

Methodology to Evaluate the Effect of Sorption in the Unsaturated Zone on the Storage of Nitrate and Other Ions and Their Transport Across the Water Table, Southern New Jersey

By Timothy J. Reilly and Arthur L. Baehr

Toxic Substances Hydrology Program

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Conversion Factors, Datums, and Abbreviations

Multiply	By	To obtain
Length		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	25.4	inch (in.)
centimeter (cm)	0.0328	foot (ft)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
Area		
square kilometer (km ²)	247.1	acre
square kilometer (km ²)	0.3861	square mile (mi ²)
Volume		
liter (L)	33.81	ounce, fluid (fl. oz)
liter (L)	61.02	cubic inch (in ³)
Mass		
gram (g)	0.0353	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound, avoirdupois (lb)

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Altitude, as used in this report, refers to distance above the vertical datum.

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

Abbreviations:

mg/L milligrams per liter

mg/kg milligrams per kilogram

L/mg liters per milligram

L/min liters per minute

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Abstract

A new field-based approach for determining sorption in the unsaturated zone and its effect on the storage of ions and their transport in recharge to ground water has been demonstrated for a small agricultural watershed in the Coastal Plain of southern New Jersey. Moisture-content and chemical-concentration data obtained from unsaturated-zone-core and shallow-ground-water samples were used to estimate the mass flux of chemical constituents across the water table, as well as sorption coefficients (K_d). The selectivity order of the K_d values for cations is consistent with the expected selectivity order: for example, $\text{Na}^+ > \text{Mg}^{++} > \text{Ca}^{++}$ for sands. Although calculated sorption coefficients, as expected, were greater for cations than for anions, sorption had a substantial effect on the transport of anions through the unsaturated zone; in particular, average K_d values for NO_3^- were 0.22 liters per milligram for sands and 0.62 liters per milligram for finer grained sediments. The unsaturated zone in the study area is a large reservoir for nitrogen. Models that do not account for sorption are likely to result in unrealistic predictions of contaminant transport rate and provide overly optimistic expectations for natural cleansing in this watershed and those in other similar hydrogeologic settings.

Introduction

Contamination of ground water as a result of fertilizer application is a well-documented occurrence around the world (Spalding and Exner, 1993; Nolan and Stoner, 2000; Fields, 2004; Norse, 2005). This problem is of particular concern in settings like southern New Jersey, where rural homeowners derive drinking water from wells screened in the same surficial aquifers that are affected by local agriculture. The U.S. Environmental Protection Agency (USEPA) has established a maximum contaminant level for nitrate-nitrogen ($\text{NO}_3\text{-N}$) of 10 mg/L in public water systems (U.S. Environmental Protec-

tion Agency, 2001). This regulation was established primarily to prevent methemoglobinemia (“blue baby syndrome”) in infants (Craun and others, 1981). In addition, recent studies have linked $\text{NO}_3\text{-N}$ contamination with an increased incidence of bladder and ovarian cancer (Weyer and others, 2001; Ward and others, 2005). Information about the transport and storage of nitrate in the unsaturated zone is needed to evaluate its effect on ground-water quality.

Agronomists and soil scientists routinely monitor the nitrogen content of the root zone underlying farm fields so that fertilizer application practices can be managed to maintain profitability and minimize leaching to ground water. Preferential flow (Ghodrati and Jury, 1990; Kung, 1990; Flury and others, 1994; Lee and others, 2001; Öhrström and others, 2002), chemical loading (Cambardella and others, 1999; Shepard and others, 2001; Al-Jabri and others, 2002), and denitrification (Tindall and others, 1995; Jacinthe and others, 2000; Tesoriero and others, 2000; Siemens and others, 2003) have been assessed to help refine these agricultural practices. Because plant-fertility studies rather than regional water-quality issues have driven much of the soil and shallow-unsaturated-zone transport research, information about the effects of the hydraulic and geochemical properties of the lower unsaturated zone (the area between the root zone and the water table) on nutrient cycling and loading (mass flux) to ground water is limited (National Research Council, 2004). The spatial variability of these properties becomes important when the focus is on regional water quality rather than evaluation of farming practices. For example, information on the spatial variability of the mass flux of chemical constituents to the water table is needed to evaluate loading to the underlying unconfined surficial aquifer because land use, farming practices, and unsaturated-zone geology, all of which affect the amount and quality of recharge, vary within the watershed (Baehr and others, 2003).

The lower unsaturated zone, in addition to being the conduit from the root zone to the shallow aquifer system, can be an important reservoir for nitrogen and requires consideration in nutrient budgets. Klein and Bradford (1979) collected sediment samples from 13 test holes on plots in a variety of

land-use areas (agricultural, urban, vacant, and feedlot) in San Bernardino, California, to determine the amount of nitrate stored in the unsaturated zone. Although nitrate concentrations were highest at the surface at most of the sites, substantial concentrations of nitrate (approximately 2–30 mg/kg) were common at depths up to 37 m, especially at the irrigated agricultural sites. In similar studies of agricultural land in Great Britain (Foster and others, 1982), pore-water nitrate concentrations of 10 to 20 mg/L persisted to depths greater than 9 m. The storage of chloride, sulfate, and other cations in the lower unsaturated zone also was noted. In other recent studies, substantial nitrate reservoirs have been documented in the lower unsaturated zone beneath a Minnesota corn field (Delin and others, 1997), Argentine farm land (Costa and others, 2002), and North American deserts (Walvoord and others, 2003).

Sorption of nitrate and the resultant increase in ion-storage capacity in the lower unsaturated zone, although well documented, commonly is neglected in unsaturated-zone transport models. Anion sorption has been measured in tropical soils (Sollins and others, 1988) and soils in the southeastern U.S. (Eick and others, 1999) and Middle Atlantic (Toner and others, 1989). In some soils, the surface charge is permanent—that is, a net negative charge exists as a result of the structural features of the clay particles and persists irrespective of pH and aqueous-phase composition. Anion sorption in these soils—for example, 2:1-layer silicate clays (illite, vermiculite, and smectite) and 2:2-layer clays (chlorite)—would be anticipated to be minimal. In contrast, variably charged soils are characterized by a surface charge that is pH- and solution-dependent. Anion sorption in these soil types could be substantial, as a positive charge can result from protonation and deprotonation of surface hydroxyl groups that occur at the edges of 1:1-layer silicate clays (kaolinite), on less-ordered aluminosilicates, on crystalline hydroxides and oxides of Al (gibbsite) and Fe (goethite, hematite), and on organic matter (Sollins and others, 1988). Sorption of anions can result from association with the cations in a secondary layer or an outersphere complex (Sparks, 2003). Other studies in which anion sorption has been documented include Sing and Kanehiro (1969), Kinjo and Pratt (1971), Hingston and others (1972), and Espinoza and others (1975).

To address these issues, the U.S. Geological Survey (USGS), as part of its Toxic Substances Hydrology Program, initiated a study to investigate the effect of sorption in the lower unsaturated zone on the storage of chemical constituents, particularly nitrate, and their transport across the water table.

Purpose and Scope

This report describes a field-based methodology developed to evaluate the flux of nitrate and other ions across the water table in a small agricultural watershed in the New Jersey Coastal Plain. This methodology is unique in that ion-concentration data from the shallow ground water are coupled with

ion-concentration data from the lower unsaturated zone to estimate the flux and partitioning of chemicals simultaneously. Recharge, as well as chemical storage and sorption within the lower unsaturated zone, is quantified. Storage, sorption, and mass flux are documented to assess the physical/chemical assimilative capacity of the entire unsaturated zone and the effect of sediment variability on the distribution of nitrate loading to the underlying aquifer.

Description of Study Area

The study was conducted primarily within a 8-km² agricultural watershed overlying the unconfined Kirkwood-Cohansey aquifer system in Upper Deerfield Township, New Jersey (fig. 1). Nitrate contamination of shallow ground water in the agricultural region that encompasses this watershed is a serious problem (Ayers and others, 2000). As part of the USGS's National Water-Quality Assessment (NAWQA) program, shallow monitoring wells installed in the region were sampled from 1996 to 1998. The median concentration of nitrate was 13 mg/L, which exceeds the USEPA maximum contaminant level of 10 mg/L (Stackelberg and others, 1997; Ayers and others, 2000). In addition to the samples collected at the Upper Deerfield Township sites, samples were collected at three sites in undeveloped areas within the New Jersey Pinelands, a portion of the 4,450-km² Pinelands National Reserve, a protected area in southern New Jersey (New Jersey Pinelands Commission, 2004). The Pinelands sites were selected to provide background concentrations of the constituents studied (fig. 1).

Most of the sediments that comprise the unsaturated zone and the unconfined Kirkwood-Cohansey aquifer system in the study area are made up of the Bridgeton Formation. This formation is characterized by coarse, pebbly, orange sands deposited under continental conditions during the late Tertiary and Quaternary Periods (Zapeczka, 1989). Distinctive strata local to this study area have been documented by Baehr and others (2003).

