

Vulnerability of Shallow Groundwater and Drinking-Water Wells to Nitrate in the United States

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Two nonlinear models were developed at the national scale to (1) predict contamination of shallow ground water (typically < 5 m deep) by nitrate from nonpoint sources and (2) to predict ambient nitrate concentration in deeper supplies used for drinking. The new models have several advantages over previous national-scale approaches. First, they predict nitrate concentration (rather than probability of occurrence), which can be directly compared with water-quality criteria. Second, the models share a mechanistic structure that segregates nitrogen (N) sources and physical factors that enhance or restrict nitrate transport and accumulation in ground water. Finally, data were spatially averaged to minimize small-scale variability so that the large-scale influences of N loading, climate, and aquifer characteristics could more readily be identified. Results indicate that areas with high N application, high water input, well-drained soils, fractured rocks or those with high effective porosity, and lack of attenuation processes have the highest predicted nitrate concentration. The shallow groundwater model (mean square error or MSE = 2.96) yielded a coefficient of determination (R^2) of 0.801, indicating that much of the variation in nitrate concentration is explained by the model. Moderate to severe nitrate contamination is predicted to occur in the High Plains, northern Midwest, and selected other areas. The drinking-water model performed comparably (MSE = 2.00, R^2 = 0.767) and predicts that the number of users on private wells and residing in moderately contaminated areas (>5 to ≤10 mg/L nitrate) decreases by 12% when simulation depth increases from 10 to 50 m.

Introduction

Groundwater is an important national resource that provides drinking water for nearly half the people in the United States (U.S.). Unfortunately, the resource is susceptible to contamination by chemicals derived from the land surface. Nitrate is considered the most widespread contaminant in groundwater (1). Because nitrate is both soluble and mobile, it is prone to leaching through soils with infiltrating water.

High nitrate concentration in groundwater is a human health concern. Prevention of methemoglobinemia in infants is the basis for the maximum contaminant level of 10 mg/L nitrate as N, established by the U.S. Environmental Protection Agency (1). Recent studies have associated nitrate in drinking

water with several types of cancer (2–5). The causal role of nitrate is not conclusive because there are few such studies for a given type of cancer, and because it is difficult to evaluate the combined effect of nitrate intake from food and water. Nevertheless, the results are a cause for concern because the adverse effects are associated with nitrate concentrations as low as 2.5 mg/L (5). Relative background concentration of nitrate in shallow groundwaters of the U.S. is about 1 mg/L (6).

Protection of drinking-water sources is a national priority and is mandated by the Safe Drinking Water Act (7). The U.S. Geological Survey's (USGS's) National Water-Quality Assessment (NAWQA) Program effectively monitors the occurrence and distribution of nitrate and other contaminants in groundwater and streams, using consistent sampling and analytical methods (8). It is impractical to monitor everywhere, however, so the availability of high-quality data is limited nationally.

Data gaps can be addressed with regional and national water-quality models that use detailed spatial data on chemical loadings and environmental characteristics. Empirical models, in particular logistic regression, have been successfully applied at a variety of scales to predict the likelihood of contamination by various chemicals (9–24). Predicted probabilities, however, cannot be directly compared with water-quality standards or other concentrations relevant to human health, and predicting concentrations is problematic because water-quality data commonly are censored at the analytical reporting limit. Use of ordinary least-squares with simple substitution of values (e.g., zero or half the reporting limit) for censored data is inappropriate because the resulting model coefficients depend on the assumed values (25).

The goal of the current study is to predict groundwater vulnerability to nitrate at the national scale, to complement measured data. Specific objectives are to reliably predict nitrate concentration in shallow groundwater and in that used for drinking and to describe the uncertainty of the predictions. We present a nonlinear approach to national-scale Ground-Water Vulnerability Assessment (GWAVA), which uses average characteristics of NAWQA monitoring networks. Use of network averages smoothes local variability that can obscure large-scale trends in nitrate concentration. By focusing on large-scale variability, the predominant processes influencing nitrate contamination at the national scale can more readily be identified. Compared with simple linear approaches, the model has a mechanistic structure with components representing nitrogen (N) sources, transport of nitrate to aquifers, and attenuation of nitrate in groundwater.

Nonlinear regression models previously were developed at large spatial scales to predict N yields and phosphorus concentrations in streams of U.S. watersheds (26, 27). The SPATIALLY REFERENCED REGRESSIONS ON WATERSHEDS (SPARROW) model relates measured chemical transport rates in streams to spatial data comprising chemical source terms, land-to-water delivery factors, and in-stream-decay factors. The SPARROW model reliably predicted contaminant transport in U.S. watersheds; the mean square error (MSE) of the N model was 0.45, and the coefficient of determination (R^2) was 0.87.

