Soil characteristics and agrichemicals in groundwater of the Midwestern United States

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Abstract A comprehensive set of soil characteristics were examined to determine the effect of soil on the transport of agrichemicals to groundwater. This paper examines the relation of soil characteristics to concentrations and occurrence nitrate, atrazine, and atrazine residue from 99 wells completed in unconsolidated aquifers across the Midwestern United States. Soil characteristics that determine the rate of water movement were directly related to the occurrence and concentrations of nitrate and atrazine in groundwater. The substantial differences in the relations found among soil characteristics and nitrate and atrazine in groundwater suggest that different processes affect the transformation, adsorption, and transport of these contaminants. A multi-variable analysis determined that the soil characteristics examined explained the amount of variability in concentrations for nitrate (19%), atrazine (33%), and atrazine residue (29%). These results document that, although soils do affect the transport of agrichemicals to groundwater, other factors such as hydrology, land use, and climate must also be considered to understand the occurrence of agrichemicals in groundwater.

Keywords Agrichemicals; atrazine; groundwater; nitrate; soil

Introduction

Agrichemicals such as herbicides, herbicide degradation products, and nitrate are commonly found in water resources and have been traced to sources associated with crop production. Recent research suggests possible negative effects of these agrichemicals on ecosystems may result, in part, from shallow aquifer contributions in natural discharge areas. A US Geological Survey (USGS) study of the regional distribution of agrichemicals in shallow bedrock and unconsolidated aquifers (Kolpin and Buckart, 1991) focused on the Midwest where agrichemicals are extensively used in corn (*Zea Mays* L.) and soybean [*Glycine max* (L.) Merr.] production. Shallow aquifers are those within about 15 m of the land surface. These aquifers represent hydrogeologic settings most vulnerable to surface application of agrichemicals (Hallberg, 1989; Mehnert *et al.*, 1995).

The initial data and interpretations resulting from the regional study of agrichemicals by the USGS were published elsewhere (Burkart and Kolpin, 1993; Kolpin *et al.*, 1993, 1994). A subsequent study (Kolpin, 1997) using the regional USGS data included correlations between land-use data near 100 of the 303 wells originally used and the agrichemicals detected in the 1991 study (Kolpin *et al.*, 1994).

This paper presents the results of a statistical evaluation of soil characteristics and concentrations and occurrence of nitrate, atrazine, and atrazine residue. This includes identifying soil characteristics that significantly correlate with agrichemical occurrence and defining the combination of soil characteristics that best predict their occurrence in groundwater. Concentrations of deisopropylatrazine (DIA) and deethylatrazine (DEA) were added to the parent compound concentrations to derive atrazine residue concentrations in the water samples. Larger frequencies of censored data (concentrations below analytical reporting limits) precluded examination of other agrichemicals (Burkart and Kolpin, 1993).

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Methods

The same subset of 100 wells used in Kolpin's (1997) regional land-use analysis were selected for this analysis of soil characteristics. The soils surrounding one of these wells, however, had not been mapped, so 99 were used for this study. The 99 wells used for this study were all completed in unconsolidated aquifers because of the significantly greater occurrence of agrichemicals compared to samples from bedrock aquifers (Burkart and Kolpin, 1993). A stratified random selection process was used to obtain 99 wells (Figure 1) in countries where at least 25% of the land area was in corn production.

Water chemistry data for the selected wells were obtained from samples collected in 1991 during two periods; March–April and July–August. The maximum concentration of the two 1991 samples for each site (usually the summer sample) was used for this analysis. This step provided the largest amount of uncensored chemical data. A summary of the water-chemistry data used for this study is provided in Table 1. Sample-collection methods are detailed in Kolpin and Buckart (1991) and Kolpin *et al.* (1994).