Methods of Sample Collection and Analysis

Unsaturated-zone sediment samples were collected at 14 sites in the study area using a Geoprobe direct push system. Sites were selected to provide areal coverage of the study area. Cores were obtained by driving a core barrel through sediment with a high-frequency (30 Hertz) pneumatic hammer. The cores were contained in 3.8-cm-diameter by 120-cm-long acrylic core liners. After the altitude of the water table was determined with a steel measuring tape, a 120-cm-long Geoprobe retractable stainless-steel 10-slot well screen (Geoprobe model SP-15) was driven to the water table to create a temporary well at each site. Temporary wells were installed at the

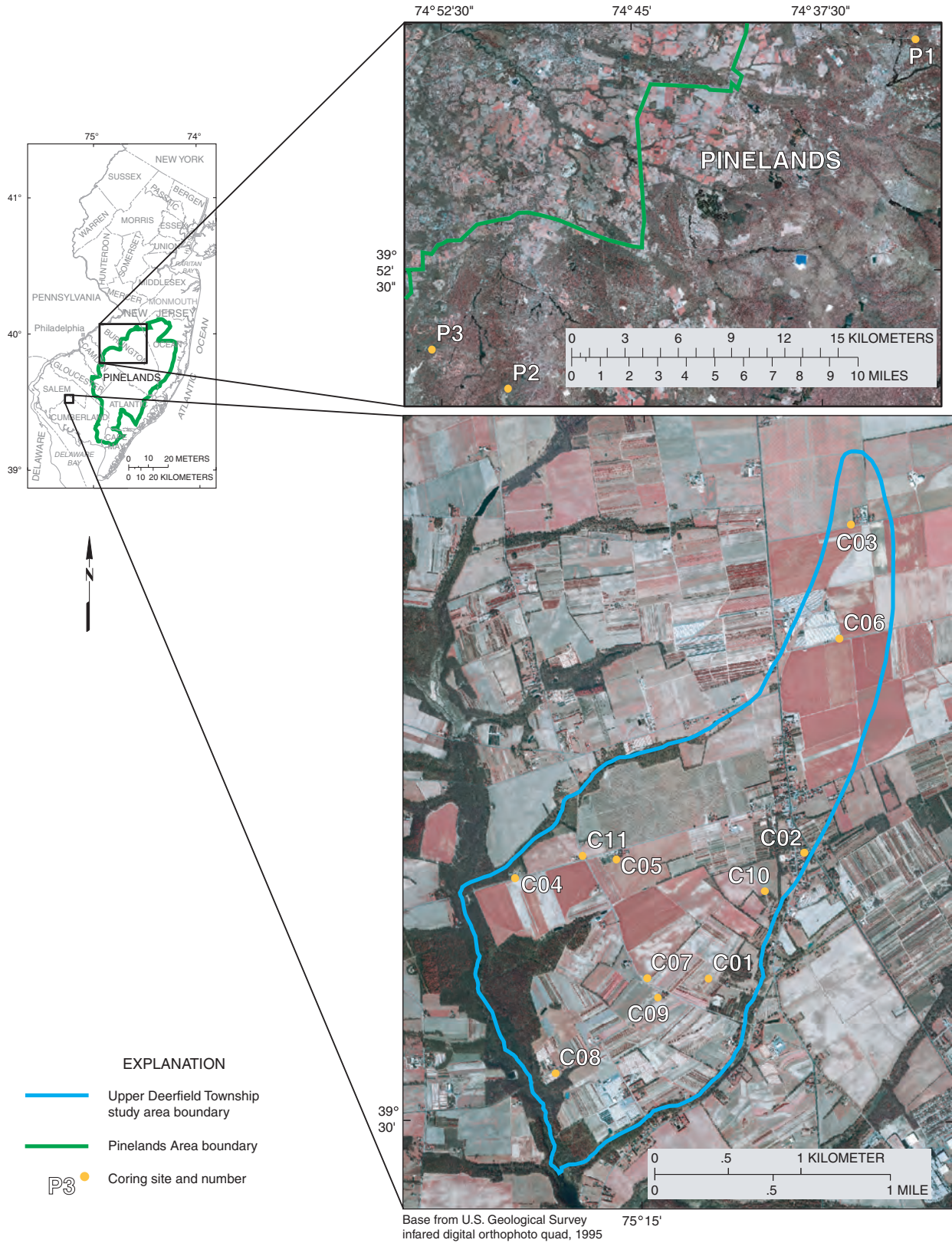


Figure 1. Location of study area, Pinelands, and coring sites, southern New Jersey.

shallowest possible depth to allow sampling at the water table. The median depth below the water table of the top of the well screen was 0.305 m and the median screen length was 0.76 m. At each site, one ground-water sample was collected by inserting a 0.64-cm-diameter PVC tube through the annular space of the driving rods to the bottom of the screen. The temporary well was developed and sampled at 1 L/min using a peristaltic pump. Development criteria included purging fine particles from the screen and pumping until temperature, specific conductance, and pH readings stabilized. Ground-water samples were analyzed at the USGS National Water Quality Laboratory (NWQL) in Denver, Colorado.

Moisture content was determined gravimetrically on four or five 30-g sediment samples collected approximately every 60 cm along the length of each core. Soil horizons and stratigraphy were determined by visual inspection. Samples were collected from selected layers (the upper soil zone and the lowermost part of the unsaturated zone at a minimum) for particle-size measurement and chemical analysis. Particle-size distribution was determined by optical diffraction using a Coulter LS-230 particle-size analyzer. These data are summarized in appendix 1A (at the end of the report).

Sediment samples were analyzed at the Rutgers University Soil Testing Laboratory in New Brunswick, New Jersey (Rutgers STL), to determine the concentrations of compounds in the unsaturated zone. Sediments were dried as part of all procedures. Therefore, the constituent concentrations reported (app. 1A) are total concentrations (aqueous and extractable-adsorbed mass partitions). Nitrate (NO_3 as N), ammonium (NH_4^+), organic nitrogen plus ammonium (TKN), calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^+), and potassium (K^+) extractions were analyzed using a Technicon AutoAnalyzer II continuous flow analysis system (Mann, 1963; Markus and others, 1985; Mulvaney, 1996; Sumner and Miller, 1996). Organic-matter concentrations were determined using a modified Mebius procedure (Nelson and Sommers, 1982).

Split samples were analyzed at a USGS research laboratory in Lakewood, Colorado, to determine concentrations of NO_3 as N, sulfate (SO_4^{--}), and chloride (Cl^-) using ion-chromatography techniques (Richard Healy, U.S. Geological Survey, written commun., 2004; McMahan and others, 2003). Nitrate concentrations, therefore, were determined by two methods. At the Rutgers STL, a 0.5-M (molar) sodium chloride (NaCl) solution was used to extract NO_3 as N (as well as NH_4^+) from sediment—a standard procedure commonly used by soil scientists (Mulvaney, 1996). At the USGS research laboratory, deionized water was used for extraction of NO_3 as N, SO_4^{--} , and Cl^- (McMahan and others, 2003) because the high ion concentrations that would result from using the 0.5-M NaCl solution would interfere with subsequent chromatographic analyses.

For samples in which both laboratories detected nitrate, the method employed by the Rutgers STL removed, on average, approximately four times more nitrate than the method used by the USGS research laboratory (app. 1, figure 1-1). This discrepancy results from the lower extraction efficiency

of deionized water compared to the 0.5-M NaCl solution. The nitrate content not extractable with deionized water may be bound in clays (Herbel and Spalding, 1993) or sorbed strongly on sediment with a large anion-exchange capacity (Bremner, 1965). The nitrate concentrations reported by the USGS laboratory are presented here to demonstrate that the use of different solvents for nitrate extraction have differing efficiencies and can produce substantially different results; however, because the focus of this study is the total nitrate stored in the unsaturated zone, only data from the Rutgers STL are analyzed in the subsequent discussion. Only data from the USGS research laboratory are available for SO_4^{--} and Cl^- ; therefore, sediment concentrations reported for SO_4^{--} and Cl^- likely underestimate actual concentrations, and reported K_d estimates for these constituents likely are lower than actual values.

Effect of Sorption on Transport and Storage

The effects of sorption on storage in the lower unsaturated zone and transport across the water table are evaluated to assess the physical/chemical assimilative capacity of the entire unsaturated zone and to determine the effect of sediment variability on the movement of selected constituents to the underlying aquifer. Background concentrations of selected constituents in precipitation and in an undeveloped area are documented to evaluate atmospheric loading to the unsaturated zone.

Calculation of Mass Fluxes and Sorption Coefficients

Chemical concentrations determined from analysis of sediment samples are combined with calculated flow rates to determine mass fluxes to the underlying unconfined Kirkwood-Cohansey aquifer system. Unsaturated-zone sorption coefficients are calculated based on differences in chemical concentrations between the lower unsaturated-zone sediments and samples of the shallow ground water beneath them.

Mass Flux of Chemicals Across the Water Table

Estimates of the mass flux of chemicals across the water table are summarized in table 1. The flux estimates were calculated by using the following equation:

$$J = qC \quad (1)$$

where J is the mass flux ($\text{mg}/\text{cm}^2/\text{yr}$), q is the recharge rate (cm/yr), and C is the concentration (mg/cm^3) in the aqueous phase. Because ground-water samples were collected at the water table, values of C are the ground-water concentrations reported in appendix 1. This method of approximating

the concentrations of chemical constituents in recharge is conservative because chemical transformations near the water table are assumed to be negligible.

Data on sediment texture and water content in the lowermost portion of the unsaturated zone were used in conjunction with Darcy's Law to approximate q . Darcy's Law for unsaturated flow is

$$q = -K \left[1 - \frac{d\Psi}{dz} \right], \quad (2)$$

where K is conductivity (cm/d), Ψ is the matric potential (cm), and z is the vertical coordinate (cm and positive upward). The functions K and Ψ were estimated using the particle-size and moisture-content data with the pedotransfer functions of the ROSETTA model version 1.0 (U.S. Department of Agriculture, 2004). Moisture content was measured throughout the unsaturated zone approximately every 60 cm. This spacing was determined to be too large to determine the matric potential gradient; therefore, the unit gradient approximation

$$q = -K \quad (3)$$

was employed. ROSETTA employs the van Genuchten-Mualem model (van Genuchten, 1980) to calculate K . The average moisture content of the lowermost layer of the unsatu-

rated zone at each site (app. 2) was used to define the required moisture content. Portions of the lowermost layers subject to increased moisture content as a result of capillary rise were neglected in the calculation. The recharge calculations and site information are summarized in appendix 2. The median value of K calculated for the 11 sites in Upper Deerfield is 48.7 cm/yr (range, 9.1-314.4 cm/yr; standard deviation, 110.4 cm/yr). In water-budget studies previously conducted in southern New Jersey, annual recharge ranges from 33.1 to 49.3 cm/yr (Baehr and others, 2003). Although the unit gradient recharge values determined during this study vary substantially, the median value is within the range of recharge values calculated in earlier studies as part of annual water budgets for the area and, therefore, is assumed to provide a realistic range of the spatial variability of recharge in Upper Deerfield.

