Published online July 6, 2006

Accuracy and Performance of Three Water Quality Models for Simulating Nitrate Nitrogen Losses under Corn

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ABSTRACT

Simulation models can be used to predict N dynamics in a soil–water–plant system. The simulation accuracy and performance of three models: LEACHM (Leaching Estimation And CHemistry Model), NCSWAP (Nitrogen and Carbon cycling in Soil, Water And Plant), and SOILN to predict NO_3–N leaching were evaluated and compared to field data from a 5-yr experiment conducted on a Hagerstown silt loam (fine, mixed, mesic Typic Hapludalf). Nitrate N losses past 1.2 m from N-fertilized and manured corn (*Zea mays* L.) were measured with zero-tension pan lysimeters for 5 yr. The models were calibrated using 1989–1990 data and validated using 1988–1989, 1990–1991, 1991–1992, and 1992–1993 NO_3–N leaching data. Statistical analyses indicated that LEACHM, NCSWAP, and SOILN models were able to provide accurate simulations of annual NO_3–N leaching losses below the 1.2-m depth for 8, 9, and 7 of 10 cases, respectively, in the validation years. The inaccuracy in the models' annual simulations for the control and manure treatments seems to be related to inadequate description of processes of N and C transformations in the models' code. The overall performance and accuracy of the SOILN model were worse than those of LEACHM and NCSWAP. The root mean square error (RMSE) and modeling efficiency (ME) were 10.7 and 0.9, 9.5 and 0.93, and 20.7 and 0.63 for LEACHM, NCSWAP, and SOILN, respectively. Overall, the three models have the potential to predict NO_3–N losses below 1.2-m depth from fertilizer and manure nitrogen applied to corn without recalibration of models from year to year.

Nitrate nitrogen (NO_3–N) levels have been of worldwide concern due to the deteriorating quality of ground and surface waters for the past four decades. Environmentalists, scientists, and citizens alike are mending bridges and melding perspectives to reach consensus that human impact on water quality must be more closely monitored. Currently, personal, agricultural, and industrial water use practices threaten the quality and preservation of indispensable natural water resources. The United States Environmental Protection Agency (USEPA) has identified nitrate contamination as an indicator of overall ground water quality (USEPA, 1999). The USEPA has set a maximum contaminant level (MCL) for NO_3–N in drinking water of 10 mg L^{-1}. Nitrate N concentrations above the 10 mg L^{-1} level have been shown to pose health risks to humans, mainly infants (blue baby syndrome), causing a condition called methemoglobinemia, which can be inherited or acquired. Methemoglobinemia is a blood disorder resulting from high levels of methemoglobin, which is blue and indicative of a nonfunctioning form of red hemoglobin that transports oxygen (McCarty, 2006). The infant's formula may be mixed with contaminated well water measuring high nitrate levels. Some other contributors to acquired methemoglobinemia are sodium nitrate, which is used in preserving meat; silver nitrate, used in treating burns; topical anesthetics; well water contaminated with oxidants; high nitrate content vegetables, such as beets, spinach, celery, turnips, and carrots; and vegetables or fruits grown in nitrate-rich soil (Kumar and Verive, 2003).

The concern about the health and environmental effects of nitrate contaminated surface and ground waters has made it imperative to estimate nitrate losses from cropland and to evaluate the impact of crop production practices on nitrate leaching.

Nearly one half of the U.S. drinking water supply comes from ground water and the majority of rural households rely on ground water for their drinking water supplies (USGS, 1999). In southeastern Pennsylvania, the area of the state with the most intensive agriculture, Swistock et al. (1993) found nearly 50% of the wells had NO_3–N concentrations above the USEPA maximum contaminant level (10 mg L^{-1}) for public drinking water. This survey also showed that nitrate levels were significantly higher in wells near corn fields. Agricultural practices such as the application of fertilizers and manure to fields potentially impact these ground water nitrate levels.

Water quality computer models are useful tools to predict the risk of agricultural chemicals' potential contamination to surface and ground waters. These models need to be calibrated and validated for the conditions under which they will be used. A properly validated model provides a fast and cost effective way of estimating NO_3–N leaching under different agricultural management practices. Thus, the farmer can more accurately determine the amount of fertilizer to use on a crop to manage yield yet avoid overfertilization, while political decision makers can identify agricultural best practices. The number of nonpoint source agricultural models used to predict nitrate leaching through the rootzone and into the underlying unsaturated soil zone has grown rapidly over the last two decades. These include NCSWAP (Nitrogen and Carbon cycling in Soil Water And Plant) by Molina and Richards (1984), PRZM (Pesticide Root Zone Model) by Carsel et al. (1985), GLEAMS (Groundwater Loading Effects of Agricultural Management System) by Leonard et al. (1987), SLIM by Addiscott and Whitmore (1991), NLEAP (Nitrate Leaching and Eco-

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Published in J. Environ. Qual. 35:1227–1236 (2006).
Technical Reports: Ground Water Quality
doi:10.2134/jeq2005.0413

Abbreviations: MD, mean difference; ME, modeling efficiency; RMSE, root mean square error.

nomic Analysis Package) by Shaffer et al. (1991), SOIL-SOILN by Eckersten et al. (1996), GRASIM (GRAzing SImulation Model) by Mohtar et al. (1997), RZWQM (Root Zone Water Quality Model) by Rojas et al. (1999), and LEACHM (Leaching Estimation And CHemistry Model) by Hutson (2003). Evaluation of these models has also received increasing attention over the last decade (Khakural and Robert, 1993; Jemison et al., 1994; Ahuja et al., 1996; Jabro et al., 1998, 2001; Sogbedji and van Es, 2001; Mahmood et al., 2002; Larocque et al., 2002; Marchetti et al., 2004). In summary, the creation, calibration, and validation of water quality computer models impact agricultural practices leading to greater awareness and potential control of environmental impacts.