Two nonlinear models are presented in the current study, to predict nitrate concentration in U.S. groundwaters. The first (GWAVA-S) predicts nitrate contamination of shallow, recently recharged groundwater, which may or may not be used for drinking. The calibration data set represents

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TABLE 1. Parameters of Nonlinear Regression Model for Nitrate in Shallow Groundwater (GWAVA-S)

model parameter	units	estimated coefficient	standard error	significance level (<i>p</i>)
Nitrogen Source (β)				
farm fertilizer	kg/ha	0.2265	0.0722	0.0024
confined manure	kg/ha	0.4049	0.1355	0.0037
orchards/vineyards	percent	1.9600	0.8466	0.0231
population density	people/km ²	0.006658	0.0014	<0.0001
cropland/pasture/fallow	percent	0.1473	0.0585	0.0138
Transport to Aquifer (α)				
water input ^a	km ² /cm	38.16	14.21	0.0088
carbonate rocks	binary indicator	0.5630	0.1640	0.0009
basalt and volcanic rocks	binary indicator	0.5182	0.3161	0.1050
drainage ditch	km ²	-6.483	1.343	<0.0001
slope	percent	-0.03861	0.0115	0.0012
glacial till	binary indicator	-0.8141	0.2440	0.0013
clay sediment	percent	-0.04751	0.0064	<0.0001
Attenuation (δ)				
fresh surface water withdrawal	MLD ^b	-1.078	0.2231	<0.0001
irrigation tailwater recovery	km ²	-8.327	1.415	<0.0001
histosol soil type	percent	-0.0185	0.0111	0.1000
wetlands	percent	-0.03213	0.0151	0.0363

^a Ratio of irrigated land to precipitation. ^b Megaliters per day.

TABLE 2. Parameters of Nonlinear Regression Model for Nitrate in Drinking-Water Wells (GWAVA-DW)

model parameter	units	estimated coefficient	standard error	significance level (<i>p</i>)
Nitrogen Source (β)				
farm fertilizer	kg/ha	0.1068	0.0220	<0.0001
confined manure	kg/ha	0.1416	0.0335	<0.0001
orchards/vineyards	percent	0.2999	0.1415	0.0367
population density	people/km ²	0.0021	0.0010	0.0435
Transport to Aquifer (α)				
water input ^a	km ² /cm	86.55	19.53	<0.0001
glacial till	binary indicator	-0.8658	0.3790	0.0245
semiconsolidated sand aquifers	binary indicator	0.5057	0.2063	0.0160
sandstone and carbonate rocks	binary indicator	0.3641	0.1274	0.0052
drainage ditch	km ²	-5.080	1.724	0.0040
Hortonian overland flow	percent of streamflow	-0.0330	0.0124	0.0093
Attenuation (δ)				
fresh surface water withdrawal	MLD ^b	-1.334	0.2973	<0.0001
irrigation tailwater recovery	km ²	-13.84	2.155	<0.0001
Dunne overland flow	percent of streamflow	-0.1443	0.0528	0.0074
well depth	m	-0.00163	0.0012	0.1809

^a Ratio of irrigated land to precipitation. ^b Megaliters per day.

monitoring wells, domestic wells, and other well types. The second model (GWAVA-DW) is based on domestic and public supply wells, which typically are deeper than monitoring wells. Although there is overlap between the two data sets, the first set better reflects overlying land use and is comparable to data used in prior national approaches. GWAVA-S results are directly comparable to previous national-scale, logistic-regression models for nitrate (17, 18). GWAVA-DW isolates drinking-water wells and is of interest to agencies that regulate drinking-water sources or that monitor diseases related to ingestion of drinking water. The GWAVA-DW data set emphasizes domestic wells, which are an important but largely unmonitored resource. Over 40 million people in the U.S. use domestic water supplies (28).

Methods

Data used in this study were collected by the NAWQA Program during 1991–2003 and represent the first full decade of sampling. The program employs consistent sampling procedures and analytical methods at a national scale (29, 30). Nitrite-plus-nitrate was analyzed by the USGS National Water Quality Laboratory, and reported concentrations are based on elemental N (e.g., NO₂⁻ plus NO₃⁻ as N). Nitrite-plus-

nitrate concentration is referred to in this paper as “nitrate” because nitrite contribution in groundwater generally is negligible (31).

The GWAVA-S data set comprises 2306 wells that sample relatively shallow groundwater beneath agricultural, urban, mining, and forested lands (see the Supporting Information). Most of these are monitoring wells. Installation of such wells, however, is impractical in some areas (such as deep fractured basalt aquifers in the Upper Snake River Plain in southeastern Idaho). Although deeper than 5 m, the basalt aquifers are recently recharged by irrigation water. Existing domestic wells are used in such cases. Thus, the GWAVA-S data set includes 488 drinking-water wells that also are in the GWAVA-DW data set, which comprises all 2490 drinking-water wells sampled by NAWQA through 2003. The drinking-water wells generally are deeper (mean depth = 48.8 m) than the monitoring wells (mean depth = 7.9 m). The number of wells in each data set reflects filtering in a geographic information system (GIS) to remove neighboring wells closer than 1000 m. Filtering objectives were to reduce spatial clustering and to avoid double counting of estimated N loading within 500-m radius circular buffers around sampled wells.