Unsaturated-Zone Sorption Coefficients

Mass partitioning between aqueous and adsorbed phases in the lower layer of the unsaturated zone defines the mass of chemical available to enter the aquifer with recharge water. The sorption coefficient K_d (L/mg) is defined as follows:

$$S = K_d C, \quad (4)$$

where S (mg/kg of dry sediment) is the concentration of the compound adsorbed onto solid surfaces and C (mg/L)

Table 1. Mass flux of selected ions across the water table at 11 agricultural and 3 undeveloped sites in southern New Jersey, 2003-04.

[Mass flux (J) = qC ; q , recharge rate; C , concentration; TKN, total Kjeldahl nitrogen; <, less than; --, not calculated. Values of C are from appendix 1; values of q are from appendix 2; cm/yr, centimeters per year; (g/m²)/yr, grams per square meter per year]

Site identifier and land use	q (cm/yr)	Mass flux ((g/m ²)/yr)							
		NO ₃ ⁻ as N	NH ₄ ⁺ as N	TKN	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	SO ₄ ⁻	Cl ⁻
C01 - nursery	86.6	10.3	< 0.1	0.1	20.7	16.4	4.4	43.8	28.8
C02 - former orchard	314.4	10.6	1.5	2.2	53.1	9.0	9.1	124.9	14.0
C03 - corn field	251.9	46.4	< 0.1	0.3	98.5	32.0	6.4	103.0	71.6
C04 - open field	19.3	< 0.1	< 0.1	< 0.1	0.6	0.9	6.2	2.8	11.0
C05 - sod farm	9.1	0.7	< 0.1	< 0.1	1.8	0.7	0.3	4.7	0.9
C06 - sod farm	38.7	6.5	< 0.1	< 0.1	13.7	8.4	1.6	24.6	13.0
C07 - sod farm	217.4	60.3	< 0.1	0.3	76.9	35.9	8.2	52.2	63.3
C08 - residential	48.7	3.1	< 0.1	0.1	5.4	1.4	3.1	7.9	6.7
C09- open field	166.5	29.0	< 0.1	0.1	39.3	20.1	56.0	49.6	102.1
C10- open field	23.0	1.8	< 0.1	--	5.1	1.6	0.9	10.0	2.9
C11- corn field	10.1	0.5	< 0.1	--	2.5	1.7	5.4	1.5	16.6
Median		8.4	< 0.1	0.2	13.7	8.4	5.4	24.6	14.0
P1 - Undeveloped		< 0.1	< 0.1	--	--	--	--	--	--
P2 - Undeveloped		< 0.1	< 0.1	--	--	--	--	--	--
P3 - Undeveloped		< 0.1	< 0.1	--	--	--	--	--	--

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is the concentration of the compound in the aqueous phase within the unsaturated zone. The unsaturated-zone chemical concentrations reported in appendix 1 are the total of adsorbed plus aqueous phase partitions:

$$T = S + w_{ave} C, \tag{5}$$

where T is the total concentration (mg/kg of dry sediment) and w_{ave} is the average moisture fraction (L of water/kg of dry sediment) of the lowermost layer. Equations (4) and (5) yield the following formula for calculating K_d from field data:

$$K_d = \frac{T}{C} - w_{ave} \tag{6}$$

As was the case for the computation of mass flux with equation (1), the shallow-ground-water chemical concentrations reported in appendix 1 were used to determine C in equation (6). The K_d values calculated for each site are summarized

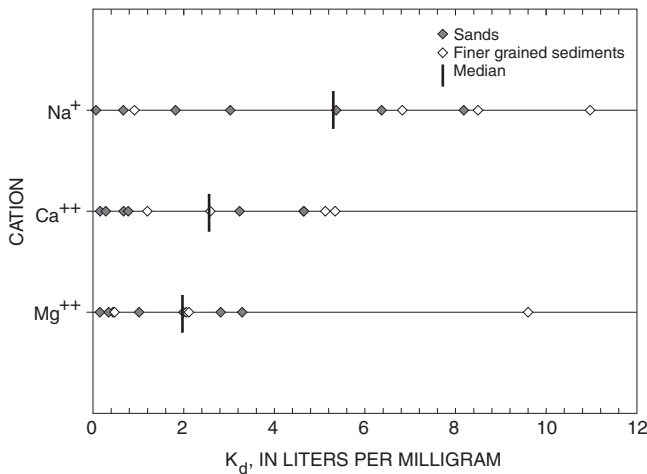


Figure 2a. Sorption coefficients (K_d) for cations in sands and in finer grained sediments, Upper Deerfield Township, New Jersey.

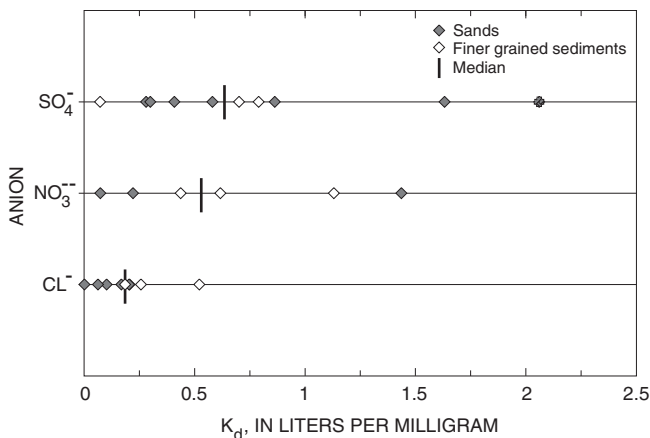


Figure 2b. Sorption coefficients (K_d) for anions in sands and in finer grained sediments, Upper Deerfield Township, New Jersey.

in appendix 3 and are depicted graphically in figures 2a and 2b.

Variability in K_d values for a given ion is expected as a result of differences in sediment properties including texture, pH, and surface chemical properties. Variability is also expected because compound mixtures vary from site to site and because compounds compete for sorption sites as they migrate to the lower unsaturated zone. The lower unsaturated zone contains little organic matter (app. 1); therefore, organic-matter content does not contribute to sorption variability. Measurement errors result in a random component of variability, especially when the collection of field data is involved.

The K_d values were calculated using field data and an operational definition of sorption—that is, the adsorbed mass is the portion of total mass that is not associated with water moving across the water table. The calculated K_d values are consistent with the properties of the adsorbed ions and variations in sediment texture. The median K_d values for cations are approximately an order of magnitude greater than those for anions (figs. 3a and 3b). This result is expected because the

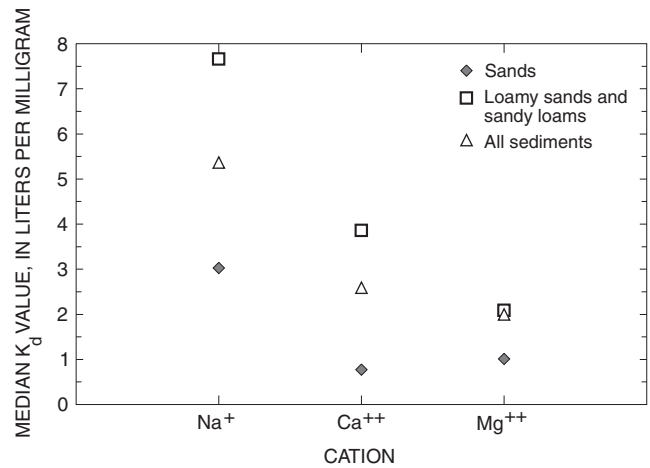


Figure 3a. Median values of sorption coefficient (K_d) for cations in sands, loamy sands and sandy loams, and all sediments, Upper Deerfield Township, New Jersey.

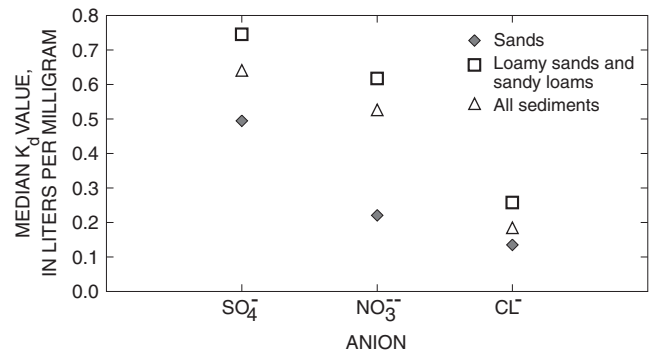


Figure 3b. Median values of sorption coefficient (K_d) for anions in sands, loamy sands and sandy loams, and all sediments, Upper Deerfield Township, New Jersey.

sediment surfaces are expected to have a net negative charge. Median K_d values for the finer grained sediments encountered in the lower unsaturated zone (three loamy sands and a sandy loam) are greater than the medians for the sediments at the seven sites where the lower unsaturated zone consisted of sand (figs. 3a and 3b). This result is expected because the surface area is greater for finer sediments than for sands.

The cation sorption selectivity order, based on median K_d values, is $\text{Na}^+ > \text{Mg}^{++} > \text{Ca}^{++}$ for sands and $\text{Na}^+ > \text{Ca}^{++} > \text{Mg}^{++}$ for finer grained sediments. The observed order for anions is $\text{SO}_4^- > \text{NO}_3^- > \text{Cl}^-$; however, as discussed above, the K_d values for SO_4^- and Cl^- likely are underestimated. The order for cations is consistent with the expected negative correlation between K_d and charge density (valence divided by ionic radius) (fig. 4). Cations with a smaller charge density create a smaller electrical field and are less likely to remain solvated given the competition for complexation by a surface functional group (Sparks, 2003). The change in order of Ca^{++} and Mg^{++} between sediment types is not contradictory because the charge densities for these divalent cations are similar. K_d values were not calculated for K^+ because its concentrations in shallow ground water were not determined. K_d values also were not calculated for NH_4^+ because its concentrations in shallow ground water were below detection limits.