Samples were analyzed for 11 pesticides and DEA and DIA by gas chromatography/mass spectrometry following solid-phase extraction on C-18 cartridges (Meyer *et al.*, 1993; Thurman *et al.*, 1992). The analytical reporting limit for this method was 0.05 $\mu g\ L^{-1}$ for all compounds. Nitrate was determined with an automated colorimetric procedure (Fishman and Friedman, 1989) with an analytical reporting limit of 0.05 $mg\ L^{-1}$.

Table 1 Summary of agricultural chemical concentrations used in this study

Constituent	Reporting limit	Drinking water standard	Percent detection	10th %-ile	Median	90th %-ile	Maximum concentration
Nitrate (mg l^{-1} as N)	0.05	10.0	77	<0.05	2.6	13.0	32.0
Atrazine (µg L^{-1})	0.05	3.0	38	<0.05	<0.05	0.36	2.1
Atrazine residue (µg L^{-1})	0.05	none	47	<0.05	<0.05	0.84	4.4

Table 2 Soil attribute names, Map Unit Interpretation Database symbols and variable type used in the statistical analysis

Soil attribute name	MUIR attribute symbol (total number of variables)	Variable Type
Organic matter	†OM (9)	Chemical
Clay content	†CLAY (9)	Texture
Silt content	†SILT (9)	Texture
Sand content	†SAND (9)	Texture
Percent passing sieve number 10	†NO10 (9)	Texture
Percent passing sieve number 200	†NO200 (9)	Texture
Available water holding capacity	†AWC (9)	Physical
Bulk density	†BD (9)	Physical
Shrink-swell potential in upper layer (Very high, high, moderate, low)	SHRINKSW (4)	Physical
Permeability rate	†PERM (9)	Water flux
Hydrologic group (A, B, C, D)	HYDGRP (4)	Water flux
Sociol drainage class (E, SE, W, MW, SP, P, VP)	DRAIN (7)	Water flux
Soil slope	‡SLOPE (3)	Landscape
Seasonally high water table depth	‡WTDEP (3)	Landscape
Hydric soil rating (Y, N)	HYDRIC (1)	Landscape

† Three sets of values were used: upper layer, deepest layer; and all layers
Averages were calculated for the upper, deepest, and all layers in addition to the maximum and minimum values for each layer

‡ Average values were calculated in addition to maximum and minimum

Soils data surrounding each well were derived from soil surveys published by the Natural Resources Conservation Service (NRCS). Analog soils maps were transformed to digital vector data for analysis in a geographic information system (GIS). Individual soil map sheets from these surveys were scanned and spliced together to create digital records of soils in a 2 km radius around each selected well.

The scanned images were registered to a transportation digital coverage with geographic coordinates and then converted to an ARC/INFO grid. The grids were processed to differentiate soil polygons representing soil map unit boundaries. The resultant polygon coverages were edited by deleting lines and shading that did not represent soil boundaries and adding missing map unit boundary lines. A complete polygon coverage for each 2-km circle was degenerated by splicing together as many as nine polygon coverages developed from soil map sheets. Within the buffer, spliced segments were edge-matched to produce continuous polygons across former soil sheet map boundaries. This was accomplished with a combination of automated and manual GIS processing. Polygons were labeled with the Map Unit Identifiers (MUID) and related to a polygon attribute table. The polygon area was used to define the area-weighted values for specific soil attributes. Soil attributes for each MUID were downloaded from the Map Unit Interpretation Records maintained by NRCS (*http://www.statlab.iastate.edu/soils/muir/download.html*).

The MUIR soil attribute table was then combined with the polygon coverage for each 2-km circle to link polygons and soil data. All polygons with the same MUID were aggregated and a single area-weighted value for each buffer was calculated for the soil variables listed in Table 2. An average value for each variable was calculated and used in the analysis where MUIR reported a maximum and minimum value.

A total of 103 variables, divided into 5 semi-independent variable types, were used in the univariate statistical analysis (Table 2). For characteristics that had data for multiple soil layers, nine different values were used representing the average (A), minimum (L), and maximum (H) values for the upper (1), lower (9), and composite (T) layers. Only the value with the largest correlation coefficient to each agrichemical examined is discussed in the statistical results. Sand and silt content were calculated from size-analysis fractions for the upper, lowest, and composite layer values.

