Grande, and Valley and Ridge Carbonate aquifer systems. The objectives are to identify the most important source, transport, and attenuation (STA) factors controlling NPS NO_3^- above relative background concentrations in recently recharged groundwater within each PA and describe how those factors vary across the U.S. by climatic, environmental, and hydro-geologic settings (Table SI-1). Explanatory variables and predictions from the PA models are compared to those from a new national model to evaluate the effects of spatial scale on model development and prediction.

MATERIALS AND METHODS

Logistic regression is a statistical method that uses explanatory variables to predict the probability of a binary or categorical response³³ and has been widely used in groundwater vulnerability assessments to predict the probability of a water-quality constituent to exceed a management threshold, such as a background concentration or drinking-water standard.¹⁹ Univariate and multivariate logistic regression analyses were

used to identify important STA factors controlling NPS NO_3^- and predict the probability of detecting concentrations of NO_3^- in recently recharged groundwater greater than or equal to the relative background concentrations established for each PA and nationally (see the Supporting Information (SI) for details).

The water-quality data used in the logistic regression includes 2,150 wells sampled in 16 PAs during 1974–2010 (not including the High Plains aquifer – see below); over 90% (1,955 wells) were sampled after 1990 and 47% (1,016 wells) after 2000 (see the SI). Approximately two-thirds (1,348 wells) were randomly selected for model calibration and one-third (802 wells) for model validation (Table SI-2). Each PA had a minimum of 30 calibration and 17 validation wells (Table SI-2). Groundwater-quality data were compiled from NAWQA and non-NAWQA samples from the USGS NWIS (National Water Information System; <http://waterdata.usgs.gov/nwis>) database to extend the spatial coverage of NAWQA wells that intercept recently recharged groundwater in each PA. Well selection criteria included using tritium (3H) to determine recently recharged groundwater and by using an aquifer-specific, age-depth relation for wells without 3H data (see the SI for details). NAWQA wells were sampled according to ref 34, and nitrite (NO_2^-)-plus- NO_3^- was analyzed by the USGS National Water-Quality Laboratory using standard procedures.³⁵ NO_2^- -plus- NO_3^- concentration is referred to as NO_3^- because NO_2^- concentrations are generally negligible in groundwater. NO_3^- concentrations are reported as elemental N. NO_3^- from the 2,150 wells sampled ranged from 0.01 to 370 mg/L, with a median concentration of 0.5 mg/L (Table SI-2). Models for the High Plains aquifer (17th aquifer of this study) were reported previously by the authors using similar data and methods.²³

The relative background concentration of NO_3^- in shallow groundwater averaged across the U.S. is about 1.0 mg/L^{15,16} but is aquifer specific and has been reported as low as 0.4 mg/L in the North Atlantic Coastal Plain aquifer³⁶ and as high as 4 mg/L in the High Plains aquifer^{23,28} (see the SI). The median NO_3^- concentrations from the calibration and validation wells were used to guide the selection of relative background concentrations for each PA, which ranged from 0.051 to 4.0 mg/L, with most (8 of 17 PAs) at 1.0 mg/L and consistent with prior studies (Table SI-2). To be consistent with national estimates, the relative background concentration of 1 mg/L was used for the national model (Table SI-2).

We tested 87 STA explanatory variables in the univariate and multivariate logistic regression analysis, including most that are available as GIS-based spatial attributes from national sources (Table SI-3). The source variables represent NO_3^- loading and include farm fertilizer, manure from confined animal feeding operations, land use/land cover including cultivated crops and irrigated cropland, atmospheric NO_3^- and N, population density, and aqueous geochemical indicators in groundwater (not available as GIS-based spatial attributes). The transport variables represent NO_3^- mobilization in the soil, unsaturated zone, and saturated zone to the well and include water inputs from precipitation and runoff, hydrologic and geochemical properties of soil and aquifer material, depth to the water table, depth to the well screen below the water table, recharge rates, and selected management practices. This is the first groundwater vulnerability assessment to evaluate depth to water from a national spatial data set.³⁷ The attenuation variables represent denitrification and/or dilution of NO_3^- .

RESULTS AND DISCUSSION

The log-likelihood ratio (LLR) p-values³³ indicate that all the PA and national models are statistically significant at the significance level of 5% (α of 0.05) except for the Rio Grande model (LLR p-value, 0.077), which is significant at the α of 0.1 (Table SI-4). The Hosmer-Lemeshow (HL) goodness-of-fit test statistic p-values indicate that the national model and 76% (13 of 17) of the PA models are well calibrated (HL p-values >0.6) (Table SI-4). Moderately well calibrated models (HL p-values 0.351 to 0.554) are found in the Cambrian-Ordovician, Central Valley, and Coastal Lowlands. The Rio Grande model is poorly calibrated (HL p-value, 0.081). A complementary goodness-of-fit statistic is the area under the Receiver Operating Characteristic (ROC) curve³³ (see SI for details), which ranges from 0.7 to 0.99 (Table SI-4) and indicates acceptable to outstanding ability of the PA and national models to discriminate between recently recharged groundwater with NO_3^- greater than the relative background concentration versus recently recharged groundwater that does not.

Principal Aquifer (PA) Models. Of the 87 explanatory variables tested, only 25 unique variables were identified as statistically significant in the multivariate logistic regression models (8-source, 9-transport, and 8-attenuation) (Table SI-5). Of the 60 nonunique variables used in the PA models, the attenuation factors were identified most frequently (46%; 28 of 60), followed by source (32%; 19 of 60) and transport (22%; 13 of 60) factors (Table SI-5). Dissolved oxygen (DO) (attenuation) was the most frequently identified factor in 13 PA models (Figure 1) and thus the most important control on

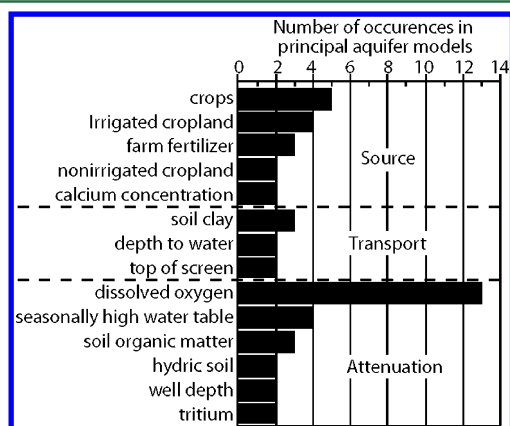


Figure 1. Occurrence of most predominant source, transport, and attenuation variables in principle aquifer (PA) logistic regression models. These variables occur in more than one PA model. Dissolved oxygen was found to be significant in 13 PA models and is the most important controlling factor of groundwater vulnerability to nonpoint-source nitrate.