Background Concentrations

Representative concentrations of ions in precipitation for 2000-03 are presented in table 2 with associated concentrations in unsaturated-zone sediments calculated according to equation (5). Concentrations of ions in precipitation are measured throughout the United States as part of the National Atmospheric Deposition Program (NADP) (<http://nadp.sws.uiuc.edu/>). The calculations show that precipitation is a negligible source of Ca^{++} , Mg^{++} , K^+ , NO_3^- , and Cl^- in unsaturated-zone sediments. Precipitation probably contributes a measurable concentration (on the order of 1-3 mg/kg) of Na^+ , NH_4^+ , and SO_4^- , but this input is small compared to most of the concentrations measured in Upper Deerfield Township (app. 1).

The sediment texture, moisture, and chemistry data and shallow-water-quality data collected at the three sites in the New Jersey Pinelands allow for evaluation of the combined effect of background sources. Land at these sites is historically undeveloped; therefore, measured concentrations of ions in the lower unsaturated zone are limited to contributions from the atmosphere, weathering, microbial respiration, and vegetation. At these sites (P1, P2, and P3 in appendix 1), concentrations of NO_3^- , Ca^{++} , Mg^{++} , and Cl^- in unsaturated-zone sediments were less than 1 mg/kg, indicating that background sources of these ions do not contribute substantially to the concentrations measured in Upper Deerfield Township. Concentrations of NH_4^+ , Na^+ , K^+ , and SO_4^- at sites P1, P2, and P3 were greater than those that can be attributed to precipitation, but less than those measured in Upper Deerfield Township and associ-

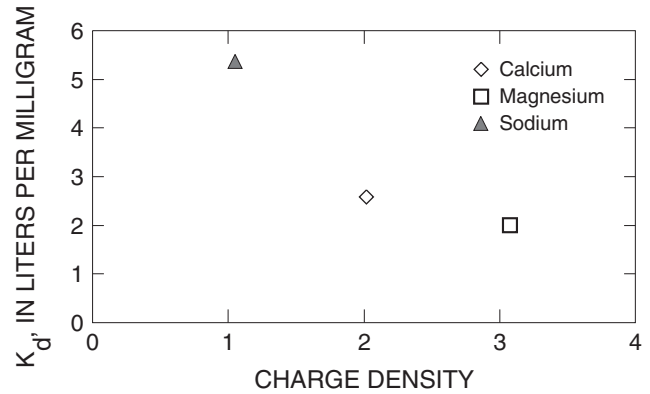


Figure 4. Sorption coefficient (K_d) as a function of charge density for cations, Upper Deerfield Township, New Jersey.

Table 2. Concentrations of selected ions in precipitation and their predicted contribution to the concentrations of selected ions in the lower unsaturated zone, southern New Jersey, 2000-03.

[mg/L, milligrams per liter; mg/kg, milligrams per kilogram; L/mg, liters per milligram; T, total concentration; K_d , sorption coefficient; W_{ave} , average moisture fraction; <, less than]

Ion	C_{precip}^1 (mg/L)	T_{precip}^2 for sands (mg/kg)	T_{precip}^2 for other sediment types (mg/kg)
Ca^{++}	<0.1	0.1	0.4
Mg^{++}	0.05	0.1	0.1
Na^+	0.4	1.2	3.1
K^+	0.04	0.2 ³	0.2 ³
NH_4^+ as N	0.2	1.1 ³	1.1 ³
NO_3^- as N	0.3	0.1	0.2
SO_4^-	1.6	0.9	1.4
Cl^-	0.5	0.1	0.2

¹ C_{precip} = concentration in precipitation; values from <http://nadp.sws.uiuc.edu/isopleths/annualmaps.asp>, accessed 1/25/2006

² $T_{precip} = (K_d + w_{ave})C_{precip}$; average K_d values from appendix 3; $w_{ave} = 0.06$ for sands and 0.10 for sandy loams and loamy sand (see appendix 1A).

³ No field K_d values calculated for K^+ and NH_4^+ ; these estimates are based on an assumed $K_d = 5.5$ L/mg.

ated with agricultural land use. The concentrations of these ions are assumed to be representative of in situ background processes unrelated to local inputs at all of the study sites. The near-ubiquitous occurrence of NO_3^- , Ca^{++} , Mg^{++} , and Cl^- in the unsaturated zone and shallow ground water in the study area is attributed to agricultural land use. Background concentrations of SO_4^- and Na^+ also were small compared to the concentrations observed in Upper Deerfield.

Effect of Sorption on Transport of Chemicals across the Water Table

In the absence of information pertaining to sorption (particularly for NO_3^- and other anions), a conservative assumption would be that all chemical mass in the lower unsaturated zone is partitioned entirely in the aqueous phase, and therefore is available to recharge. The following ratio (γ) can be used to estimate the extent to which this assumption would cause contaminant loading to the underlying aquifer to be overestimated:

$$\gamma = \frac{T/w_{ave}}{C} = \frac{K_d + w_{ave}}{w_{ave}} \quad (7)$$

The value is the hypothetical unsaturated-zone aqueous concentration under the assumption that all mass resides in the aqueous phase. This value is divided by C , the actual unsaturated-zone aqueous concentration, to obtain γ . Values of γ calculated (where possible) for the lowermost layer of the unsaturated zone in Upper Deerfield Township are listed in table 3.

Neglecting sorption would result in a gross overestimation of the rate of mass transfer to the water table. For

example, the median γ for NO_3^- is 6.8, so the mass-transfer rate would be overestimated by a factor of 6.8. Residence-time calculations likewise would be affected, resulting in an under-prediction of the time required for natural cleansing if the land were to be reclaimed. Geochemical transport models that did not account for the sorption of NO_3^- to the sediments would be highly inaccurate. Because γ varies spatially with differences in sediment properties and the mixture of compounds that have migrated to the lower unsaturated zone, transport models would yield inaccurate predictions of compound loading at individual sites without specific information on sediment properties.

In a previous study, a mathematical model of the local ground-water flow system was used to evaluate the effects of various nitrate-management options on the concentration of NO_3^- in streams and water-supply wells in the New Jersey Coastal Plain (Kauffman and others, 2001). NO_3^- concentrations were simulated under the assumption of an immediate ban on nitrate input and the conservative assumption that all nitrate resides in the aqueous phase. Even under this most optimistic assumption, NO_3^- concentrations were predicted to remain elevated above background concentrations in streams and wells for decades as a result of the time required for ground water to flow through the aquifer.

Table 3. Ratio (γ) of the hypothetical aqueous concentration of selected ions in the unsaturated zone under the assumption that all mass on the sediment resides in the aqueous phase to the actual unsaturated-zone aqueous concentration, Upper Deerfield Township, New Jersey, 2003-04.

[--, the ratio cannot be calculated because the ion was not detected in the aqueous phase; *, the ratio cannot be calculated because the ion was not detected in the lower unsaturated zone; #, the ratio is not reported because the ion concentration in ground water was very large]

Site identifier and land use	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	Cl ⁻	NO ₃ ⁻ as N	SO ₄ ⁻⁻
C01 - nursery	66.6	9.9	109.9	5.2	2.5	--
C02 - former orchard	60.5	37.1	105.7	3.6	19.4	6.2
C03 - corn	11.9	6.5	104.8	2.7	4.6	5.6
C04 - open field	114.9	81.6	17.3	2.5	--	40.9
C05 - sod farm	43.4	80.5	57.5	3.1	10.4	1.6
C06 - sod farm	13.9	3.4	51.3	3.8	*	6.0
C07 - sod farm	17.8	7.6	154.4	3.6	*	12.0
C08 - residential	3.7	36.8	33.6	*	*	16.5
C09- open field	5.5	17.6	2.0	1.0	*	10.5
C10- open field	46.8	37.4	151.2	10.2	8.7	13.4
C11- corn	35.4	14.6	6.9	#	5.0	14.3
Median	35.4	17.6	57.5	3.6	6.8	11.3

$$\gamma = \frac{T/w_{ave}}{C} = \frac{K_d + w_{ave}}{w_{ave}}$$

T = total concentration (mg/kg of dry sediment)

w_{ave} = moisture fraction (L of water/kg of dry sediment)

C = concentration in the aqueous phase (mg/L)

K_d = sorption coefficient (L/mg).

Effect of Sorption on Unsaturated-Zone Storage

Sorption affects the storage capacity and residence time of each compound in the unsaturated zone. The mass of a compound stored within an interval of the unsaturated zone is obtained as follows:

$$M_{[z_1, z_2]} = \int_{z_1}^{z_2} T \rho_b dz \quad (8)$$

where M (g/m^2) is the mass of the compound stored per unit area over the depth interval $[z_1, z_2]$, T is the total concentration of the compound sorbed to the sediment (g/kg), and ρ_b is the dry bulk density of the sediment (kg/m^3). The value

$$\bar{M}_{[z_1, z_2]} = \frac{M_{[z_1, z_2]}}{z_2 - z_1} \quad (9)$$

is the average total concentration of the compound (g/m^3) for the interval $[z_1, z_2]$ (table 4). The intervals defined were the soil and the lower unsaturated zone—that is, the unsaturated zone beneath the soil. Concentrations representative of the soil layer were obtained at each site. For the lower unsaturated-zone integration, if concentration data were not available for a distinguishable layer, then the concentration in an adjacent layer was assumed. These calculations for the lower unsaturated zone are limited in accuracy because the data collected were insufficient to develop functional descriptions of variations in concentration with depth; however, they provide a scale for estimates of storage and residence time and a basis for comparing the difference in sorption between compounds.

On the basis of median values (table 4), concentrations of NO_3^- , NH_4^+ , SO_4^{2-} , and Na^+ in the soil layer and the lower unsaturated zone are similar in magnitude. Therefore, storage of these chemicals can be assumed, on average, to be approximately uniform throughout the unsaturated zone in Upper Deerfield. For the cations Ca^{++} , Mg^{++} , and K^+ , concentrations in the lower unsaturated zone are, on average, 12 to 20 percent of those in soils. The results for Cl^- may be anomalous, as concentrations in the lower unsaturated zone are higher, on average, than those in soils.

Although NH_4^+ is present throughout the unsaturated zone (table 4), the recharge flux of NH_4^+ is immeasurably low at all sites (table 1). It is presumed that NH_4^+ has a high sorption coefficient as it is a monovalent cation, which renders NH_4^+ effectively immobile through the lower unsaturated zone. Therefore, NH_4^+ is presumed to reside in the lower unsaturated zone because nitrogen was transported in a mobile form and subsequently converted to NH_4^+ . For example, a soluble fraction of organic nitrogen (TKN) may travel through the unsaturated zone and be subject to mineralization reactions at depth, resulting in the observed accumulation of NH_4^+ .