Spearman's rank correlation coefficients (Helsel and Hirsch, 1992) were calculated to identify continuous soil variables having significant relations with concentrations of agrichemicals. This test is a measure of the monotonic relation between response variables (nitrate, atrazine, or atrazine residue concentrations) and explanatory variables (soil characteristics). Non-continuous soil characteristics, such as drainage class (Table 2), were transformed to continuous variables by calculating the percent of the total area in the 2-km buffer occupied by soils in each class.

Mann-Whitney tests were also used to identify those soil characteristics having significant relations with the occurrence of agrichemicals in groundwater. Mann-Whitney tests defined differences between two groups of data. The thresholds used to subdivide the data were: nitrate (2.0 mg L^{-1} ; suggestive of anthropogenic sources of nitrate [Mueller and Helsel, 1996]); atriazine (0.05 $\mu g\ L^{-1}$; reporting limit for atrazine used for this study), and atrazine residue (0.05 $\mu g\ L^{-1}$; reporting limit for atrazine, DEA, and DIA used for this study).

Multi-variate analyses were conducted to determine what set of characteristics best predict the concentration (linear regression) and occurrence (logistic regression; [Helsel and Hirsh, 1992]) of agrichemicals in groundwater. All variables were log-transformed, which results in relatively normal distributions. Many of the soil characteristics compiled for this study are strongly correlated with each other. To reduce the effects of multi-collinearity among potential explanatory variables, only the most significant characteristic in each variable type (Table 3) was included in the multi-variabe part of this study.

Table 3 Summary of soil attributes, Spearman rank correlation coefficients (upper number), and significance (lower number) to agrichemical concentrations for the most significant soil characteristic of each variable type

Variable type	Nitrate	Atrazine	Atrazine residue
Chemical	–	Organic matter maximum in upper layer (OMH_1) –0.301 0.002	Organic matter average in composite of layers (OMA_T) –0.240 0.017
Texture	Clay content maximum in composite of layers (CLAYH–T) –0.216 0.032	Silt minimum in upper layer (SILTL–1) 0.348 <0.001	Silt minimum in upper layer (SILTL_1) 0.208 0.039
Physical	Bulk density maximum in composite of layers (BDH_T) –0.226 0.011	Available water holding capacity minimum in lower layer (AWCL_9) 0.306 0.002	Bulk density minimum in lowest layer (BDL_9) –0.239 0.017
Water flux	Hydrologic group C (HYDGP–C) –0.334 <0.001	Drainage class very poor (DRAIN_VP) –0.527 <0.001	Drainage class very poor (DRAIN_VP) –0.458 <0.001

Results and discussion

Nitrate

The soil characteristics having the strongest relation to nitrate concentration within each variable type are shown in Table 3 and Figure 1. Seasonally shallow water table depth (WTDEPH; Figure 1D) had the strongest relation to nitrate concentration. The positive correlation suggests the lowest nitrate concentrations were generally associated with the shallowest WTDEPH. Shallow water tables generally reflect poorly drained soils and anaerobic conditions. Under these conditions, denitrification of nitrate can occur in the presence of organic carbon and denitrifying bacteria (Korom, 1992). Indeed, a significant negative relation exists ($r=0.446$, $p<0.001$; Spearman's rank correlation) between WTDEPH and dissolved oxygen for this study.

Hydrologic group C (HYDGP_C) was negatively related to nitrate concentration (Table 3, Figure 1C). These are soils with slow infiltration rates caused by layers that impede downward movement of water and hence, nitrate. Slow draining soils maintain longer periods of saturation than faster drained soils. Saturated soils are more oxygen deficient, thus promoting denitrification (Meisinger and Randall, 1991). These soils are also more likely to be artificially drained, diverting nitrate to nearby streams rather than leaching to groundwater.