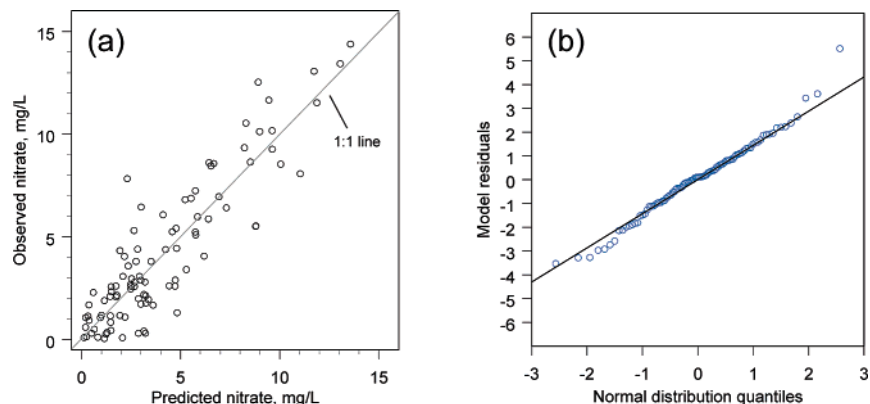


FIGURE 1. Observed nitrate concentration versus that predicted by GWAVA-S for shallow, recently recharged groundwater (a) and distribution of model residuals (b).

Spatial Attributes. Spatial attributes representing N loading and transport and attenuation factors were compiled in a GIS prior to model development. The N source variables include farm fertilizer, manure from confined animal feeding operations, and loading surrogates that reflect additional sources of N (Tables 1 and 2). Transport factors include water input, sediments, rock type, and selected management practices. “Water input” is an interaction term expressed as the ratio of the total area of irrigated land in well buffers to precipitation. Attenuation factors include variables that are surrogates for dilution and/or denitrification. Details on these variables and GIS procedures are given in the Supporting Information.

Spatial Averaging of Small-Scale Variability. Nitrate data and spatial attributes were averaged within GIS polygons representing NAWQA groundwater monitoring networks before developing the models, to smooth small-scale variability associated with point measurements of nitrate concentration. Mean nitrate concentration in networks was calculated using log probability regression to accommodate nitrate values <0.05 mg/L. The N sources and transport and attenuation factors were spatially averaged by computing means for the network polygons. The final GWAVA-S data set consists of 97 networks that monitor shallow groundwater; the final GWAVA-DW data set is based on drinking-water wells in 111 networks. Details on spatial averaging and log-probability regression are given in the Supporting Information.

Model Development. The GWAVA models have a non-linear structure comprising an additive linear submodel for N sources and multiplicative exponential terms that proportionally increase or decrease the amount of nitrate transferred to and accumulating in groundwater

$$c_{gwi} = S_i \cdot T_i \cdot A_i + \epsilon_i \quad (1)$$

where

$$\text{N sources: } S_i = \sum_{n=1}^N \beta_n X_{n,i} \quad (2)$$

$$\text{Transport: } T_i = \exp\left(\sum_{j=1}^J \alpha_j Z_{j,i}\right) \quad (3)$$

$$\text{Attenuation: } A_i = \exp\left(\sum_{k=1}^K -\delta_k Z_{k,i}\right) \quad (4)$$

and c_{gwi} = observed mean ambient nitrate concentration in groundwater associated with network polygon i , mg/L; $X_{n,i}$ = average N load from source n in network polygon i ; $Z_{j,i}$ =

average transport factor j in network polygon i ; $Z_{k,i}$ = average attenuation factor k in network polygon i ; β_n = coefficient for N source n ; α_j = coefficient for transport factor j ; δ_k = coefficient for attenuation factor k ; and ϵ_i = model error for network polygon i .

Although shown as positive in eq 3, transport factors can have positive or negative signs depending on whether water movement and contaminant delivery are enhanced or restricted. In contrast, attenuation factors in eq 4 all have negative signs and represent dilution and/or reactive processes (e.g., denitrification) in the aquifer itself.

Spatially, the predicted nitrate concentration represents average conditions in a nominal area of about 20 km², which is the minimum size of a NAWQA groundwater monitoring network. Although the networks vary in size, model residuals are fairly constant as the size increases (data not shown). Temporally, the predictions represent mid-1990s land-use and N-loading conditions.

Model performance was evaluated based on the significance level of estimated coefficients, the coefficient of determination (R^2), mean square error (MSE), probability plots of model residuals, and plots of predicted versus observed values. The MSE is defined as

$$s^2 = \frac{\sum_{i=1}^n \epsilon_i^2}{n - 2} \quad (5)$$

where s^2 = mean square error of fitted model, (mg/L)²; ϵ_i = model error for network polygon i ; and n = number of networks in the data set.

Prediction uncertainty was estimated stochastically by computing variances based on 500 Monte Carlo simulations per monitoring network. The Monte Carlo simulations involved simultaneous perturbation of parameters and model errors, based on a multivariate normal distribution with expected value of 0 and variance described by a covariance matrix of parameter estimates or equation residuals.