Summary and Conclusions

Contamination of ground water as a result of fertilizer application is of particular concern in settings like southern New Jersey, where rural homeowners derive drinking water from wells screened in the same surficial aquifers that are affected by local agriculture. Information about the storage of nitrate in the unsaturated zone and its transport across the water table is needed to evaluate its effect on ground-water quality. Because plant-fertility studies rather than regional water-quality issues have driven much of the soil and shallow-unsaturated-zone transport research, information is limited about the effects of the hydraulic and geochemical properties of the lower unsaturated zone (the area between the root zone and the water table) on nutrient cycling and loading (mass flux) to ground water. To address these issues, the U.S. Geological Survey (USGS), as part of its Toxic Substances Hydrology Program, initiated a study to investigate the role of sorption in the storage of chemical constituents, particularly nitrate, in the lower unsaturated zone and their transport across the water table to the unconfined Kirkwood-Cohansey aquifer system.

The effects of sorption on storage in the lower unsaturated zone and transport across the water table were evaluated to assess the physical/chemical assimilative capacity of the entire unsaturated zone and the effect of sediment variability on the movement of selected chemicals to the underlying aquifer. Background concentrations of selected chemicals in precipitation and in an undeveloped area were documented to evaluate atmospheric loading to the unsaturated zone. Chemical concentrations determined from analysis of sediment samples were combined with calculated flow rates to determine mass fluxes to the aquifer system. Unsaturated-zone sorption coefficients were calculated based on differences in chemical concentrations between the lower-unsaturated-zone sediments and samples of the shallow ground water beneath them. Mass partitioning between aqueous and adsorbed phases in the lower layer of the unsaturated zone defines the mass of chemical available to enter the aquifer with recharge water.

In this study, anion sorption accounted for a much greater storage capacity for NO_3^- , SO_4^{2-} , and Cl^- in the unsaturated zone than would be calculated if mass were assumed to reside only in the aqueous phase. The increased residence times indicated as a result of this study imply that natural cleansing of the unconfined Kirkwood-Cohansey aquifer system is likely to take much longer than previously predicted. Similar results are likely in comparable hydrogeologic settings throughout the Atlantic Coastal Plain. Additional investigations of the occurrence and phase-partitioning of compounds relevant to the nitrogen cycle in the lower unsaturated zone and shallow ground water and of the storage properties of the unsaturated zone—particularly the anion-exchange capacity and kinetics of nitrate remobilization—would permit a more thorough evaluation of the long-term effects of agricultural land use on ground-water quality.

Table 4. Storage of selected ions in soil and the lower unsaturated zone, Upper Deerfield Township, New Jersey, 2003-04.[m, meter; g/m², grams per square meter; mg/m³, milligrams per cubic meter; --, not measured; I.unsat, lower unsaturated]

Site identifier and land use	Depth interval, soil (m)	Depth interval, unsaturated zone (m)	Depth interval, lower unsaturated									
			M _{(soil)¹} (g/m ²)	M _(Lunsat) (g/m ²)	M _{(soil)²} (mg/m ²)	M _(Lunsat) (mg/m ²)	M _{(Lunsat)/M_(soil)}	M _{(soil)¹} (g/m ²)	M _(Lunsat) (g/m ²)	M _{(soil)²} (mg/m ²)	M _(Lunsat) (mg/m ²)	M _{(Lunsat)/M_(soil)}
Ca ⁺⁺												
C01 - nursery	0.0-0.49	0.49-9.80	328.2	1240.0	673.0	133.2	0.20	76.3	171.1	156.6	18.4	0.12
C02 - former orchard	0.0-0.40	0.40-3.08	271.4	352.2	684.9	131.3	0.19	97.411	73.880	245.8	27.5	0.11
C03 - corn field	0.0-0.49	0.49-10.09	645.7	1260.9	1324.0	131.3	0.01	239.221	283.549	490.5	29.5	0.06
C04 - open field	0.0-0.50	0.50-2.59	27.9	54.3	55.4	26.0	0.47	29.335	27.845	58.3	13.3	0.23
C05 - sod farm	0.0-0.53	0.53-5.32	964.9	2077.0	1809.0	434.3	0.24	243.700	1249.648	456.9	261.3	0.57
C06 - sod farm	0.0-0.49	0.49-7.68	318.7	1333.2	653.4	185.3	0.28	105.991	237.544	217.3	33.0	0.15
C07 - sod farm	0.0-0.49	0.49-6.13	576.3	614.4	1181.7	109.0	0.09	167.181	175.761	342.8	31.2	0.09
C08 - residential	0.0-0.47	0.47-4.93	11.3	16.8	23.9	3.8	0.16	34.186	132.771	72.4	29.8	0.41
C09 - open field	0.0-0.50	0.50-7.30	467.9	208.7	930.5	30.7	0.03	137.999	155.198	274.4	22.8	0.08
C10 - open field	0.0-0.49	0.49-7.01	74.6	559.0	153.1	85.7	0.56	23.989	105.331	49.2	16.1	0.33
C11 - corn field	0.0-0.43	0.43-5.68	280.1	1102.9	656.5	209.8	0.32	119.931	204.910	281.052	39.0	0.14
Median			318.7	614.4	673.0	131.3	0.20	106.0	171.1	245.8	29.5	0.12
Mg ⁺⁺												
C01 - nursery	0.0-0.49	0.49-9.80	68.7	295.2	140.9	31.7	0.23	27.1	439.3	55.5	47.2	0.85
C02 - former orchard	0.0-0.40	0.40-3.08	42.5	38.5	107.3	14.3	0.13	42.120	98.536	106.3	36.7	0.35
C03 - corn field	0.0-0.49	0.49-10.09	127.5	393.5	261.5	41.0	0.16	35.657	320.105	73.1	33.3	0.46
C04 - open field	0.0-0.50	0.50-2.59	33.0	54.0	65.5	25.9	0.39	31.442	79.465	62.5	38.1	0.61
C05 - sod farm	0.0-0.53	0.53-5.32	182.8	926.8	342.7	193.8	0.57	18.247	123.898	34.2	25.9	0.76
C06 - sod farm	0.0-0.49	0.49-7.68	100.0	645.2	205.0	89.7	0.44	34.440	294.187	70.6	40.9	0.58
C07 - sod farm	0.0-0.49	0.49-6.13	135.7	169.3	278.3	30.0	0.11	15.437	303.689	31.7	53.9	1.70
C08 - residential	0.0-0.47	0.47-4.93	12.5	44.6	26.4	10.0	0.38	9.963	120.236	21.1	27.0	1.28
C09 - open field	0.0-0.50	0.50-7.30	152.1	178.3	302.5	26.2	0.09	14.208	126.599	28.3	18.6	0.66
C10 - open field	0.0-0.49	0.49-7.01	15.1	127.2	30.9	19.5	0.63	9.957	315.012	20.417	48.295	2.37
C11 - corn field	0.0-0.43	0.43-5.68	89.4	397.3	209.4	75.6	0.36	12.682	636.846	29.720	121.124	4.08
Median			89.4	178.3	205.0	30.0	0.15	18.2	294.2	34.2	38.1	1.11

Table 4. Storage of selected ions in soil and the lower unsaturated zone, Upper Deerfield Township, New Jersey, 2003-04—Continued.

[m, meter; g/m², grams per square meter; mg/m³, milligrams per cubic meter; --, not measured; I.unsat, lower unsaturated]

Site identifier and land use	Depth interval, soil (m)	Depth interval, unsaturated zone (m)	Depth interval, lower unsaturated zone (m)									
			M _{(soil)¹} (g/m ²)	M _(L.unsat) (g/m ²)	M _{(soil)²} (mg/m ²)	M _(L.unsat) (mg/m ²)	M _{(L.unsat)/M_(soil)}	M _{(soil)¹} (g/m ²)	M _(L.unsat) (g/m ²)	M _{(soil)²} (mg/m ³)	M _(L.unsat) (mg/m ³)	M _{(L.unsat)/M_(soil)}
NH ₄ ⁺ as N												
C01 - nursery	0.0-0.49	0.49-9.80	7.6	214.1	15.7	23.0	1.47	3.2	138.2	6.7	14.8	2.23
C02 - former orchard	0.0-0.40	0.40-3.08	6.4	35.4	16.1	13.2	0.82	0.6	4.8	1.4	1.8	1.23
C03 - corn field	0.0-0.49	0.49-10.09	7.8	138.5	15.9	14.4	0.91	1.2	79.7	2.5	8.3	3.38
C04 - open field	0.0-0.50	0.50-2.59	7.4	27.1	14.7	13.0	0.88	1.8	20.6	3.6	9.8	2.73
C05 - sod farm	0.0-0.53	0.53-5.32	4.2	37.5	7.8	7.8	1.00	1.9	40.9	3.6	8.6	2.41
C06 - sod farm	0.0-0.49	0.49-7.68	6.4	74.3	13.1	10.3	0.79	15.4	128.9	31.5	17.9	0.57
C07 - sod farm	0.0-0.49	0.49-6.13	4.9	57.1	10.1	10.1	1.00	2.6	74.6	5.3	13.2	2.48
C08 - residential	0.0-0.47	0.47-4.93	4.9	46.8	10.3	10.5	1.02	0.7	0.0	1.4	0.0	0.00
C09 - open field	0.0-0.50	0.50-7.30	12.0	143.5	23.8	21.1	0.89	1.7	21.6	3.4	3.2	0.94
C10 - open field	0.0-0.49	0.49-7.01	6.9	129.5	14.2	19.9	1.40	0.7	77.8	1.4	11.9	8.78
C11 - corn field	0.0-0.43	0.43-5.68	4.1	124.4	9.5	23.7	2.49	5.7	261.4	13.3	49.7	3.75
Median			6.4	74.3	14.2	13.2	0.93	1.8	74.6	3.6	9.8	2.77
NO ₃ ⁻ as N												
C01 - nursery	0.0-0.49	0.49-9.80	4.6	11.5	9.5	1.2	0.13	63.7	49.6	130.6	5.3	0.04
C02 - former orchard	0.0-0.40	0.40-3.08	3.7	23.7	9.3	8.8	0.95	10.9	83.6	27.5	31.1	1.13
C03 - corn field	0.0-0.49	0.49-10.09	8.3	78.4	17.0	8.2	0.48	11.0	385.1	22.6	40.1	1.77
C04 - open field	0.0-0.50	0.50-2.59	3.7	17.2	7.3	8.2	1.13	36.7	85.6	72.9	41.0	0.56
C05 - sod farm	0.0-0.53	0.53-5.32	6.1	66.0	11.4	13.8	1.21	7.1	125.8	13.3	26.3	1.98
C06 - sod farm	0.0-0.49	0.49-7.68	5.0	49.3	10.2	6.9	0.67	62.9	373.3	128.9	51.9	0.40
C07 - sod farm	0.0-0.49	0.49-6.13	9.3	0.0	19.0	0.0	0.00	7.4	227.5	15.3	40.4	2.64
C08 - residential	0.0-0.47	0.47-4.93	0.0	0.0	0.0	0.0	--	3.3	94.6	7.1	21.2	3.00
C09 - open field	0.0-0.50	0.50-7.30	5.0	0.0	9.9	0.0	0.00	3.9	332.6	7.7	48.9	6.34
C10 - open field	0.0-0.49	0.49-7.01	1.5	19.7	3.1	3.0	0.97	24.5	244.9	50.3	37.5	0.75
C11 - corn field	0.0-0.43	0.43-5.68	5.3	50.4	12.4	9.6	0.78	30.4	199.4	71.3	37.9	0.53
Median			5.0	19.7	9.9	6.9	0.69	11.0	199.4	27.5	37.9	1.38