NO_3^- exceeding the relative background concentration. Although the explanatory variables are categorized as distinct STA processes, many of the variables may each represent a combination or interaction of multiple STA factors. The sign and magnitude of the standardized coefficients (Table SI-5) indicate the predominant STA processes.

For all source variables, the sign of standardized coefficient is positive and indicates a positive relation between increases in N sources and increases in the probability of NO_3^- exceeding the relative background concentration (Table SI-5). In most PA models, source variables ranked second or third in terms of the

magnitude of the standardized coefficient, typically behind DO (attenuation), except in the northern High Plains aquifer, New England Crystalline, Piedmont and Blue Ridge, and Valley and Ridge Carbonate where source variables, primarily from agriculture, have the greatest influence.

The most important source variables (Figure 1) represent agricultural land and/or fertilizer loading, which is well supported by local^{20,21,23} and national-scale studies.^{15,25–27} Much of the variation in NO_3^- exceeding the relative background is explained by the different N source proxies in agricultural settings (Table SI-5). Irrigated croplands often receive greater N application rates compared to nonirrigated cropland.²⁴ The resulting pore-water NO_3^- reservoirs in many vadose zones beneath irrigated cropland, especially in the arid and semiarid western U.S., often exceed pore-water NO_3^- reservoirs beneath other land uses.³⁸ However, in semiarid and arid PAs such as the High Plains, some of the largest pore-water NO_3^- reservoirs are found beneath natural rangeland settings because of evapoconcentration processes.³⁸ These naturally occurring reservoirs can be mobilized by irrigation return flow after the natural rangeland has been converted to irrigated cropland³⁸ and from climate variability.³⁹ Therefore, irrigated cropland represents source and transport processes for naturally occurring and anthropogenic NO_3^- .⁴⁰ Calcium concentrations were a significant source indicator in the Rio Grande model (Table SI-5) and previously have been positively correlated with NO_3^- in groundwater beneath U.S. agricultural areas.⁴¹ The nitrification of reduced N from fertilizers and manure generates acidity that results in elevated calcium concentrations in recharging groundwater because of the buffering by naturally occurring carbonate minerals and/or dolomite [$\text{CaMg}(\text{CO}_3)_2$] that is commonly applied to agricultural land to provide Ca and Mg for plant growth and to neutralize the soil acidity.⁴² Agricultural source variables were not identified in models for the Biscayne, Cambrian-Ordovician, Edwards-Trinity, Mississippi Embayment, and New England Crystalline, which may indicate a lesser relative importance of agricultural N sources and/or the greater relative effect of attenuation processes in some parts of the more humid eastern U.S. In fact, no source variables were identified in the Biscayne, Cambrian-Ordovician, or Mississippi Embayment models, which all have low relative background concentrations of NO_3^- (1 mg/L or less). Population density was one of three source variables identified in the Denver Basin and is likely a surrogate for NO_3^- sources in urban areas, including nonfarm fertilizer and sewer exfiltration.²⁷ Atmospheric NO_3^- was significant only in the New England Crystalline model (Table SI-5), which is consistent with the forest-dominated landscape and some of the highest rates of U.S. atmospheric N deposition.^{43,44} This finding is consistent with the USGS SPARROW model results in New England⁴⁵ that indicate a portion of the atmospheric N is mobilized through permeable soil and shallow groundwater before delivery to streams (Doug A. Burns, USGS, personal communication, 2011). No other source variables were identified in the New England Crystalline model. Although acid deposition has been shown to affect groundwater quality,⁴⁶ to the authors' knowledge this is the first study that has identified a correlation between atmospheric NO_3^- deposition and NO_3^- in groundwater greater than the relative background concentration. Atmospheric NO_3^- was also significant in the univariate analysis of 9 other PAs (Table SI-3) but was not significant in the multivariate models indicating

that atmospheric NO_3^- has less effect on NO_3^- than agricultural sources in most PAs (Table SI-5).

Variables that impede transport have negative coefficients (inverse relation to NO_3^-) and are identified in more total models and more frequently in PAs of the arid and semiarid western U.S. (Figure 2, Table SI-5). These transport variables

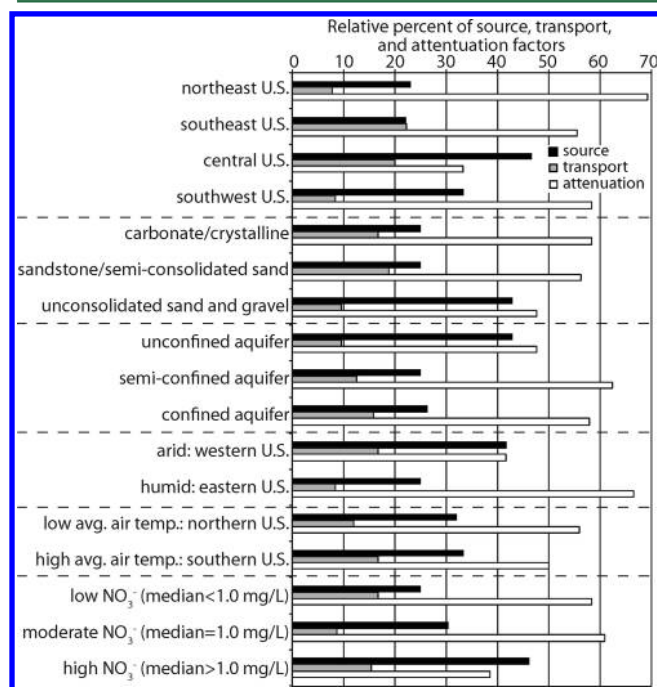


Figure 2. Relative percent of source, transport, and attenuation variables in principle aquifer logistic regression models, grouped by climatic, environmental, and hydrogeologic setting.

represent smaller rates of infiltration (soil clay and soil group D) and recharge (average clay in vadose zone) and longer flowpaths (soil thickness, depth to water table, and top of screen) (Table SI-5), which all increase transit times and impede NO_3^- transport. Clay in the soil is the most commonly identified transport variable, followed by depth to water and top of screen below the water table (Figure 1). The depth to water table is identified as a significant factor in the Denver Basin and High Plains aquifers where the water table can be tens of meters below land surface. Depth to water has the greatest influence on the central and southern High Plains model and is second behind DO in the Denver Basin (Table SI-5). Surface-derived NO_3^- must travel farther to reach the groundwater in areas with greater depth to water.¹⁷ Depth to water and top of screen may also be a surrogate for attenuation processes. Depth to water and DO are positively correlated in most PAs, with generally greater depths to water in the arid, western U.S. compared the humid, eastern U.S.³⁰ and DO controls redox conditions.