Results and Discussion

Shallow GWAVA Model. The GWAVA-S model yielded an R^2 of 0.801, indicating that much of the variation in nitrate concentration is explained by the model. The nonlinear model outperformed alternative approaches that were tried with individual wells (tobit) and network averages (multiple linear regression), based on the MSE of 2.96 (see the Supporting Information). A plot of observed versus predicted nitrate concentrations indicates that GWAVA-S fits the data reasonably well (Figure 1a). A probability plot of model residuals indicates that they follow a normal distribution (Figure 1b);

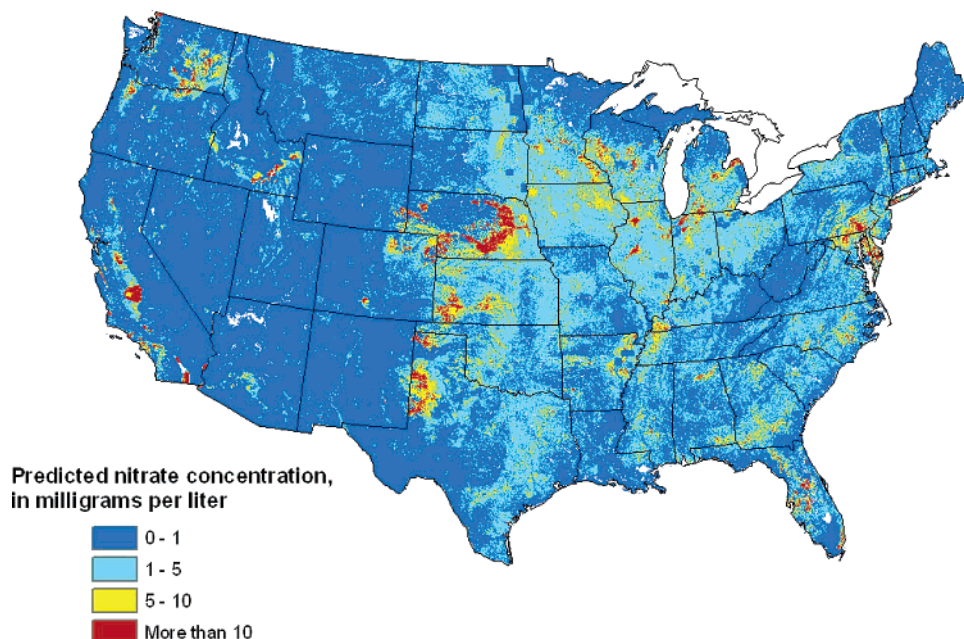


FIGURE 2. Nitrate concentration in shallow, recently recharged U.S. groundwater, as predicted by the GWAVA-S model.

therefore, transformation of dependent and independent variables for regression was unnecessary. We performed the Kolmogorov-Smirnov test as an additional check on the distribution of GWAVA-S residuals. Because the probability associated with the test statistic is > 0.05 , we accept the null hypothesis that the residuals follow a normal distribution.

Parameter coefficients in Table 1 shed light on predominant processes influencing nitrate transport and accumulation in shallow groundwater at the national scale. The coefficient sign of all N sources is positive, indicating that as N loading at the land surface increases, nitrate concentration in shallow groundwater increases. The model corroborates the results of prior studies that show a positive relation between agricultural land and/or fertilizer loading and nitrate concentration in groundwater (9, 13, 15, 17, 18). Several of the variables in Table 1 are believed to function as surrogates for additional sources of N or different management practices. Orchards/vineyards may represent unique management practices in such areas, and cropland/pasture/fallow land may represent additional N sources such as septic systems and unconfined manure. The latter two variables were tested in both models but found to be statistically insignificant. Population density likely is a surrogate for N sources in urban areas, including nonfarm fertilizer, sewer exfiltration, and atmospheric deposition. The latter three variables were insignificant in the regressions.

Parameter coefficients for transport factors have positive or negative signs depending on whether they proportionally increase or decrease the amount of N delivered to groundwater. Factors having positive signs include water input and rock type (Table 1). Nitrate concentration increases with increasing water input, here defined as the ratio of irrigated land to precipitation. The latter variable was tested separately but was statistically insignificant in the regressions, indicating that irrigation-enhanced transport dominates in more arid regions; however, the wetlands variable likely embodies precipitation in humid regions. Water inputs interact with selected rocks to enhance delivery of nitrate to aquifers. Carbonate rocks and basalt and volcanic rocks commonly contain solution channels and/or fractures that promote flow of water and chemicals to wells. Both rock types have positive coefficient signs in the model.

The remaining transport factors have negative coefficients. Fine-grained sediment—represented in the model by clay

and poorly sorted glacial till—typically restricts water and chemical fluxes to groundwater. Ditches in agricultural areas with poorly drained soils divert contaminated water to nearby streams, which short circuits nitrate leaching. Areas with increased slope have low nitrate concentration in groundwater, which could indicate reduced vertical permeability or increased overland flow. Increased slope is more likely a surrogate for minimally developed land, which has lower N loading compared with agricultural and urban areas. Among sampled areas, high slopes are found in minimally developed areas of West Virginia, northwestern Virginia and Maryland, and western Colorado.