$$1 \quad M_{[z_1, z_2]} = \int_{z_1}^{z_2} \rho_b dz$$

$$2 \quad \bar{M}_{[z_1, z_2]} = \frac{M_{[z_1, z_2]}}{z_2 - z_1}$$

M_[z₁, z₂] = mass of the compound stored per unit area over the depth interval [z₁, z₂] (grams per cubic meter).

T = total concentration of the compound sorbed to the sediment (grams per kilogram).

ρ_b = dry bulk density of the sediment (kilograms per cubic meter).

$\bar{M}_{[z_1, z_2]}$ = average total concentration of the compound for the interval [z₁, z₂] (grams per cubic meter).

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14 Effect of sorption on storage and transport of nitrate and other ions, southern New Jersey

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Appendixes 1-3

Appendix 1. Results of analysis of unsaturated-zone sediment and ground water, southern New Jersey, 2003-04.

[m, meter; mbils, meters below land surface; mg/L, milligrams per liter; ρ_b , bulk density; g/cm³, grams per cubic centimeter; W_{ave} , average moisture fraction for interval; L/kg, liters per kilogram; mg/kg as N, milligrams of chemical per kilogram of dry sediment as nitrogen; mg/kg, milligrams of chemical per kilogram of dry sediment; CEC, cation exchange capacity; meq/100g, milliequivalents per 100 grams of dry sediment; TKN, total Kjeldahl nitrogen (ammonium-N plus organic nitrogen); OM, organic matter; %, grams of organic matter per gram of dry sediment multiplied by 100; --, not applicable or not measured. A repeated sampling interval indicates a replicate sample; site locations shown in figure 1]

Site C01																	
Land use (1)	Nursery	Depth to water table (m)	9.8														
Latitude	N 39 30 38.5	Unsaturated-zone sampling date	6/3/2003														
Longitude	W 075 14 35.9	Ground-water sampling date	6/3/2003														
Unsaturated-zone sampling interval (mbils) (2)		Sediment texture	ρ_b (3)	W_{ave}	NO ₃ -lab 1 (4)	NO ₃ -lab 2 (4)	NH ₄ ⁺	TKN	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	SO ₄ ⁻²	Cl ⁻	pH	OM	CEC
Top	Bottom		g/cm ³	L/kg	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	standard units	%	meq/100g
0.00	0.49	silt	1.46	0.104	6.5	10.7	10.7	790	460.9	96.5	38.0	107.2	89.4	4.6	5.2	1.0	6.4
1.65	2.07	loamy sand	1.65	0.093	<0.1	3.8	16.0	170	87.0	32.9	46.5	16.9	12.5	9.1	4.8	<0.1om	2.5
5.33	5.90	coarse sand	1.67	0.066	0.4	<0.1	15.3	90	76.4	20.8	14.7	13.3	<0.5	9.4	4.9	0.1	0.9
7.80	8.28	coarse sand	1.67	0.049	2.9	<0.1	12.1	100	79.3	7.6	28.2	5.5	<0.5	8.1	5.0	<0.1om	0.4
7.80	8.28	coarse sand	1.67	0.049	<0.1	<0.1	10.5	90	77.6	10.9	27.2	6.0	<0.5	8.9	5.0	<0.1om	0.3
Ground-water sampling interval (mbils)		mg/L as N															
10.09	10.24	11.9															
		mg/L															
		23.9 18.9 5.1 -- 50.5 33.2 5.9 -- --															
Site C02																	
Land use	Former orchard	Depth to water table (m)	3.08														
Latitude	N 39 31 11.7	Unsaturated-zone sampling date	6/12/2003														
Longitude	W 075 14 03.4	Ground-water sampling date	6/12/2003														
Unsaturated-zone sampling interval (mbils) (2)		Sediment texture	ρ_b (3)	W_{ave}	NO ₃ -lab 1 (4)	NO ₃ -lab 2 (4)	NH ₄ ⁺	TKN	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	SO ₄ ⁻²	Cl ⁻	pH	OM	CEC
Top	Bottom		g/cm ³	L/kg	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	standard units	%	meq/100g
0.00	0.46	silty clay	1.56	0.150	6.0	8.6	10.4	1870	440.4	69.0	68.3	158.1	17.7	0.9	5.2	3.0	7.2
1.65	2.13	v. coarse sand	1.67	0.071	5.1	2.1	8.1	90	79.5	9.5	17.4	16.6	17.9	0.9	5.1	0.3	0.9
1.65	2.13	v. coarse sand	1.67	0.071	6.1	2.0	11.0	80	77.6	8.7	22.6	12.5	18.5	0.9	5.2	0.1	0.7
2.44	2.74	v. coarse sand	1.67	0.078	5.1	1.0	6.6	130	79.8	8.3	24.0	18.4	19.3	1.3	5.2	0.3	0.7
Ground-water sampling interval (mbils)		mg/L as N															
3.81	4.57	3.4															
		mg/L															
		16.9 2.9 2.9 -- 39.7 4.4 6.2 -- --															
Site C03																	
Land use	Corn field	Depth to water table (m)	10.09														
Latitude	N 39 32 38.8	Unsaturated-zone sampling date	6/17/2003														
Longitude	W 075 13 47.7	Ground-water sampling date	6/17/2003														
Unsaturated-zone sampling interval (mbils) (2)		Sediment texture	ρ_b (3)	W_{ave}	NO ₃ -lab 1 (4)	NO ₃ -lab 2 (4)	NH ₄ ⁺	TKN	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	SO ₄ ⁻²	Cl ⁻	pH	OM	CEC
Top	Bottom		g/cm ³	L/kg	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	standard units	%	meq/100g
0.00	0.49	silty loam	1.47	0.250	11.6	10.9	10.9	1390	903.4	178.4	49.9	334.7	15.4	1.7	7.4	2.2	8.0
1.74	2.13	loamy sand	1.65	0.148	6.5	1.5	8.9	360	187.2	70.5	30.6	94.6	47.0	7.6	6.2	0.3	3.5
1.74	2.13	loamy sand	1.65	0.148	5.7	1.5	9.5	150	250.3	73.9	48.7	95.0	48.0	7.4	6.2	0.3	2.8
4.18	4.69	loamy sand	1.65	0.137	4.7	1.0	8.9	140	74.9	24.2	18.4	8.6	24.4	4.8	5.6	0.2	1.4
7.74	8.17	v. coarse sand	1.68	0.061	5.2	0.9	8.3	90	28.7	5.1	16.3	5.9	13.9	4.6	6.8	0.2	0.3
Ground-water sampling interval (mbils)		mg/L as N															
10.21	10.82	18.4															
		mg/L															
		39.1 12.7 2.5 -- 40.9 28.4 5.8 -- --															

Appendix 1. Results of analysis of unsaturated-zone sediment and ground water, southern New Jersey, 2003-04.—Continued.