Variables that promote transport have positive coefficients and are identified only in 3 PA models, all in the humid, eastern U.S. (Biscayne, New England Crystalline, and Valley and Ridge Carbonate PAs), and include soil group B (moderate infiltration), recharge, and the presence of carbonate aquifer, which is a surrogate of recharge because solution channels in carbonate rocks commonly enhance water flow and transport of dissolved constituents to wells²⁷ (Table SI-5). Moderate infiltration rates in soil above the Biscayne aquifer potentially

enhance NO_3^- transport, but the low DO concentrations in groundwater promote NO_3^- reduction, resulting in some of the lowest NO_3^- concentrations of PAs studied (Table SI-2). Given the importance of recharge in contaminant transport and other groundwater vulnerability models,¹⁹ including the widely used USEPA DRASTIC model,⁴⁷ it is somewhat surprising that recharge was a significant transport variable in only 1 PA model (New England Crystalline). Recharge was compiled from the only known national-scale estimate of natural recharge, which was developed using the base-flow index method that uses a ratio of base flow to total flow in a stream.⁴⁸ Although the base-flow recharge estimates are positively correlated with estimates of recharge based on groundwater apparent-ages, the base-flow estimates are substantially lower than age-based estimates in irrigation-dominated aquifers of the U.S.⁴⁹ Base-flow and age-based estimates likely represent different spatiotemporal scales of recharge,⁴⁹ and base-flow estimates may likely represent more of the shallow groundwater system that is the focus of the current study. It is likely that the lack of significance of recharge is some combination of the base-flow recharge estimate underestimating actual recharge rates and the strong influence of attenuation variables masking the influence of recharge.

The coefficient sign of the attenuation variables are positive (negative) if NO_3^- attenuation increases (decreases) in the soil, vadose zone, and saturated zone (Table SI-5). In most PA models, attenuation variables, particularly DO, had the greatest magnitude standardized coefficients (Table SI-5), indicating that redox and denitrification have a stronger influence than N sources or transport processes and are the most important control on groundwater vulnerability to NPS NO_3^- (Figure 1). It is well documented that reduced conditions promote denitrification and are commonly found in groundwater with large amounts of organic carbon and depleted oxygen along flow paths in low permeability, waterlogged, poorly drained soils, and histosols.^{15,23,24,27} DO is such an important controlling factor that in some PAs, particularly the Mississippi Embayment that has considerable agriculture, no source variables were significant (Table SI-5). The Mississippi Embayment has fine-grained sediments and clay-rich soils⁵⁰ that slow NO_3^- transport, enhance denitrification, and result in low NO_3^- concentrations (Table SI-2). Tile drains that are used in agricultural fields of some PAs may further diminish the signal of source and transport variables, but it is beyond the scope to delineate tile drains at the field scale.

DO was significant in 13 PA models, while redox classification³⁰ was significant (and DO was not significant) in only the New England Crystalline and North Atlantic Coastal Plain models (Table SI-5). DO was not evaluated in the previous development of the High Plains models.¹⁹ The lack of significance for the redox classification may indicate that the categories of oxic ($\text{DO} \geq 0.5$ mg/L), anoxic ($\text{DO} < 0.5$ mg/L), and other redox classifications (Table SI-3), while important controls on many water-quality issues may not be as sensitive an indicator as the actual DO concentration in terms of predicting NPS NO_3^- at various relative background concentrations. The findings here further support and qualify the recommendation made in ref 30 that DO should be included in water-quality monitoring programs whenever the objective is to quantify groundwater vulnerability to NPS NO_3^- .

Attenuation factors are a more important control on NPS NO_3^- in the humid, eastern U.S. as compared to the more arid, western U.S. (Figure 2, Table SI-5). Depth to seasonally high