Attenuation factors thought to represent dilution and denitrification have negative signs in GWAVA-S. Fresh surface water withdrawal suggests dilution in irrigated areas overlying highly transmissive rocks. Some irrigation districts in the Upper Snake River Basin in southeastern Idaho apply surface water to thin soils (about 5 m deep) overlying fractured basalt, which results in massive recharge of low-nitrate water and flushing (Michael G. Rupert, personal communication, 2005). Tailwater recovery in these same areas may result in more efficient use of irrigation water, which can minimize leaching, or reapplication of recovered, relatively clean water may enhance the dilution effect. In contrast, other irrigation districts in the region apply and recycle groundwater, which typically degrades groundwater quality.

Areas with increased percentages of histosols and/or wetlands have increased potential for denitrification, a bacterially mediated process that converts nitrate to N_2 . Denitrification occurs under reducing conditions in the presence of electron donors such as organic carbon or ferrous iron (32). Histosols are soils that contain large amounts of organic matter in the upper profile. Together, these factors suggest denitrification potential in saturated soils with high organic carbon content.

The GWAVA-S model was used to predict nitrate concentration in shallow groundwaters of the U.S. (Figure 2). Model inputs were obtained by compiling the spatial attributes shown in Table 1 for 1-km²-grid cells representing the conterminous U.S. Areas with high N load, low-to-moderate clay content, sufficient water input, and low denitrification potential have the highest predicted nitrate concentration. The most extensive areas of predicted, severe contamination (nitrate > 10 mg/L) occur in the High Plains,

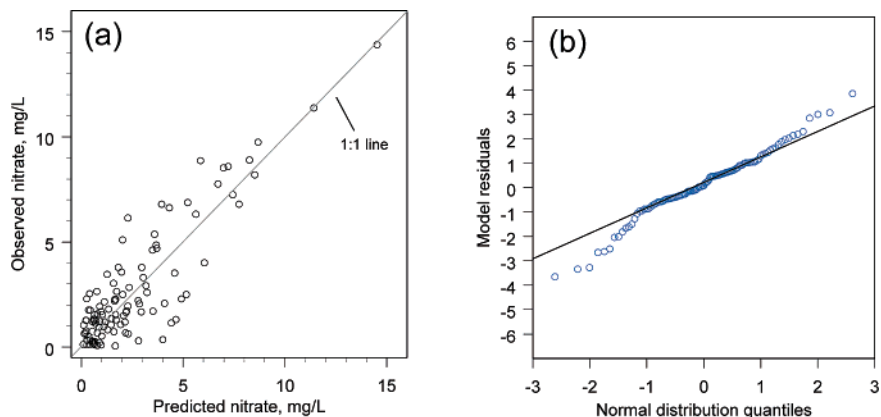


FIGURE 3. Observed nitrate concentration versus that predicted by GWAVA-DW for drinking-water wells (a) and distribution of model residuals (b).

and areas of predicted, moderate contamination (>5 to ≤ 10 mg/L nitrate) occur extensively in the northern Midwest. These results compare favorably with geographic areas predicted to have increased probability of nitrate contamination in previous research (18).

Model errors for monitoring networks (ϵ_i in eq 1) were analyzed for spatial patterns and to evaluate model performance for individual observations. A national map indicates no apparent spatial patterns in the errors; hence, the predictions appear to lack systematic bias (see Figure 1 in the Supporting Information). The model performs well in areas such as southern California, where observed and predicted nitrate concentrations are 6.95 and 6.94 mg/L, respectively ($\epsilon_i = 0.015$ mg/L). Agriculture, landscape irrigation, and wastewater generation and disposal adversely affect groundwater quality in the region (33). Large errors indicate where the model does not perform as well. Groundwater in the coastal plain of South Carolina has moderately low predicted nitrate concentration (2.32 mg/L) but high observed nitrate (7.83 mg/L). The model apparently overestimates nitrate attenuation in the area, based on high values of wetlands and histosols in the data set. In fact, sandy soils in the region promote rapid transport of contaminants to groundwater (34).

Drinking-Water GWAVA Model. The GWAVA-DW model performed comparably to GWAVA-S (MSE = 2.00 and $R^2 = 0.767$). Observed and predicted nitrate concentrations generally follow a one-to-one line (Figure 3a). The median of the predicted nitrate values (1.6 mg/L) is somewhat less overall than that of GWAVA-S (3.0 mg/L), which shows the influence of deeper wells in the GWAVA-DW data set. A probability plot of GWAVA-DW residuals suggests that they follow a normal distribution (Figure 3b). The bulk of the data in Figure 3b are linear; they fall on the straight line representing the theoretical distribution. Additionally, the probability of the Kolmogorov-Smirnov test statistic is >0.05 for the GWAVA-DW residuals, so we accept the null hypothesis that they follow a normal distribution.

GWAVA-DW is conceptually similar to GWAVA-S, but some factors differ. Significant rock types include semiconsolidated sand aquifers present in the north Atlantic coastal plain, and sandstone and carbonate rocks in southern Pennsylvania, Maryland, northwestern Virginia, and eastern Tennessee (Table 2). These rocks have high interconnected porosity and/or solution channels that can readily transmit water and chemicals to groundwater.