[m, meter; mbils, meters below land surface; mg/L, milligrams per liter; ρ_b , bulk density; g/cm³, grams per cubic centimeter; W_{ave} , average moisture fraction for interval; L/kg, liters per kilogram; mg/kg as N, milligrams of chemical per kilogram of dry sediment as nitrogen; mg/kg, milligrams of chemical per kilogram of dry sediment; CEC, cation exchange capacity; meq/100g, milliequivalents per 100 grams of dry sediment; TKN, total Kjeldahl nitrogen (ammonium-N plus organic nitrogen); OM, organic matter; %, grams of organic matter per gram of dry sediment multiplied by 100; --, not applicable or not measured. A repeated sampling interval indicates a replicate sample; site locations shown in figure 1]

Site C07																	
Land use		Sod farm		Depth to water table (m)		6.13											
Latitude		N 39 30 38.3		Unsaturated-zone sampling date		7/16/2003											
Longitude		W 075 14 57.1		Ground-water sampling date		7/16/2003											
Unsaturated-zone sampling interval (mbils) ⁽²⁾																	
Top	Bottom	ρ_b ⁽³⁾ g/cm ³	W_{ave} L/kg	NO ₃ ⁻ lab 1 ⁽⁴⁾ mg/kg as N	NO ₃ ⁻ lab 2 ⁽⁴⁾ mg/kg as N	NH ₄ ⁺ mg/kg as N	TKN mg/kg as N	Ca ⁺⁺ mg/kg	Mg ⁺⁺ mg/kg	Na ⁺ mg/kg	K ⁺ mg/kg	SO ₄ ⁻² mg/kg	Cl ⁻ mg/kg	pH standard units	OM %	CEC meq/100g	
0.00	0.49	1.58	0.138	12.0	5.9	6.4	1200	746.7	175.8	20.0	216.6	9.6	3.4	6.5	1.7	7.3	
2.44	2.85	1.64	0.085	<0.1	0.3	6.4	200	97.2	32.6	7.6	29.7	30.6	9.0	5.3	0.3	1.8	
2.44	2.85	1.64	0.085	<0.1	0.2	5.1	100	93.4	29.4	31.5	30.1	28.6	8.4	5.1	0.2	1.6	
4.05	4.45	1.66	0.072	<0.1	0.3	6.4	100	44.9	9.0	41.8	10.9	20.7	7.5	5.1	0.1	0.8	
Ground-water sampling interval (mbils)																	
7.17	7.93			27.8	<0.04	<0.04	0.2	35.4	16.5	3.8	--	24.0	29.1	5.3	--	--	
Site C08																	
Land use		Residential		Depth to water table (m)		4.93											
Latitude		N 39 30 13.0		Unsaturated-zone sampling date		7/22/2003											
Longitude		W 075 15 28.4		Ground-water sampling date		7/22/2003											
Unsaturated-zone sampling interval (mbils) ⁽²⁾																	
Top	Bottom	ρ_b ⁽³⁾ g/cm ³	W_{ave} L/kg	NO ₃ ⁻ lab 1 ⁽⁴⁾ mg/kg as N	NO ₃ ⁻ lab 2 ⁽⁴⁾ mg/kg as N	NH ₄ ⁺ mg/kg as N	TKN mg/kg as N	Ca ⁺⁺ mg/kg	Mg ⁺⁺ mg/kg	Na ⁺ mg/kg	K ⁺ mg/kg	SO ₄ ⁻² mg/kg	Cl ⁻ mg/kg	pH standard units	OM %	CEC meq/100g	
0.00	0.46	1.61	0.198	<0.1	1.2	6.4	900	14.8	16.4	13.1	45.0	4.4	0.9	4.6	1.2	4.0	
1.68	2.13	1.66	0.052	<0.1	<0.1	5.1	200	2.2	6.4	23.4	16.8	9.2	<0.5	5.2	0.2	0.6	
3.66	4.15	1.67	0.056	<0.1	<0.1	6.4	100	2.8	6.3	14.7	18.8	14.5	<0.5	5.1	<0.1om	0.8	
3.66	4.15	1.67	0.056	<0.1	<0.1	7.7	100	1.8	5.2	9.2	18.4	15.2	<0.5	5.1	<0.1om	0.7	
Ground-water sampling interval (mbils)																	
5.65	6.42			6.4	<0.04	<0.04	0.1	11.1	2.8	6.4	--	16.2	13.7	5.58	--	--	
Site C09																	
Land use		Open field		Depth to water table (m)		7.30											
Latitude		N 39 30 33.1		Unsaturated-zone sampling date		7/29/2003											
Longitude		W 075 14 53.3		Ground-water sampling date		7/29/2003											
Unsaturated-zone sampling interval (mbils) ⁽²⁾																	
Top	Bottom	ρ_b ⁽³⁾ g/cm ³	W_{ave} L/kg	NO ₃ ⁻ lab 1 ⁽⁴⁾ mg/kg as N	NO ₃ ⁻ lab 2 ⁽⁴⁾ mg/kg as N	NH ₄ ⁺ mg/kg as N	TKN mg/kg as N	Ca ⁺⁺ mg/kg	Mg ⁺⁺ mg/kg	Na ⁺ mg/kg	K ⁺ mg/kg	SO ₄ ⁻² mg/kg	Cl ⁻ mg/kg	pH standard units	OM %	CEC meq/100g	
0.00	0.00	1.48	0.258	6.7	1.7	16.1	1130	628.4	204.3	19.1	185.3	5.2	2.3	6.8	1.7	6.8	
2.90	0.88	1.66	0.112	<0.1	<0.1	11.1	140	25.6	18.7	9.2	15.6	35.2	2.9	5.2	0.0	1.7	
2.90	0.88	1.66	0.112	<0.1	<0.1	14.6	130	23.0	16.0	21.1	17.2	35.4	3.1	5.3	0.1	1.5	
5.29	1.61	1.66	0.061	<0.1	<0.1	12.5	100	8.0	13.0	4.1	9.0	19.1	3.8	5.7	<0.1om	0.8	
Ground-water sampling interval (mbils)																	
7.91	8.67			17.4	<0.04	<0.04	0.1	23.6	12.1	33.6	--	29.8	61.3	5.4	--	--	

Appendix 1. Results of analysis of unsaturated-zone sediment and ground water, southern New Jersey, 2003-04.—Continued.

[m, meter; mbils, meters below land surface; mg/L, milligrams per liter; ρ_b , bulk density; g/cm³, grams per cubic centimeter; W_{ave} , average moisture fraction for interval; L/kg, liters per kilogram; mg/kg as N, milligrams of chemical per kilogram of dry sediment as nitrogen; mg/kg, milligrams of chemical per kilogram of dry sediment; CEC, cation exchange capacity; meq/100g, milliequivalents per 100 grams of dry sediment; TKN, total Kjeldahl nitrogen (ammonium-N plus organic nitrogen); OM, organic matter; %, grams of organic matter per gram of dry sediment multiplied by 100; --, not applicable or not measured. A repeated sampling interval indicates a replicate sample; site locations shown in figure 1.]

Site C10																	
Land use		Open field		Depth to water table (m)		6.89											
Latitude		N 39 31 01.4		Unsaturated-zone sampling date		11/13/03											
Longitude		W 075 14 16.9		Ground-water sampling date		11/13/03											
Unsaturated-zone sampling interval (mbils) ⁽²⁾																	
Top	Bottom	ρ_b ⁽³⁾ g/cm ³	W_{ave} L/kg	NO ₃ -lab 1 ⁽⁴⁾ mg/kg as N	NO ₃ -lab 2 ⁽⁴⁾ mg/kg as N	NH ₄ ⁺ mg/kg as N	TKN mg/kg as N	Ca ⁺⁺ mg/kg	Mg ⁺⁺ mg/kg	Na ⁺ mg/kg	K ⁺ mg/kg	SO ₄ ⁻ mg/kg	Cl ⁻ mg/kg	pH standard units	OM %	CEC meq/100g	
0.00	0.49	1.48	0.209	2.1	0.5	9.6	1020	103.4	20.9	13.8	33.2	34.0	0.9	4.3	0.5	4.2	
1.68	2.13	1.57	0.059	0.2	<0.1	10.5	580	55.3	4.1	26.4	12.5	21.4	2.0	4.5	0.1	5.9	
3.66	4.11	1.66	0.076	1.6	<0.1	12.9	800	46.3	14.0	29.0	7.8	18.0	9.8	4.7	<0.1om	0.9	
4.88	5.33	1.65	0.057	1.3	<0.1	6.7	890	58.7	14.7	25.3	11.3	34.6	7.8	4.4	<0.1om	1.3	
4.88	5.33	1.65	0.057	6.4	<0.1	16.8	1080	58.9	15.6	39.3	10.2	31.4	6.8	4.4	0.2	1.3	
Ground-water sampling interval (mbils)																	
				mg/L as N		mg/L as N		mg/L		mg/L		mg/L					
				7.8		<0.04		22.2		7.1		3.8				5.24	
Site C11																	
Land use		Corn field		Depth to water table (m)		5.68											
Latitude		N 39 31 10.7		Unsaturated-zone sampling date		11/18/03											
Longitude		W 075 15 19.3		Ground-water sampling date		11/18/03											
Unsaturated-zone sampling interval (mbils) ⁽²⁾																	
Top	Bottom	ρ_b ⁽³⁾ g/cm ³	W_{ave} L/kg	NO ₃ -lab 1 ⁽⁴⁾ mg/kg as N	NO ₃ -lab 2 ⁽⁴⁾ mg/kg as N	NH ₄ ⁺ mg/kg as N	TKN mg/kg as N	Ca ⁺⁺ mg/kg	Mg ⁺⁺ mg/kg	Na ⁺ mg/kg	K ⁺ mg/kg	SO ₄ ⁻ mg/kg	Cl ⁻ mg/kg	pH standard units	OM %	CEC meq/100g	
0.00	0.43	1.42	0.213	8.7	3.7	6.7	1710	462.1	147.4	20.9	197.8	50.2	9.3	6.0	1.9	7.0	
2.87	3.29	1.65	0.107	6.9	0.6	15.6	630	120.8	50.6	83.0	19.2	17.3	44.5	5.5	0.1	2.3	
4.15	4.63	1.55	0.155	2.5	0.8	7.6	840	152.7	43.1	32.4	34.0	30.7	5.5	4.7	0.3	5.0	
4.15	4.63	1.55	0.155	5.5	1.0	16.7	940	118.8	32.2	82.1	27.0	33.1	8.1	4.7	0.1	4.2	
Ground-water sampling interval (mbils)																	
				mg/L as N		mg/L as N		mg/L		mg/L		mg/L					
				5.2		0.03		24.7		16.6		53.5				4.8	
Site P1																	
Land use		Undeveloped		Depth to water table (m)		4.39											
Latitude		N 39 52 45.0		Unsaturated-zone sampling date		5/20/04											
Longitude		W 074 29 28.4		Ground-water sampling date		6/9/04											
Unsaturated-zone sampling interval (mbils) ⁽²⁾																	
Top	Bottom	ρ_b ⁽³⁾ g/cm ³	W_{ave} L/kg	NO ₃ -lab 1 ⁽⁴⁾ mg/kg as N	NO ₃ -lab 2 ⁽⁴⁾ mg/kg as N	NH ₄ ⁺ mg/kg as N	TKN mg/kg as N	Ca ⁺⁺ mg/kg	Mg ⁺⁺ mg/kg	Na ⁺ mg/kg	K ⁺ mg/kg	SO ₄ ⁻ mg/kg	Cl ⁻ mg/kg	pH standard units	OM %	CEC meq/100g	
0.37	0.79	1.65	0.050	1.0	<0.1	8.0	<100x	0.1	0.1	55.2	3.0	9.4	<0.5	4.7	0.3	1.1	
1.22	2.23	1.67	0.045	<0.1	<0.1	10.0	<100x	0.1	0.1	38.9	3.0	8.3	<0.5	4.5	0.1	0.5	
2.90	3.66	1.65	0.092	<0.1	<0.1	13.0	<100x	0.9	1.1	51.9	3.4	14.2	<0.5	4.3	0.1	1.4	
Ground-water sampling interval (mbils)																	
				mg/L as N		mg/L as N		mg/L		mg/L		mg/L					
				<0.06		<0.04		---		---		---				4.5	

Appendix 1. Results of analysis of unsaturated-zone sediment and ground water, southern New Jersey, 2003-04.—Continued.