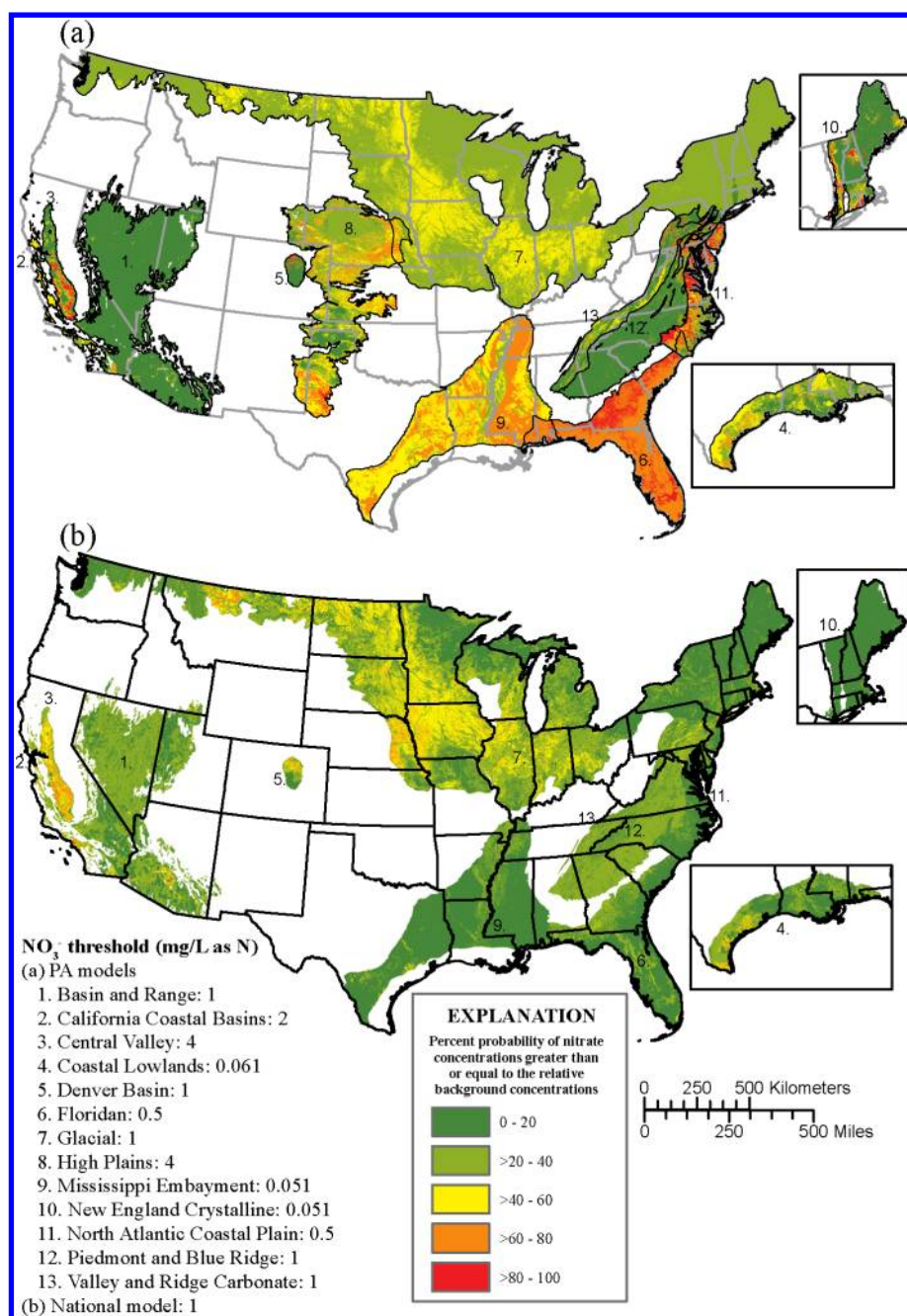


Figure 3. Probability of detecting nitrate concentrations greater than or equal to the relative background concentrations (NO_3^- thresholds in Table SI-4) in recently recharged groundwater of selected principal aquifers (PA), as predicted by (a) the individual PA models and (b) the national model. The models with redox variables are applied using dissolved oxygen = 2.0 mg/L, except for the Mississippi Embayment where DO = 0.5 mg/L, and represents geochemical conditions if actual redox conditions in each PA limit denitrification and enhance vulnerability to NO_3^- .

water table follows this general east–west spatial pattern (Table SI-5). Depth to seasonally high water table is a characteristic of the soil, not necessarily representative of the regional water table, and indicates the potential for saturated conditions in near-surface, poorly drained soils to promote denitrification in the presence of organic carbon. A shallow seasonal water table, typical of the eastern U.S., promotes reduced conditions and denitrification, while deep seasonal water tables, typical of the western U.S., do not.¹⁵ Depth to seasonally high water table was found to have a statistically significant, positive relation on NO_3^- in the North Atlantic Coastal Plain and Valley and Ridge Carbonate PAs (eastern U.S.), as well as in the basin-fill alluvial California Coastal Basins and Central Valley aquifers (western

U.S.) (Table SI-5). The positive relation between seasonally high water table and NO_3^- is generally consistent with the regional flow system of a basin-fill alluvial aquifer;⁵¹ alluvium becomes increasingly fine-grained and organic-rich toward the axial trough of the basin where the regional groundwater flow converges and a shallow water table exists in some locations.⁵²

The importance of attenuation over source and transport factors is also illustrated by general lithology and aquifer type (Figure 2, Table SI-1). The relative percent of source and attenuation variables in PA models is approximately the same in the unconsolidated sand and gravel aquifers and unconfined aquifers, while the relative percent of attenuation variables is much higher in the carbonate/crystalline, sandstone/semi-

consolidated lithology and semiconfined and confined aquifer type (Figure 2). Compared to other lithology and aquifer types, NO_3^- sources may be greater for unconsolidated sand and gravel and unconfined aquifers that include some of the most productive and heavily used PAs that support agriculture, including the Central Valley, Glacial, High Plains, and parts of the California Coastal Basin aquifers.

Using the PA models and GIS map-algebra,²³ we constructed maps for each PA that predict the probability of recently recharged groundwater having NO_3^- greater than or equal to the relative background concentrations (NO_3^- thresholds, Table SI-4) (Figure 3a). The maps (Figures 3ab, SI-2, SI-3) incorporate explanatory variables that are available as spatially continuous GIS data and some that are not such as DO, which is incorporated in the maps based on PA-specific median concentrations (Table SI-2) that are also consistent with important thresholds of denitrification (see the SI). Figure 3a uses DO = 2.0 mg/L and redox variable = oxic for all PAs except the Mississippi Embayment where DO = 0.5 and generally represents geochemical conditions if actual DO concentrations limit denitrification and enhance vulnerability to NO_3^- . Alternatively, Figure SI-2 uses DO = 0.5 mg/L and redox variable = reduced for all PAs except the Mississippi Embayment where DO = 2.0, and generally represents geochemical conditions if actual DO concentrations in each PA enhance denitrification and limit vulnerability to NO_3^- . Unlike other PAs, actual DO concentrations are generally anoxic in the Mississippi Embayment, which has a median DO concentration of 0.10 mg/L (Table SI-2). Comparison of Figure 3a and Figure SI-2 indicate areas of a PA that are more or less at risk based on DO closer to the true concentration (whether map Figure 3a or SI-2 applies depends on the measured DO concentration (Table SI-2)). Due to the use of spatially uniform DO values in Figure SI-2 that may not represent actual geochemical conditions, the predicted probabilities are spatially uniform across some PAs such as the Mississippi Embayment and Glacial. We did not make maps for the Biscayne, Cambrian-Ordovician, Edwards-Trinity, and Rio Grande because of poor model calibration and validation that is attributed to limitations of logistic regression to identify and model some controlling factors, particularly in these systems that have spatially homogeneous and low NO_3^- concentrations (Biscayne),⁵³ and deeply, confined (Cambrian-Ordovician)¹³ and karst (Edwards-Trinity)⁵⁴ aquifers with complex flow and NO_3^- STA factors (Rio Grande).⁵⁵

Of all the PA models, the Central Valley and High Plains aquifers have the highest relative background concentrations of NO_3^- (4 mg/L); the San Joaquin Valley (southern Central Valley) and Texas panhandle (southern High Plains) have the greatest spatial extent of highest predicted probabilities (>80%) (Figure 3a), which is a function of agriculture and elevated NO_3^- loading. The high predicted probabilities in the San Joaquin Valley is consistent with ref 52 that identified a relatively small proportion of wells with anoxic conditions and concluded that the effects of denitrification on NO_3^- are small under current conditions. Of the PA models with a 1-mg/L NO_3^- threshold, the greatest spatial extent of highest predicted probabilities (>80%) are in the northern areas of the Denver Basin and Valley and Ridge Carbonate aquifers, while the greatest spatial extent of lowest predicted probabilities (<20%) are in the Basin and Range and Piedmont and Blue Ridge aquifers. Notable intra-PA variability is present in the Glacial (1-mg/L NO_3^- threshold), with higher predicted probabilities

in the midwestern corn belt and lower predicted probabilities in New England and the northeastern U.S. Moderately high (>60%) and high (>80%) predicted probabilities are in the Coastal Lowlands, Floridan, Mississippi Embayment, New England Crystalline, and North Atlantic Coastal Plain aquifers. However, these predicted areas have relatively low NO_3^- (all NO_3^- thresholds ≤ 0.5 mg/L) compared to other PAs and the national relative background concentrations of 1 mg/L.