Bulk density maximum in all layers (BDH_T; Figure 1B) and clay content maximum of all layers (CLAYH_T; 1A) negatively correlate to nitrate concentration. Both are indicators of reduced vertical water flux associated with smaller matrix permeability.

An exploratory analysis was also conducted to determine which soil characteristics were significantly related to nitrate concentrations exceeding 2.0 mg L^{-1} (Table 4). Characteristics identified were similar to those that relate to nitrate concentration (Table 3). However, there were no significant texture variables identified, and the combination of soil drainage classes poor, somewhat poor, and very poor (DRAIN_B) was the most significant characteristics for the water flux variable type.

All the soil characteristics that significantly relate to nitrate concentration (Figure 1) are direct or indirect measures of water flux. Consequently, rates of water movement are clearly important in transporting nitrate to groundwater.

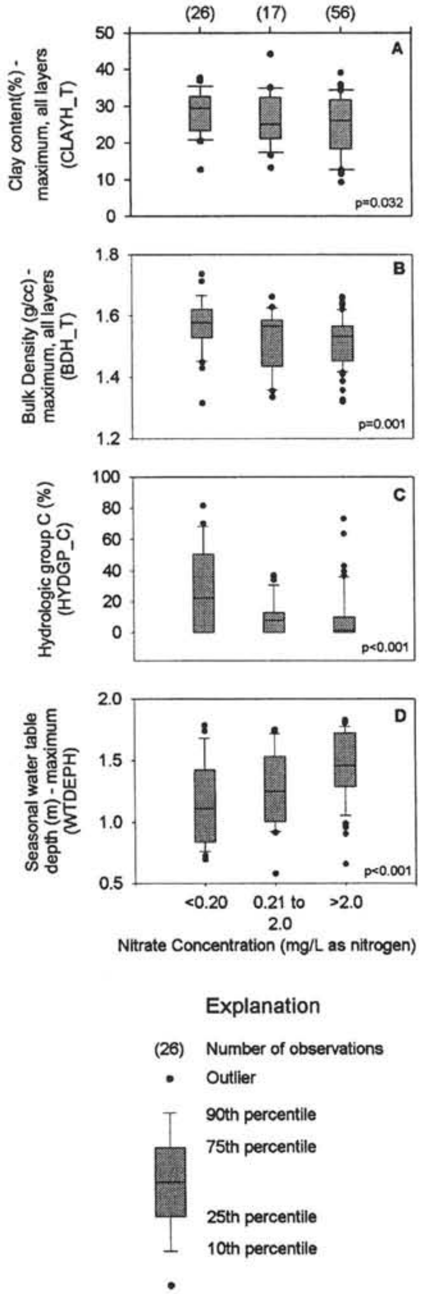

Figure 1 Soil characteristics correlated to nitrate concentrations

The maximum variance in the log-transformed nitrate concentration that was explained by the various soil characteristics was found to be 19% for the combination of WTDEPH + HYDGP_C + BDH_T + CLAYH_T ($R^2 = 0.19$). Thus, even though the soil characteristics help explain nitrate concentration in groundwater, there are obviously many other important characteristics involved (i.e., land use, hydrogeology, climate, and chemical use) that would help capture the remaining 81% of the variance in nitrate concentrations left unexplained.

Logistic regression analysis was used to predict the presence or absence of anthropogenic sources of nitrate (>2.0 mg/L) from characteristics identified in Table 4. The model that had the highest accuracy (most correct predictions) was WTDEPH + DRAIN_B with an accuracy of 66%.