[m, meter; mbils, meters below land surface; mg/L, milligrams per liter; ρ_b , bulk density; g/cm³, grams per cubic centimeter; W_{ave} , average moisture fraction for interval; L/kg, liters per kilogram; mg/kg as N, milligrams of chemical per kilogram of dry sediment as nitrogen; mg/kg, milligrams of chemical per kilogram of dry sediment; CEC, cation exchange capacity; meq/100g, milliequivalents per 100 grams of dry sediment; TKN, total Kjeldahl nitrogen (ammonium-N plus organic nitrogen); OM, organic matter; %, grams of organic matter per gram of dry sediment multiplied by 100; --, not applicable or not measured. A repeated sampling interval indicates a replicate sample; site locations shown in figure 1]

Site P2																					
Land use		Depth to water table (m)		Sediment texture		ρ_b ^(b)	W_{ave}	NO_3^- lab 1 ⁽⁴⁾	NO_3^- lab 2 ⁽⁴⁾	NH_4^+	TKN	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	SO_4^{--}	Cl ⁻	pH	OM	CEC	
Top	Bottom	g/cm ³	L/kg	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	standard units	%	meq/100g	
0.30	0.46	1.65	0.066	<0.1	<0.1	7.0	100	0.4	0.3	281.1	0.7	6.0	<0.5	4.5	0.7	2.7		4.5	0.7	2.7	
1.52	1.83	1.66	0.035	1.0	<0.1	8.0	<100x	0.1	0.2	33.5	3.0	8.2	<0.5	4.6	0.2	0.4		4.6	0.2	0.4	
2.29	2.44	1.65	0.859	1.0	<0.1	7.0	<100x	0.1	0.2	22.5	2.8	15.7	0.7	4.5	0.3	0.7		4.5	0.3	0.7	
Ground-water sampling interval																					
(mbils)		98145.452		mg/L as N		mg/L as N		mg/L		mg/L		mg/L		mg/L		mg/L		mg/L		4.6	
2.44	3.05																				
Site P3																					
Land use		Depth to water table (m)		Sediment texture		ρ_b ^(b)	W_{ave}	NO_3^- lab 1 ⁽⁴⁾	NO_3^- lab 2 ⁽⁴⁾	NH_4^+	TKN	Ca ⁺⁺	Mg ⁺⁺	Na ⁺	K ⁺	SO_4^{--}	Cl ⁻	pH	OM	CEC	
Top	Bottom	g/cm ³	L/kg	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg as N	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	standard units	%	meq/100g	
0.61	1.22	1.65	0.036	<0.1	<0.1	1.0	<100x	0.1	0.1	43.6	3.1	38.4	0.8	4.30	0.2	2.2		4.30	0.2	2.2	
0.61	1.22	1.65	0.036	<0.1	<0.1	2.0	<100x	0.1	0.1	28.2	2.7	38.1	0.8	3.90	0.2	1.9		3.90	0.2	1.9	
1.83	2.29	1.67	0.020	<0.1	<0.1	2.0	<100x	<0.1c	<0.1m	9.1	1.1	10.7	0.6	4.20	0.1	0.4		4.20	0.1	0.4	
2.74	3.35	1.67	0.018	<0.1	<0.1	3.0	20	0.1	0.1	62.6	1.7	5.6	0.5	4.40	<0.1om	0.4		4.40	<0.1om	0.4	
2.74	3.35	1.67	0.018	<0.1	<0.1	2.0	<100x	0.1	0.1	16.7	1.5	5.8	0.5	4.35	<0.1om	0.3		4.35	<0.1om	0.3	
Ground-water sampling interval																					
(mbils)		<0.06		mg/L as N		mg/L as N		mg/L		mg/L		mg/L		mg/L		mg/L		mg/L		4.5	
3.56	4.17																				

(1) Land use at each site is provided for descriptive purposes only.

(2) A repeated interval indicates that two samples were collected from the interval for chemical analysis.

(3) ρ_b (dry bulk density) was estimated from particle-size data using the pedotransfer functions of the ROSETTA model (U.S. Department of Agriculture, 2004).

(4) The Rutgers Soils Testing lab in New Brunswick, New Jersey, is designated as lab 1 and the U.S. Geological Survey lab in Lakewood, Colorado, is designated as lab 2.

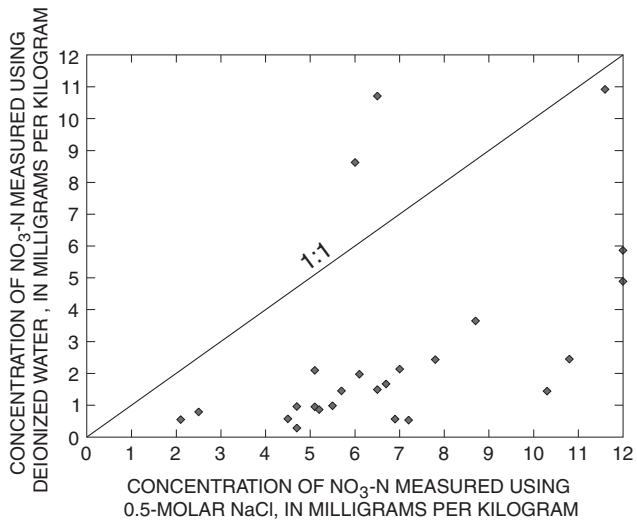


Figure 1-1. Relation between NO₃-N concentrations measured using 0.5-molar NaCl as an extractant and NO₃-N concentrations measured using deionized water as an extractant.

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Appendix 2. Summary of recharge estimates for selected sites, Upper Deerfield Township, New Jersey.

[vol/vol, volume per volume; cm/yr, centimeters per year]

Site identifier and land use	Latitude (degrees, minutes, seconds)	Longitude (degrees, minutes, seconds)	Depth to water table (meters below land surface)	Depth of lowermost unsaturated-zone layer (meters below land surface)		U.S. Department of Agriculture sediment type	Average moisture content (θ) for lowermost layer (vol/vol)	Recharge estimate (cm/yr)
				Top	Bottom			
C01 - nursery	39 30 38.2	075 14 35.9	9.80	6.74	9.75	coarse sand	0.090	86.6
C02 - former orchard	39 31 11.7	075 14 03.4	3.08	1.40	3.08	very coarse sand	0.118	314.4
C03 - corn field	39 32 38.8	075 13 47.7	10.09	7.68	10.09	very coarse sand	0.103	251.9
C04 - open field	39 31 04.7	075 15 42.4	2.59	0.87	2.44	very coarse sand	0.068	19.3
C05 - sod farm	39 31 09.8	075 15 07.6	5.32	4.11	5.32	loamy sand	0.240	9.1
C06 - sod farm	39 32 08.5	075 13 51.5	7.68	5.67	7.68	coarse sand	0.085	38.7
C07 - sod farm	39 30 38.3	075 14 57.1	6.13	1.80	6.13	loamy sand	0.141	217.4
C08 - residential	39 30 13.0	075 15 28.4	4.93	3.66	4.93	very coarse sand	0.093	48.7
C09- open field	39 30 33.1	075 14 53.3	7.30	5.29	7.32	very coarse sand	0.120	166.5
C10- open field	39 31 01.4	075 14 16.9	6.89	2.13	6.89	loamy sand	0.121	23.0
C11- corn field	39 31 10.7	075 15 19.3	5.68	4.15	4.57	sandy loam	0.247	10.1
Median			6.1					48.7

Appendix 3. Summary of sorption coefficients for selected ions in sediments, Upper Deerfield Township, New Jersey.

[K_d , sorption coefficient; --, K_d cannot be calculated because ion not detected in lowermost unsaturated zone; #, negative K_d calculated]

Site identifier and land use	Description of lowermost layer	K_d (liters per milligram)					
		Ca ⁺⁺	Mg ⁺⁺	Na ⁺	Cl ⁻	NO ₃ ⁻ as N	SO ₄ ⁻⁻
C01 - nursery	coarse sand	3.23	0.44	5.37	0.21	0.07	--
C02 - former orchard	very coarse sand	4.65	2.82	8.18	0.20	1.44	0.41
C03 - corn field	very coarse sand	0.67	0.34	6.37	0.10	0.22	0.28
C04 - open field	very coarse sand	4.65	3.29	0.67	0.06	--	1.63
C05 - sod farm	loamy sand	0.78	0.15	3.03	0.17	--	0.30
C06 - sod farm	coarse sand	0.15	2.00	1.82	--	--	0.86
C07 - sod farm	loamy sand	0.28	1.01	0.06	0.00	--	0.58
C08 - residential	very coarse sand	5.12	9.60	6.82	0.26	1.13	0.07
C09- open field	very coarse sand	1.20	0.47	10.97	0.19	--	0.79
C10- open field	loamy sand	2.59	2.06	8.50	0.52	0.44	0.70
C11- corn field	sandy loam	5.34	2.11	0.91	#	0.62	2.06
Median — sands		0.78	1.01	3.03	0.13	0.22	0.49
Median — loamy sands and sandy loams		3.86	2.09	7.66	0.26	0.62	0.75
Median — all sites		2.59	2.00	5.37	0.19	0.53	0.64