We evaluated the predictive ability of the vulnerability map (Figure 3a) using validation NO_3^- data (Table SI-2) converted to binary classification (< or > the thresholds, Table SI-5), which allowed for the percentage of observed detections from the validation wells to be compared to the predicted probabilities from the PA models. The R^2 (0.475) between the observed and predicted for validation wells in all PAs indicates a moderate predictive ability and some systematic bias with respect to the 1:1 ratio line, with the PA models generally overpredicting low probabilities and underpredicting high probabilities (Figure SI-1a). The R^2 is much higher for most individual PA models, with good ($R^2 > 0.6$) to excellent ($R^2 > 0.8$) predictive ability (Table SI-4). The Central Valley and Glacial models have moderate ($R^2 > 0.4$) predictive ability, and the California Coastal Basin and Coastal Lowlands models have poor ($R^2 < 0.2$) predictive ability. These poorly predictive models are likely overtrained on the calibration data and may not appropriately capture the controlling factors. To improve the poor predictive ability, future modeling efforts must evaluate sources of errors from the GIS-based explanatory variables and the inability of the monitoring network to capture the spatial variability of important explanatory variables and NO_3^- in groundwater.⁴⁰

National Model. The national model is well calibrated (HL p-values = 0.686) and has an excellent discrimination ability (ROC = 0.83) (Table SI-4). The explanatory variables in the national model are similar to many in the PA models, including (source) crops, confined manure (kg/km² applied to cropland), and population density; (transport) depth to water; and (attenuation) DO and seasonally high water table (Table SI-5). Similar to many PA models with attenuation factors, DO has the greatest influence on the national model followed by the source variable crops and reinforces the finding that DO and redox conditions are the most important mitigation of groundwater vulnerability to agricultural sources.

The vulnerability map constructed using the national model (NO_3^- threshold 1 mg/L) (Figure 3b) has an excellent predictive ability when comparing the predicted values versus the observed national-scale validation set ($R^2 = 0.981$, Figure SI-1b). However, the national model slightly overpredicts at probabilities of about 60% and greater (Figure SI-1b). The overprediction may be caused by a combination of the relative background concentration in some PAs being much lower than the national 1-mg/L NO_3^- threshold and that the national model may be lacking attenuation factors in some regions of high source factors. Figure 3b uses DO = 2.0 mg/L and represents geochemical conditions if actual DO concentrations at the national scale limit denitrification and enhance vulnerability to NO_3^- . Alternatively, Figure SI-3 uses DO = 0.5 mg/L and represents geochemical conditions if actual DO concentrations at the national scale enhance denitrification and limit vulnerability to NO_3^- . To evaluate the appropriateness of using the national model at finer spatial scales, the explanatory variables from the national model were tested in PA-scale logistic regression models. As to be expected from model

results (Table SI-5), the use of all 6 nationally important explanatory variables with PA specific NO_3^- data in logistic regression models resulted in poorly calibrated models for most PAs and indicate that use of the national model at the PA scale may not appropriately capture the important controlling factors and have a poor predictive ability. The map from the national model (Figure 3b) shows different patterns than the PA models (Figure 3a) in terms of the magnitude and variability of the predicted vulnerability within and among PAs. Comparing the national and PA maps (Figure 3ab), focusing on PA models with 1-mg/L NO_3^- thresholds, indicates that the national model overpredicts NO_3^- vulnerability across much of the Basin and Range, southeastern areas of the Denver Basin, and Piedmont and Blue Ridge aquifers, and underpredicts NO_3^- vulnerability across much Glacial, northwestern areas of the Denver Basin, and some northern areas of the Valley and Ridge Carbonate. It is difficult to directly compare the predictive ability of the national model to PAs with NO_3^- thresholds other than 1 mg/L.

Uses and Limitations. The PAs and national maps can be used to identify and prioritize areas for additional monitoring, remediation, and implementation of best-management practices and to help make policy decisions. The maps do not indicate actual groundwater contamination but rather areas that have the potential of recently recharged groundwater with NO_3^- that exceed the relative background concentrations. The probability maps may represent an important loading or source explanatory variables for older (>60 years) and deeper components of the flow system and may be used to predict elevated NO_3^- in parts of the used resource where water supply and irrigation wells are typically screened.

The probability maps are most appropriate for use at the regional and subregional scale and may have limitations at the site- or field-scale. The maps do not account for local NO_3^- point sources or attenuation processes or features that promote preferential flow and transport.⁵⁶ Although, the maps may not appropriately support some local-scale decisions, the important controlling factors and approach described here could be instructive in supporting some site- or field-scale decisions. As discussed, the vulnerability models and maps are highly sensitive to the scale of the explanatory variables and the model domain. Therefore, vulnerability modeling in support of management and policy needs to be developed at approximately the same scale as the decision making.

Findings from this study have important implications for management decisions and policy that are based on other, more subjective modeling approaches that use predetermined controlling factors for all aquifers, such as the widely used DRASTIC model⁴⁷ (Depth to water, net Recharge, Aquifer media, Soil media, Topography, Impact of vadose zone, and hydraulic Conductivity). We show that many DRASTIC factors are not important at the PA or national scale. Furthermore, DRASTIC does not include DO, which is the most important controlling factor, and would likely result in poorly predictive NO_3^- vulnerability models in most PAs. We recommend that DO be incorporated in groundwater modeling approaches to improve predictive ability.

The models and maps were created using data that were collected from 1974 to 2010 to illustrate spatial predictions of NO_3^- vulnerability. Because many agricultural practices that cause N loading and mobilization have remained relatively constant during this time period,¹⁷ these maps represent the probability of detecting NO_3^- under current conditions.

Temporal validation of these maps using data collected from previous time periods has not been evaluated. Because these maps were based on observations at point locations from a discrete time period, forecasting of future groundwater vulnerability conditions using the models or maps presented here may not be appropriate and would require additional validation beyond the scope of this study. New groundwater vulnerability modeling approaches are needed that can account for spatial and temporal variability of controlling STA factors, especially in light of changing patterns of land use, biogeochemical soil processes, intensification of the hydrologic cycle because of climate variability and change, and other global change processes that may affect groundwater quality.^{57,58}

The identified factors and predicted spatial patterns of NO_3^- have important implications for the current availability and future sustainability of groundwater resources in PAs as NO_3^- STA factors may change in the future. Models and maps presented here may be helpful to resource managers, policy makers, regulators, and other stakeholders across various spatial scales in their efforts to better monitor, manage, protect, and remediate vulnerable groundwater resources. An important finding is that vulnerability models are highly sensitive to the scale of the explanatory variables and model domain and support the conclusion that best management and policy objectives need vulnerability models that are developed at the same spatial scale as the decision making.