Table 4 Summary of Mann-Whitney test of agrichemical occurrence to the most significant characteristic of each variable type. Significance is shown below each variable name

Variable type	Nitrate	Atrazine	Atrazine residue
Chemical	–	Organic matter maximum in upper layer (OMH_1) 0.002	Organic matter maximum in upper layer (OMH_1) 0.015
Texture	–	Silt content minimum in upper layer (SILTL_1) <0.001	–
Physical	Bulk density maximum in composite of layers (BDH_T) <0.001	Bulk density minimum in lowest layer (BDL_9) 0.002	Bulk density maximum in composite of layers (BDH_T) 0.007
Water flux	Drainage classes poor, somewhat poor, and very poor combined (DRAIN+B)† <0.001	Drainage class, very poor (DRAIN_VP) <0.001	Drainage class, very poor (DRAIN_VP) <0.001
Landscape	Seasonally high water table maximum (WTDEPH) <0.001	Seasonally high water table maximum (WTDEPH) <0.001	Seasonally high water table maximum (WTDEPH) 0.001

† DRAIN_B - DRAIN_P + DRAIN_SP + DRAIN_VP

Atrazine

The soil characteristics having the strongest relation to atrazine concentration within each variable type are shown in Table 3 and Figure 2. The soils with very poor drainage (DRAIN_VP; Figure 2D) were most strongly related to atrazine concentration. These solids contain low-permeable layers that impede downward movement of water and hence, atrazine. In addition, atrazine is highly adsorbed to clay particles (Moreau-Kervevan and Mouvert, 1998), which may further explain the inverse relation to DRAIN_VP in soils where drainage is tied to the clay fraction. These very poorly drained soils are more likely to be artificially drained, diverting water and atrazine to nearby streams and reducing infiltration to groundwater.

The positive correlation of WTDEPH to atrazine concentration may be intuitively enigmatic. It may be expected that a deeper water table would increase travel times to groundwater and increase the distance through which atrazine is exposed to an oxygenated environment where atrazine degrades more readily (Dhileepan and Schnoor, 1992). However, WTDEPH does not exceed 1.83 m in the MUIR database. Thus, the relation determined for this study could change if a greater range in WTDEPH was encountered.

Silt content minimum in the upper layer (SILT_1) was positively correlated with atrazine concentration and was the most significant characteristic among the texture variables (Table 3, Figure 2B). It is not clear why silt was more significantly related to atrazine concentration than either sand or clay. It may be that soils with larger silt fractions are better suited for crops treated with atrazine, such as corn.

Available water holding capacity minimum in the lowest level (AWCL_9) was positively correlated with atrazine concentration and was the most significant among the physical soil characteristics (Table 3, Figure 2C). Soils with the potential to hold more water may sustain saturation accompanied by oxygen deficiency. Under these conditions, atrazine degradation rates would be slower than under better drained conditions. Alternatively, soils with high available water holding capacity may develop macropores that allow more rapid leaching of atrazine. Available water holding capacity is a particularly significant soil characteristic in the deepest layer adjacent to the deep vadose zone or underlying aquifer.