Overland flow variables in GWAVA-DW have negative coefficient signs and represent either transport or attenuation. Hortonian flow indicates overland transport of water and nitrate to streams, rather than leaching to groundwater. This type of flow occurs when the infiltration capacity of the soil

has been exceeded, and precipitation is transported downslope as sheet flow over the land surface. Alternatively, Dunne overland flow suggests saturated soils with denitrification potential, similar to wetlands in the GWAVA-S model—therefore in GWAVA-DW this factor represents attenuation rather than transport. Dunne overland flow is generated by precipitation (regardless of intensity) on soil that is already saturated.

The GWAVA-DW model includes well depth as an attenuation factor, to accommodate the wide range of sampling depths found in the data set (up to 440 m deep for individual wells). This variable was not incorporated in previous national models (17, 18) or in GWAVA-S, which primarily emphasizes shallow wells. Well depth is the least significant variable in the model ($p = 0.18$) but is retained to evaluate different water-supply scenarios. The negative coefficient sign indicates that nitrate concentration decreases as sampling depth increases. Reducing conditions at depth in some aquifers are less favorable to nitrate formation and accumulation. Additionally, deeper groundwater is older and predates recent periods (1950s to present) of increased fertilizer use. Finally, with increasing depth there is greater likelihood of intervening, less permeable layers that restrict the downward migration of nitrate.

We used the GWAVA-DW model to predict nitrate concentration in groundwater used for drinking in the U.S., based on a simulation depth of 50 m (Figure 4). Patterns of nitrate contamination are similar to those predicted by GWAVA-S. Areas of moderate to severe contamination (>5 mg/L), however, are less extensive for GWAVA-DW, particularly in the northern Midwest. This likely reflects differences in well depth; GWAVA-DW is based on data with a mean well depth of 48.8 m, compared with 9.8 m for the shallow groundwater data set.

A national map of GWAVA-DW model errors indicates that there is no apparent, systematic bias to the predictions (see Figure 2 in the Supporting Information). The model performs well in areas such as the Trinity aquifer in south central Texas, where observed and predicted nitrate concentrations are 0.30 and 0.28 mg/L, respectively. Effects from human activity are minimal because the region is largely undeveloped (35). The model does not perform as well in southern Kansas, where predicted and observed nitrate concentrations are 2.29 mg/L and 6.14 mg/L, respectively. Estimated, percent Hortonian overland flow is high in the area, so GWAVA-DW likely underestimates leaching of nitrate to groundwater. In fact, overland flows in the High Plains commonly accumulate in surface depressions, ditches, dry stream beds, and playas, which can focus recharge of water and contaminants to groundwater (Breton W. Bruce, personal communication, 2006).

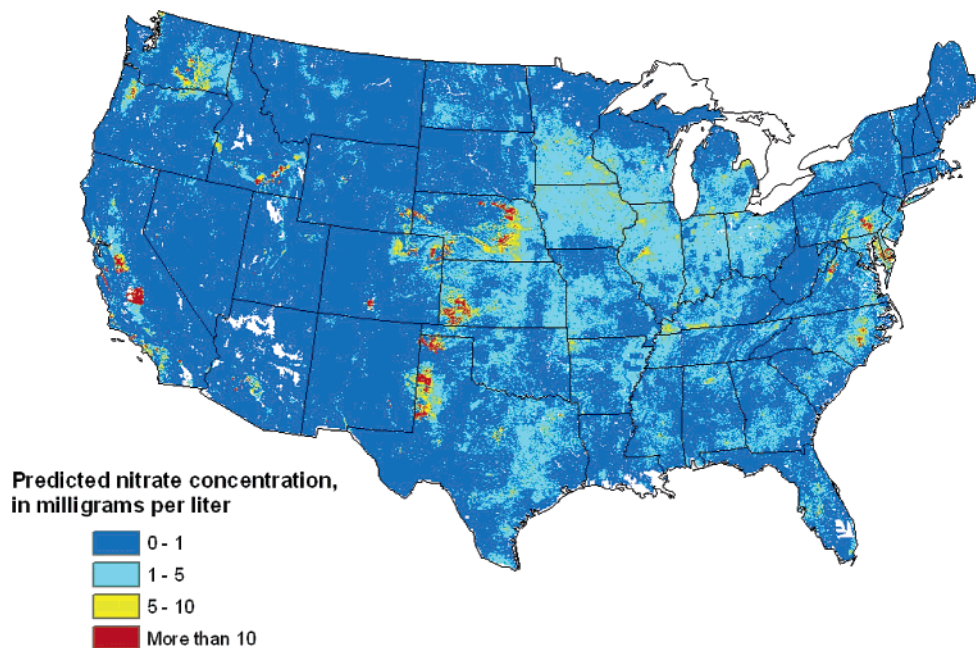


FIGURE 4. Nitrate concentration in U.S. groundwater used for drinking, as predicted by the GWAVA-DW model (simulation depth = 50 m).