■ ASSOCIATED CONTENT

■ Supporting Information

Five additional tables including climatic, environmental, and hydrogeologic settings of PAs (Table SI-1), summary of NO_3^- and DO data and redox classification (Table SI-2), list of explanatory variables and results of univariate logistic regression modeling (Table SI-3), calibration, goodness-of-fit, and validation statistics for the multivariate logistic regression models (Table SI-4), and explanatory variables and coefficients used in the models (Table SI-5). Three additional figures including evaluation of validation for PA and national models (Figure SI-1), and alternative maps of the probability of detecting NO_3^- greater than or equal to the relative background concentration in recently recharged groundwater, as predicted by the PA models (Figure SI-2) and national model (Figure SI-3). Additional text including selection criteria for data and wells, establishing relative background concentrations, GIS compilation of explanatory variables, logistic regression and interpretation of model parameters, and creating PA and national vulnerability maps. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: 415/338-6869. Fax: 415/338-7705. E-mail: jgurdak@sfsu.edu. Corresponding author address: Department of Geosciences, San Francisco State University, 1600 Holloway Avenue, San Francisco, CA 94132.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the USGS NAWQA water-quality assessment of PAs. We thank the NAWQA personnel who designed networks and collected the data used in this study. We

are grateful for the comments on earlier drafts from three anonymous reviewers and the NAWQA and other USGS scientists, including Scott Anderholm, Dave Anning, Terri Arnold, Joseph Ayotte, Nancy Bauch, Marian Berndt, Laura Bexfield, Doug Burns, Karen Burow, Judith Denver, Sarah Flanagan, Karie Hitt, Chip Hunt, Jim Kingsbury, Wayne Lapham, Bruce Lindsey, Peter McMahon, Tom Nolan, Suzanne Paschke, Gary Rowe, Michael Rupert, Sue Thiros, and Kelly Warner.