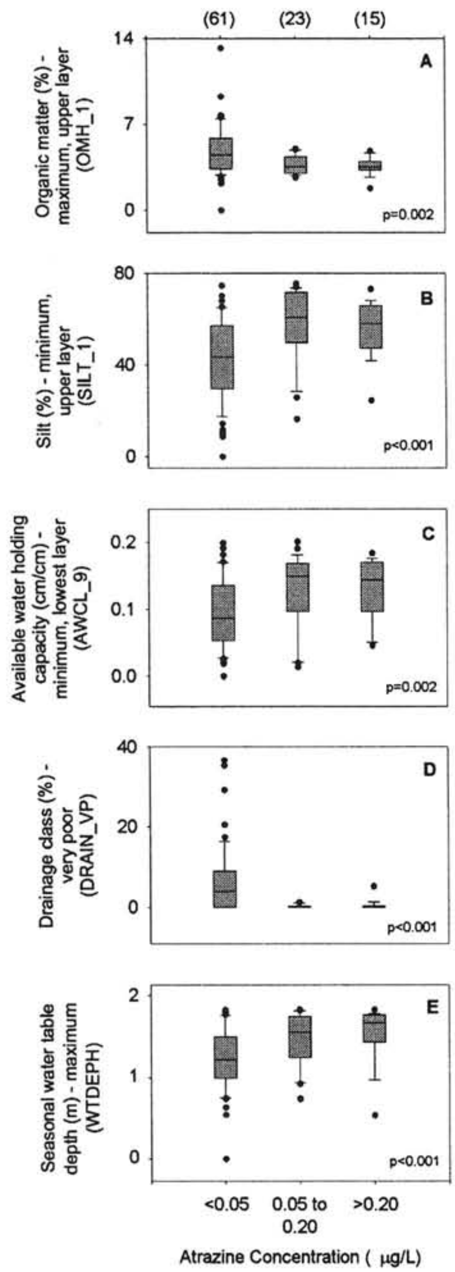

Figure 2 Soil characteristics correlated to atrazine concentrations

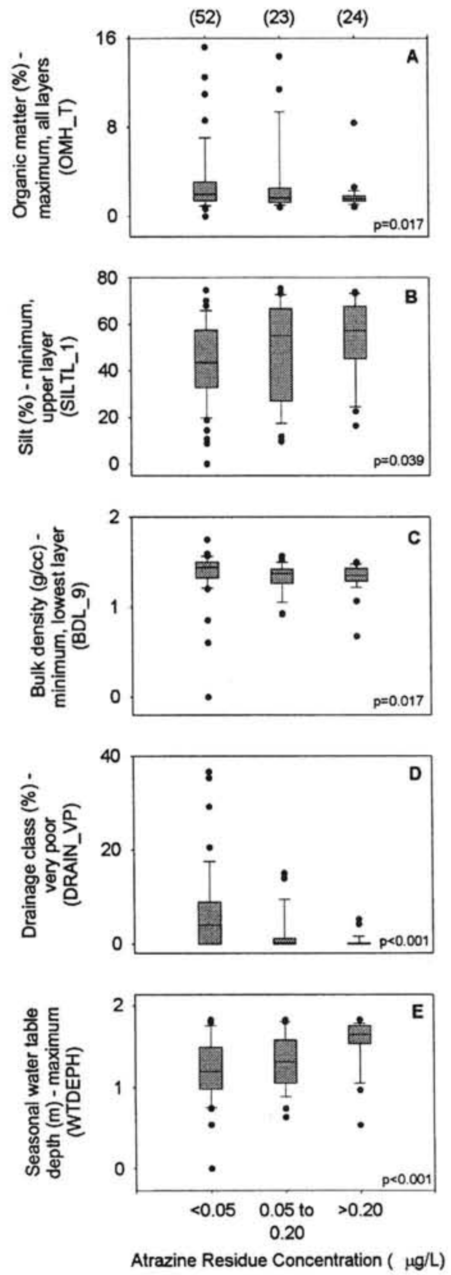

Figure 3 Soil characteristics correlated to atrazine residue concentrations

Organic matter maximum in the upper layer (OMH_1) was negatively correlated with atrazine concentration and was the most significant characteristic among the chemical variables (Table 3, Figure 2A). Higher soil organic matter content is associated with both increased atrazine degradation rates and adsorption sites (Jenks *et al.*, 1998). Interestingly, no significant relation to atrazine concentration was noted for organic matter in the lower soil layer. Thus, organic matter in lower soil layers may play less of a role in degrading and adsorbing atrazine than that of upper soil layers.

An exploratory analysis was also conducted to determine which soil characteristics were significantly related to atrazine occurrence (Table 4). With the exception of bulk density minimum in the lowest layer (BDL_9), the characteristics were identical to those related to atrazine concentration (Table 3).

The maximum amount of variance in the log-transformed atrazine concentration explained by soil characteristics was 34% for the combination DRAIN_VP + WTDEPH + SILTL_1 + AWCL_9 + OMH_1 ($R^2 = 0.34$). As with nitrate, there are other important factors that affect atrazine transport to groundwater that would help capture the remaining 66.4% of the variance in atrazine concentration unexplained by soils.