TABLE 3. Numbers of People on Private Wells in Areas with Nitrate Concentration Ranges Predicted by the Drinking-Water Model (GWAVA-DW), for Two Well-Depth Scenarios^a

predicted nitrate concn range	population counts for simulation depth		percent change
	10 m	50 m	
no data	1 710 000	1 710 000	
	Background		
0 to ≤1 mg/L	19 400 000	20 000 000	+3.2
	Elevated		
>1 to ≤5 mg/L	13 300 000	13 000 000	-3.0
	Moderate		
>5 to ≤10 mg/L	1 400 000	1 240 000	-12.0
	Severe		
>10 mg/L	528 000	467 000	-11.5

^a Percent changes were calculated before population counts were rounded for inclusion in the table.

Prediction uncertainty was evaluated for both GWAVA-S and GWAVA-DW using Monte Carlo simulations. The uncertainty generally is highest for networks with high values of one or more sensitive variables, such as N loading and water input (see Figures 3 and 4 in the Supporting Information).

Model Application. The GWAVA-DW model was applied at two simulation depths to estimate numbers of groundwater users on private wells in contaminated areas. The first simulation depth (10 m) represents a worst-case scenario and is the mean well depth in the shallow groundwater data set. The second scenario represents mean well depth in the drinking-water data set (50 m) and corresponds to predictions shown in Figure 4. Areas with predicted nitrate-concentration ranges in Table 3 (“background,” “elevated,” and so on) were delineated in a GIS to generate counts of people on wells serving four or fewer housing units, based on census data (36). The model predicts that exposure risk is reduced by seeking deeper supplies. Contaminated areas are less extensive under the 50-m scenario and encompass fewer users on private wells, compared with the 10-m scenario. The number of users in moderately contaminated areas (>5 to

≤10 mg/L nitrate) decreases by 12% to 1.2 million, when well depth increases from 10 to 50 m (Table 3). For both well depth scenarios, areas with >5 mg/L predicted nitrate concentration are 78% agricultural and 4% urban.

Although GWAVA-DW predicts more widespread contamination at the 10-m depth, users in these areas may or may not be consuming shallow groundwater. Also, public supplies of groundwater commonly are treated to remove contaminants. Rather, the model indicates the potential for exposure based on numbers of self-supplied users residing in areas having a predicted nitrate concentration range.

Acknowledgments

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Supporting Information Available