REFERENCES

- (1) Spalding, R. F.; Exner, M. E. Occurrence of nitrate in groundwater – A Review. *J. Environ. Qual.* **1993**, *22* (3), 392–402.
- (2) McMahon, P. B.; Bruce, B. W.; Becker, M. F.; Pope, L. M.; Dennehy, K. F. Occurrence of nitrous oxide in the central High Plains aquifer, 1999. *Environ. Sci. Technol.* **2000**, *34* (23), 4873–4877.
- (3) Galloway, J. N.; Aber, J. D.; Erisman, J. W.; Seitzinger, S. P.; Howarth, R. W.; Cowling, E. B.; Cosby, B. J. The nitrogen cascade. *BioScience* **2003**, *53* (4), 341–356.
- (4) Fan, A. M.; Steinberg, V. E. Health implications of nitrate and nitrite in drinking water: An update on methemoglobinemia occurrence and reproductive and developmental toxicity. *Regul. Toxicol. Pharmacol.* **1996**, *23* (1), 35–43.
- (5) U.S. Environmental Protection Agency. Drinking water contaminants 2012. <http://water.epa.gov/drink/contaminants/index.cfm> (accessed May 22, 2012).
- (6) Weyer, P. J.; Cerhan, J. R.; Kross, B. C.; Hallberg, G. R.; Kantamneni, J.; Breuer, G. Municipal drinking water nitrate level and cancer risk in older women: the Iowa Women's Health Study. *Epidemiology* **2001**, *12* (3), 327–338.
- (7) Fewtrell, L. Drinking-water nitrate, methemoglobinemia, and global burden of disease: a discussion. *Environ. Health Perspect.* **2004**, *112* (14), 1371–1374.
- (8) Centers for Disease Control and Prevention. Spontaneous abortions possibly related to ingestion of nitrate-contaminated well water, La Grange County, Indiana, 1991–1994. *Morbidity Mortality Weekly Rep.* **1996**, *45* (26), 569–572.
- (9) Ward, M. H.; Mark, S. D.; Cantor, K. P.; Weisenburger, D. D.; Correa-Villaseñor, A.; Zahm, S. H. Drinking water nitrate and the risk of non-Hodgkins lymphoma. *Epidemiology* **1996**, *7* (5), 465–471.
- (10) Tegtmeier, E. M.; Duffy, M. D. External costs of agricultural production in the United States. *Int. J. Agric. Sustainability* **2004**, *2* (1), 1–20.
- (11) Ribaud, M.; Gollehon, N.; Aillery, M.; Kaplan, J.; Johansson, R.; Agapoff, J.; Christensen, L.; Breneman, V.; Peters, M. Manure management for water quality: Costs to animal feeding operations of applying manure nutrients to land: Agricultural Economic Report 824; U.S. Department of Agriculture, Econ. Res. Serv.: Washington, DC, 2003; 90 p. <http://www.ers.usda.gov/publications/aer824/aer824.pdf> (accessed May 22, 2012).
- (12) Alley, W. M.; Reilly, T. E.; Franke, O. L. Sustainability of ground-water resources, Circular 1186; U.S. Geological Survey: Reston, VA, 1999; 79 p. <http://pubs.usgs.gov/circ/circ1186/> (accessed May 22, 2012).
- (13) U.S. Geological Survey, *Principal aquifers of the 48 conterminous United States, Hawaii, Puerto Rico, and the U.S. Virgin Islands*, 2003. <http://www.nationalatlas.gov/mld/aquifrp.html> (accessed May 22, 2012).
- (14) Maupin, M. A.; Barber, N. L. *Estimated withdrawals from principal aquifers in the United States, 2000*, Circular 1279; U.S. Geological Survey: Reston, VA, 2005; 47 p. <http://pubs.usgs.gov/circ/2005/1279/> (accessed May 22, 2012).
- (15) Burow, K. R.; Nolan, B. T.; Rupert, M. G.; Dubrovsky, N. M. Nitrate in groundwater of the United States, 1991–2003. *Environ. Sci. Technol.* **2010**, *44* (13), 4988–4997.
- (16) Nolan, B. T.; Hitt, K. J. *Nutrients in shallow ground waters beneath relatively undeveloped areas of the conterminous United States*, Water-Resources Investigations Report 02-4289; U.S. Geological Survey: Reston, VA, 2003; 17 p. <http://pubs.usgs.gov/wri/wri024289/> (accessed May 22, 2012).
- (17) McMahon, P. B.; Dennehy, K. F.; Bruce, B. W.; Gurdak, J. J.; Qi, S. L. *Water-quality assessment of the High Plains aquifer, 1999–2004*, Professional Paper 1749; U.S. Geological Survey: Reston, VA, 2007; 212 p. <http://pubs.usgs.gov/pp/1749/> (accessed May 22, 2012).
- (18) Gurdak, J. J.; McMahon, P. B.; Dennehy, K. F.; Qi, S. L. *Water quality in the High Plains Aquifer, Colorado, Kansas, Nebraska, New Mexico, Oklahoma, South Dakota, Texas, and Wyoming, 1999–2004*, Circular 1337; U.S. Geological Survey: Reston, VA, 2009; 63 p. <http://pubs.usgs.gov/circ/1337/> (accessed May 22, 2012).
- (19) Gurdak, J. J. *Ground-water vulnerability: Nonpoint-source contamination, climate variability, and the High Plains aquifer*; VDM Verlag Publishing: Saarbrücken, Germany, 2008; ISBN: 978-3-639-09427-5, 223 p.
- (20) Tesoriero, A. J.; Voss, F. D. Predicting the probability of elevated nitrate concentrations in the Puget Sound Basin – Implications for aquifer susceptibility and vulnerability. *Ground Water* **1997**, *35* (6), 1029–1039.
- (21) Rupert, M. G. *Probability of detecting atrazine/desethyl-atrazine and elevated concentrations of nitrate (NO₂+NO₃-N) in ground water of the Idaho part of the upper Snake River Basin*, Water-Resources Investigations Report 98-4203; U.S. Geological Survey: Boise, ID, 1998; 32 p. <http://id.water.usgs.gov/PDF/wri984203/> (accessed May 22, 2012).
- (22) Rupert, M. G. *Probability of detecting atrazine/desethyl-atrazine and elevated concentrations of nitrate in ground water in Colorado*, Water-Resources Investigations Report 02-4269; U.S. Geological Survey: Denver, CO, 2003; 35 p. <http://pubs.usgs.gov/wri/wri02-4269/> (accessed May 22, 2012).
- (23) Gurdak, J. J.; Qi, S. L. *Vulnerability of recently recharged ground water in the High Plains regional aquifer to nitrate contamination*, Scientific Investigations Report 2006-5050; U.S. Geological Survey: Reston, VA, 2006; 39 p. <http://pubs.usgs.gov/sir/2006/5050/> (accessed May 22, 2012).
- (24) Nolan, B. T.; Stoner, J. D. Nutrients in groundwater of the conterminous United States, 1992–1995. *Environ. Sci. Technol.* **2000**, *34* (7), 1156–1165.
- (25) Nolan, B. T. Relating nitrogen sources and aquifer susceptibility to nitrate in shallow ground waters of the United States. *Ground Water* **2001**, *39* (2), 290–299.
- (26) Nolan, B. T.; Hitt, K. J.; Ruddy, B. C. Probability of nitrate contamination of recently recharged groundwaters in the conterminous United States. *Environ. Sci. Technol.* **2002**, *36* (10), 2138–2145.
- (27) Nolan, B. T.; Hitt, K. J. Vulnerability of shallow groundwater and drinking-water wells to nitrate in the United States. *Environ. Sci. Technol.* **2006**, *40* (24), 7834–7840.
- (28) McMahon, P. B.; Böhlke, J. K.; Christenson, S. C. Geochemistry, radiocarbon ages, and paleorecharge conditions along a transect in the central High Plains aquifer, southwestern Kansas, USA. *Appl. Geochem.* **2004**, *19* (11), 1655–1686.
- (29) McMahon, P. B.; Böhlke, J. K.; Lehman, T. M. *Vertical gradients in water chemistry and age in the Southern High Plains aquifer, Texas*, 2002, Scientific Investigations Report 2004-5053; U.S. Geological Survey: Reston, VA, 2004, 53 p. <http://pubs.usgs.gov/sir/2004/5053/> (accessed May 22, 2012).
- (30) McMahon, P. B.; Chapelle, F. H. Redox processes and water quality of selected principal aquifer systems. *Ground Water* **2008**, *46* (2), 259–271.
- (31) Lapham, W. W.; Hamilton, P. A.; Myers, D. N. *National water-quality assessment program—Cycle II Regional assessments of aquifers*, Fact Sheet 2005-3013; U.S. Geological Survey: Reston, VA, 2005; 4 p. <http://pubs.usgs.gov/fs/2005/3013/> (accessed May 22, 2012).
- (32) Focazio, M. J.; Reilly, T. E.; Rupert, M. G.; Helsel, D. R. *Assessing ground-water vulnerability to contamination – providing scientifically defensible information for decision makers*, Circular 1224; U.S. Geological Survey: Reston, VA, 2002; 33 p. <http://pubs.usgs.gov/circ/2002/circ1224/> (accessed May 22, 2012).