A logistic regression analysis was used to predict the presence or absence of atrazine using a concentration threshold of 0.05 μg L^{-1}. The model with the highest accuracy (correct predictions) was DRAIN_VP + WTDEPH + SILT_1 + OMH_1 at 79%.

Atrazine residue

The soil characteristics having the strongest relation to atrazine residue concentration within each variable type are shown in Table 3 and Figure 3. For landscape, texture, and water flux variable types, the most significant characteristics were identical for both atrazine and atrazine residue concentration (Table 3). However, the strength of the correlations decreased between atrazine and atrazine residue for each variable type. It was anticipated that adding the concentrations of DEA and DIA to those of atrazine would lead to increased correlations with the soil characteristics. However, the relative mobility of these three compounds differs in soils (Kruger *et al.*, 1996), which may affect the correlations with atrazine and atrazine residue.

An exploratory analysis was conducted to determine which soil characteristics were significantly related to atrazine residue occurrence (Table 4). The only major difference from atrazine-residue concentration was that no texture variables were significantly related to atrazine residue occurrence (Table 4).

The amount of variance in the log-transformed atrazine residue concentration that was explained by soil characteristics was 29% for DRAIN_VP + WTDEPH + OMA_T + BDL_9 + SILTL_1 ($R^2 = 0.29$). These results suggest that, although statistically significant, the input of other physical and texture variable types account for only about one-fourth of the variation in atrazine residue concentrations.

Logistic regression was used to predict the presence or absence of atrazine residue (using an atrazine residue threshold of 0.05 μg L^{-1}). The model with the highest accuracy (correct predictions) was DRAIN_VP + WTDEPH + BDT_T + OMH_1 at 75%.

Conclusions

Aggregated soil characteristics in areas within 2 km of 99 wells in unconsolidated aquifers across the Midwestern United States explained 19% of the variability in nitrate, 33% in atrazine, and 29% in atrazine residue concentrations. Other characteristics not included in this analysis (i.e., land use, hydrogeology, climate, and chemical use) may help account for at least part of the remaining variance (67–81%). Generally, soil characteristics that affect rates of water movement were found to have the strongest relations to concentrations of agrichemicals in groundwater. Substantial differences exist among the types of soil characteristics that significantly correlate with nitrate, atrazine, and atrazine residue. For example, organic matter is a significant factor when correlated to concentrations of atrazine and atrazine residue, but is not significantly correlated to nitrate concentrations.

The soil characteristics that are significantly related to both atrazine and atrazine residue were similar. However, the strength of the correlations was consistently lower for atrazine residue. This trend could have been caused b the summation of three compounds that have differed mobilities in soil. Thus, rather than reinforcing the relations found for atrazine, the summation reduced or confounded the relations to soil characteristics slightly.

All soil characteristics found to be significantly related to nitrate concentrations were either direct or indirect measures of water flux. Thus, rates of water movement through soil must be considered an important process in the transport of nitrate to groundwater.

A significant inverse correlation between atrazine concentration and organic matter in the upper soil layer was found suggesting that organic matter variation in lower layers may be less critical in degrading or adsorbing atrazine. In contrast, a stronger direct correlation to atrazine concentration was found for available water capacity in the deepest layer. This may be particularly important because of this layer's proximity to the deep vadose zone or underlying aquifer.

The knowledge of which soil characteristics correlate with agrichemicals can be applied to a variety of research, monitoring, and policy objectives. These may include locating critical areas for research on groundwater contamination, establishing criteria for groundwater monitoring, developing policy to manage agrichemicals, or developing land management plans. All of these applications, however, will be enhanced by including other components such as land use, climate, chemical use, and particularly hydrology in a similar analysis. An extension of the analysis presented in this paper to include these other comopnents is underway. When completed, the results should provide a more comprehensive explanation of the regional occurrence of agrichemicals in groundwater.

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