Discussion of GIS processing of spatial data; spatial averaging of point measurements to reduce small-scale variability; comparison of nonlinear regression with alternative approaches tried; interpretation of model parameter coefficients; the spatial distribution of model errors; and results of uncertainty analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Spalding, R. F.; Exner, M. E. Occurrence of nitrate in groundwater—a review. *J. Environ. Qual.* **1993**, *22*, 392–402.
- DeRoos, A. J.; Ward, M. H.; Lynch, C. F.; Cantor, K. P. Nitrate in public water systems and the risk of colon and rectum cancers. *Epidemiology* **2003**, *14*, 640–636.
- Ward, M. H.; deKok, T.; Levallois, P.; Brender, J.; Gulis, G.; Nolan, B. T.; VanDerslice, J. Drinking water nitrate and health - recent findings and research needs. *Environ. Health Perspect.* **2005**, *115*, 1607–1614.
- 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-Hodgkin's lymphoma. *Epidemiology* **1996**, *7*, 465–471.
- (5) 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*, 327–338.
 - (6) Nolan, B. T.; Hitt, K. J. *Nutrients in shallow ground waters beneath relatively undeveloped areas in the conterminous United States*; U.S. Geological Survey Water-Resources Investigations Report 02-4289; 2003.
 - (7) U.S. Environmental Protection Agency. *Safe Drinking Water Act Amendments of 1996*; Office of Ground Water and Drinking Water; Washington, DC, 1996. <http://www.epa.gov/safewater/sdwa/> (accessed February 2006).
 - (8) Fuhrer, G. A.; Gilliom, R. J.; Hamilton, P. A.; Morace, J. L.; Nowell, L. H.; Rinella, J. F.; Stoner, J. D.; Wentz, D. A. *The quality of our nation's waters-nutrients and pesticides*; U.S. Geological Survey Circular 1225; 1999.
 - (9) Eckhardt, D. A. V.; Stackelberg, P. E. Relation of ground-water quality to land use on Long Island, New York. *Ground Water* **1995**, *33*, 1019–1033.
 - (10) Teso, R. R.; Poe, M. P.; Younglove, T.; McCool, P. M. Use of logistic regression and GIS modeling to predict groundwater vulnerability to pesticides. *J. Environ. Qual.* **1996**, *25*, 425–432.
 - (11) Mueller, D. K.; Ruddy, B. C.; Battaglin, W. A. Logistic model of nitrate in streams of the upper-midwestern United States. *J. Environ. Qual.* **1997**, *26*, 1223–1230.
 - (12) Nolan, B. T.; Ruddy, B. C.; Hitt, K. J.; Helsel, D. R. Risk of nitrate in groundwaters of the United States: a national perspective. *Environ. Sci. Technol.* **1997**, *31*, 2229–2236.
 - (13) 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*, 1029–1039.
 - (14) Rupert, M. G. *Probability of detecting atrazine/desethyl-atrazine and elevated concentrations of nitrate (NO₂ + NO₃ N) in ground water in the Idaho part of the Upper Snake River Basin*; U.S. Geological Survey Water-Resources Investigations Report 98-4203; 1998.
 - (15) Rupert, M. G. *Probability of detecting atrazine/desethyl-atrazine and elevated concentrations of nitrate in ground water in Colorado*; U.S. Geological Survey Water-Resources Investigations Report 02-4269; 2003.
 - (16) Squillace, P. J.; Moran, M. J.; Lapham, W. W.; Price, C. V.; Clawges, R. M.; Zogorski, J. S. Volatile organic compounds in untreated ambient groundwater of the United States, 1985–1995. *Environ. Sci. Technol.* **1999**, *33*, 4176–4187.
 - (17) Nolan, B. T. Relating nitrogen sources and aquifer susceptibility to nitrate in shallow ground waters of the United States. *Ground Water* **2001**, *39*, 290–299.
 - (18) 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*, 2138–2145.
 - (19) Ayotte, J. D.; Nolan, B. T.; Nuckols, J. R.; Cantor, K. P.; Gilpin, R. Robinson, J.; Baris, D.; Hayes, L.; Karagas, M. R.; Bress, W.; Silverman, D. T.; Lubin, J. H. Modeling the probability of arsenic in groundwater in New England as a tool for exposure assessment. *Environ. Sci. Technol.* **2006**, *40*, 3578–3585.
 - (20) Nolan, B. T.; Clark, M. L. Selenium in irrigated areas of the western United States. *J. Environ. Qual.* **1997**, *26*, 849–857.
 - (21) Nuckols, J. R.; Cantor, K.; Ayotte, J.; Lubin, J.; Airola, M.; Baris, D.; Silverman, D. In *14th Annual Conference of the International Society of Exposure Analysis*; Philadelphia, PA, 2004.
 - (22) Worrall, F.; Wooff, D. A.; Seheult, A. H.; Coolen, F. P. A. New approaches to assessing the risk of groundwater contamination by pesticides. *J. Geol. Soc.* **2000**, *157*, 877–884.
 - (23) Howard, G.; Pedley, S.; Barrett, M.; Nalubega, M.; Johal, K. Risk factors contributing to microbiological contamination of shallow groundwater in Kampala, Uganda. *Water Res.* **2003**, *37*, 3421–3429.
 - (24) Aelion, C. M.; Conte, B. C. Susceptibility of residential wells to VOC and nitrate contamination. *Environ. Sci. Technol.* **2004**, *38*, 1648–1653.
 - (25) Helsel, D. R.; Hirsch, R. M. *Statistical methods in water resources*; Elsevier: New York, 1992.
 - (26) Alexander, R. B.; Smith, R. A.; Schwarz, G. E. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature* **2000**, *403*.
 - (27) Smith, R. A.; Schwarz, G. E.; Alexander, R. B. Regional interpretation of water-quality monitoring data. *Water Resour. Res.* **1997**, *33*, 2781–2798.
 - (28) Hutson, S. S.; Barber, N. L.; Kenny, J. F.; Linsey, K. S.; Lumia, D. S.; Maupin, M. A. *Estimated use of water in the United States in 2000*; U.S. Geological Survey Circular 1268; 2004.
 - (29) 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*; U.S. Geological Survey Open-File Report 93-125; 1993.
 - (30) 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*; U.S. Geological Survey Open-File Report 95-399; 1995.
 - (31) Nolan, B. T.; Stoner, J. D. Nutrients in groundwaters of the conterminous United States, 1992-1995. *Environ. Sci. Technol.* **2000**, *34*, 1156–1165.
 - (32) Böhlke, J. K.; Denver, J. M. Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. *Water Resour. Res.* **1995**, *31*, 2319–2339.
 - (33) Belitz, K.; Hamlin, S. N.; Burton, C. A.; Kent, R.; Fay, R. G.; Johnson, T. *Water quality in the Santa Ana Basin, California, 1999-2001*; U.S. Geological Survey Circular 1238; 2004.
 - (34) Hughes, W. B.; Abrahamsen, T. A.; Maluk, T. L.; Reuber, E. J.; Wilhelm, L. J. *Water quality in the Santee River Basin and Coastal Drainages, North and South Carolina, 1995–98*; U.S. Geological Survey Circular 1206; 2000.
 - (35) Bush, P. W.; Ardis, A. F.; Fahlquist, L.; Ging, P. B.; Hornig, C. E.; Lanning-Rush, J. *Water quality in South-Central Texas, Texas, 1996–98*; U.S. Geological Survey Circular 1212; 2000.
 - (36) U.S. Bureau of the Census. *1990 Census of Population and Housing, Public Law 94-171 Data (United States)*; 1991. <http://water.usgs.gov/lookup/getspatial?usp90> (accessed February 2006).

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