- (33) Hosmer, D. W.; Lemeshow, S. *Applied logistic regression*; John Wiley & Sons, Inc.: New York, 2000; 373 p.
- (34) Koterba, M. T.; Wilde, F. D.; Lapham, W. W. *Ground-water data-collection protocols and procedures for the National Water-Quality Assessment Program – Collection and documentation of water-quality samples and related data*, Open-File Report 95-399; U.S. Geological Survey: Reston, VA, 1995; 113 p. <http://pubs.usgs.gov/of/1995/ofr-95-399/> (accessed May 22, 2012).
- (35) Fishman, M. J. *Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments*, Open-File Report 93-125; U.S. Geological Survey: Reston, VA, 1993; 217 p. <http://pubs.er.usgs.gov/usgspubs/ofr/ofr93125> (accessed May 22, 2012).
- (36) Hamilton, P. A.; Denver, J. M.; Phillips, P. J.; Shedlock, R. J. *Water-quality assessment of the Delmarva Peninsula—Delaware, Maryland, and Virginia—Effects of agricultural activities on, and distribution of nitrate and other inorganic constituents in the surficial aquifer*, Open-File Report 93-40; U.S. Geological Survey: Reston, VA, 1993; 87 p. <http://pubs.er.usgs.gov/publication/ofr9340> (accessed May 22, 2012).
- (37) Fan, Y.; Miguez-Macho, G.; Weaver, C. P.; Walko, R.; Robock, A. Incorporating water table dynamics in climate modeling: 1. Water table observations and equilibrium water table simulations. *J. Geophys. Res.* **2007**, *112*, D10125 DOI: 10.1029/2006JD008111.
- (38) McMahon, P. B.; Dennehy, K. F.; Bruce, B. W.; Böhlke, J. K.; Michel, R. L.; Gurdak, J. J.; Hurlbut, D. B. Storage and transit time of chemicals in thick unsaturated zones under rangeland and irrigated cropland, High Plains, United States. *Water Resour. Res.* **2006**, *42*, W03413 DOI: 10.1029/2005WR004417.
- (39) Gurdak, J. J.; Hanson, R. T.; McMahon, P. B.; Bruce, B. W.; McCray, J. E.; Thyne, G. D.; Reedy, R. C. Climate variability controls on unsaturated water and chemical movement, High Plains aquifer, USA. *Vadose Zone J.* **2007**, *6* (3), 533–547, DOI: 10.2136/vzj2006.0087.
- (40) Gurdak, J. J.; McCray, J. E.; Thyne, G. D.; Qi, S. L. Latin hypercube approach to estimate uncertainty in ground water vulnerability. *Ground Water* **2007**, *45* (3), 348–361, DOI: 10.1111/j.1745-6584.2006.00298.x.
- (41) Green, C. T.; Puckett, L. J.; Böhlke, J. K.; Bekins, B. A.; Phillips, S. P.; Kauffman, L. J.; Denver, J. M.; Johnson, H. M. Limited occurrence of denitrification in four shallow aquifers in agricultural areas of the United States. *J. Environ. Qual.* **2008**, *37*, 994–1009, DOI: 10.2134/jeq2006.0419.
- (42) Böhlke, J. K. Groundwater recharge and agricultural contamination. *Hydrogeol. J.* **2002**, *10* (1), 153–179 [Erratum, *Hydrogeol. J.* **2002**, *10*(3): 438–439].
- (43) Boyer, E. W.; Goodale, C. L.; Jaworski, N. A.; Howarth, R. W. Anthropogenic nitrogen sources and relationships to riverine nitrogen exports in the northeastern U.S.A. *Biogeochemistry* **2002**, *57* (1), 137–169.
- (44) National Atmospheric Deposition Program, *National Atmospheric Deposition Program 2000 Annual Summary*, NADP Program Office: Champaign, IL, 2000. <http://nadp.sws.uiuc.edu> (accessed May 22, 2012).
- (45) Moore, R. B.; Johnston, C. M.; Robinson, K. W.; Deacon, J. R. *Estimation of total nitrogen and phosphorus in New England streams using spatially referenced regression models*, Scientific Investigations Report 2004-5012; U.S. Geological Survey: Reston, VA, 2004; 42 p. <http://pubs.usgs.gov/sir/2004/5012/> (accessed May 22, 2012).
- (46) Hrkál, Z. Vulnerability of groundwater to acid deposition, Jizerské Mountains, northern Czech Republic: construction and reliability of a GIS-based vulnerability map. *Hydrogeol. J.* **2001**, *9* (4), 348–357.
- (47) Aller, L.; Truman, B.; Lehr, J. H.; Petty, R. J. DRASTIC - a standardized system for evaluating ground water pollution potential using hydrogeologic settings, U.S. Environmental Protection Agency: EPA/600/2-85/018: 1985; 163 p.
- (48) Wolock, D. M. *Estimated mean annual natural groundwater recharge in the conterminous United States*, Open-File Report 03-311; U.S. Geological Survey: Reston, VA, 2003, digital dataset. <http://water.usgs.gov/GIS/metadata/usgswrd/XML/rech48grd.xml> (accessed May 22, 2012).
- (49) McMahon, P. B.; Plummer, L. N.; Böhlke, J. K.; Shapiro, S. D.; Hinkle, S. R. A comparison of recharge rates in aquifers of the United States based on groundwater-age data. *Hydrogeol. J.* **2011**, *19* (4), 779–800.
- (50) Welch, H. L.; Kingsbury, J. A.; Tollett, R. W.; Seanor, R. C. *Quality of shallow groundwater and drinking water in the Mississippi embayment-Texas coastal uplands aquifer system and the Mississippi River Valley alluvial aquifer, south-central United States, 1994–2004*, Scientific Investigations Report 2009-5091; U.S. Geological Survey: Reston, VA, 2009; 51 p.
- (51) *Groundwater Availability of the Central Valley Aquifer, California*, Professional Paper 1766; Faunt, C. C., Ed.; U.S. Geological Survey: Reston, VA, 2009; 225 p.
- (52) Landon, M. K.; Green, C. T.; Belitz, K.; Singleton, M. J.; Esser, B. K. Relations of hydrogeologic factors, groundwater reduction-oxidation conditions, and temporal and spatial distributions of nitrate, Central-Eastside San Joaquin Valley, California, USA. *Hydrogeol. J.* **2011**, *19* (6), 1203–1224.
- (53) Bradner, A.; McPherson, B. F.; Miller, R. L.; Kish, G.; Bernard, B. *Quality of ground water in the Biscayne aquifer in Miami-Dade, Broward, and Palm Beach counties, Florida, 1996–1998, with emphasis on contaminants*, Open-File Report 2004-1428; U.S. Geological Survey: Reston, VA, 2005; 20 p.
- (54) Lindsey, B. D.; Berndt, M. P.; Katz, B. G.; Ardis, A. F.; Skach, K. A. *Factors affecting water quality in selected carbonate aquifers in the United States, 1993–2005*, Scientific Investigations Report 2008–5240; U.S. Geological Survey: Reston, VA, 2009; 117 p.
- (55) Bexfield, L. M.; Thiros, S. A.; Anning, D. W.; Huntington, J. M.; McKinney, T. S. *Effects of natural and human factors on groundwater quality of basin-fill aquifers in the Southwestern United States—Conceptual models for selected contaminants*, Scientific Investigations Report 2011-5020; U.S. Geological Survey: Reston, VA, 2011; 90 p.
- (56) Gurdak, J. J.; Walvoord, M. A.; McMahon, P. B. Susceptibility to enhanced chemical migration from depression-focused preferential flow, High Plains aquifer. *Vadose Zone J.* **2009**, *7* (4), 1172–1184, DOI: 10.2136/vzj2007.0145.
- (57) Gurdak, J. J.; McMahon, P. B.; Bruce, B. W. *Vulnerability of groundwater quality to human activity and climate change and variability, High Plains aquifer, USA*, 145–167. In *Climate change effects on groundwater resources: A global synthesis of findings and recommendations*; Treidel, H., Martin-Bordes, J. L., Gurdak, J. J., Eds.; CRC Press, Taylor & Francis Group: New York, NY, 2011; 414 p.
- (58) Green, T. R.; Taniguchi, M.; Kooi, H.; Gurdak, J. J.; Allen, D. M.; Hiscock, K. M.; Treidel, H.; Aureli, A. Beneath the surface of global change: Impacts of climate change on groundwater. *J. Hydrol.* **2011**, *405* (3–4), 532–560, DOI: 10.1016/j.jhydrol.2011.05.002.