The main objective of this paper was to evaluate and compare the overall performance and accuracy of LEACHM, NCSWAP, and SOILN models for their ability to predict annual NO_3–N leaching losses under continuous corn system. Five years (1988–1992) of field data were collected using zero-tension pan lysimeters placed 1.2 m below the soil surface within a long-term water quality study conducted in central Pennsylvania.

Although a number of other models are available, myriad reasons contributed to the selection of LEACHM, NCSWAP, and SOILN models: they are field-scale research-type models; they are well documented; they are user-friendly; they require manageable computer time; they are able to simulate water and nitrate leaching, N transformations (i.e., nitrification, denitrification, mineralization), soil nitrate distribution, and plant total N uptake; they use different approaches and equations for water flow and N transport; they provide a relatively manageable number of input parameters that can potentially be adjusted with acceptable levels to achieve optimal simulation of measured values; and they have been evaluated in other parts of the world under various conditions.

If these models are properly validated with respect to their simulative capability under various conditions, the models would significantly improve the quantitative understanding of N cycling processes, which can be valuable tools in designing environmentally compatible and economically suitable agricultural systems.

MATERIALS AND METHODS

Soil and Site Description

The experimental site is located in the R.E. Larson Agricultural Research Center of the Pennsylvania State University (40°42′55″ N, 77°56′15″ W), at Rock Springs (Fig. 1A). It is about 16 km west of downtown State College, Pennsylvania. The field site is nearly level, with soil series mapped as a Hagerstown silt loam developed from limestone residuum parent material. The Ap horizon is about 20 to 30 cm deep and has a weak, fine, granular structure. The B horizon is silty clay to clay textured with well-developed blocky structural peds.

The experimental field is approximately 0.9 ha (49 m wide × 183 m long). The width was divided into three longitudinal strips, oriented approximately northeast-southwest, with plot and non-plot areas in six blocks (Fig. 1B). Each block was divided into five plots to accommodate five N rate treatments, which were randomly assigned to the five plots within a block (Fig. 1B). Each plot has an area of 0.016 ha (10.6 × 15.2 m). The three blocks in Strip 2 were used for manured corn during 1988 to 1991, alfalfa during 1991 to 1994, and no-till after 1995. The other three blocks had been in continuous chisel-tilled corn since 1986 (Toth, 1996; Zhu, 2002).

Undisturbed soil cores (7.6 cm long × 7.6 cm in diameter) were collected in 0.20-m increments to a depth of 1.2 m (the rootzone depth for corn) from each of the 18 plots (six cores per plot) (Jabro et al., 1996). The soil cores were analyzed for soil bulk density (Blake and Hartge, 1986), particle size distribution (Gee and Bauder, 1986), and soil water retention characteristics (Klute, 1986) using standard methods. Soil infiltration rates were measured using a double-ring infiltrometer (Bouwer, 1986) while saturated hydraulic conductivities were measured in situ using a constant head well permeameter (Reynolds and Elrick, 1985). Physical and hydraulic characteristics of Hagerstown soil are reported in Tables 1 and 2.

Nitrogen Treatments

A field experiment was designed to monitor nitrate leaching losses from N fertilized and manured corn. The experimental design was a split-plot with three replicates, with the whole plot treatments being manure or no manure and the split plot treatments being five application rates of NH_4NO_3 fertilizer. The nitrate leaching experiment, extending from 1988 to 1992, examined nitrate leaching from non-manured, fertilized corn receiving 0 to 200 kg fertilizer N ha^{-1} annually in 50-kg increments and from manured, fertilized corn receiving 0 to 100 kg fertilizer N ha^{-1} annually in 25-kg increments. In addition to the fertilizer N, manured corn received dairy manure slurry in amounts supplying 264, 132, and 158 kg total N ha^{-1} in 1988, 1989, and 1990, respectively (Jemison et al., 1994).

Three sets of results within the N leaching treatments were selected for model evaluation. The data set includes (i) the control treatment consisting of zero N addition for all years, (ii) the fertilizer treatment with N supplied as NH_4NO_3 at a rate of 200 kg N ha^{-1} for all years, and (iii) the manure treatment with N supplied as dairy manure slurry for the years 1988–1989, 1989–1990, and 1990–1991. In addition, two treatments from one array of nine lysimeters planted to corn were selected to evaluate the accuracy of LEACHM, NCSWAP, and SOILN models. This data set included treatments of 0 kg N ha^{-1} and 200 kg N ha^{-1} for years 1991–1992 and 1992–1993.

The manure was incorporated within 2 d following application each year. All plots were chisel tilled each year followed by light disking. Before the emergence of corn crop, NH_4NO_3 fertilizer was hand-broadcast on the experimental plots. Corn was planted annually in early to mid-May and harvested for grain in mid-September to early October during the five years of study (Jemison et al., 1994; Toth, 1996).

Weather conditions during the five years of the study were normal for the area, with an exception of a 45-d period of drought in June and July of 1988, during which supplemental irrigation of 152 mm was applied to maintain the crops (Jemison, 1991; Lengnick, 1992). The weather records for each year were collected at a weather station established at the experimental site. The data included daily precipitation; maximum, mean, and minimum daily air temperatures; pan evaporation; and solar radiation. Soil temperatures were also measured on a weekly basis at the site with thermocouple thermometers placed at the 10-, 20-, 40-, 60-, and 100-cm depths (Stevenson and Pennypacker, 1993; Toth, 1996). Annual cumulative precipitation and annual cumulative pan evapotranspiration for the five years of study are presented in Table 3.

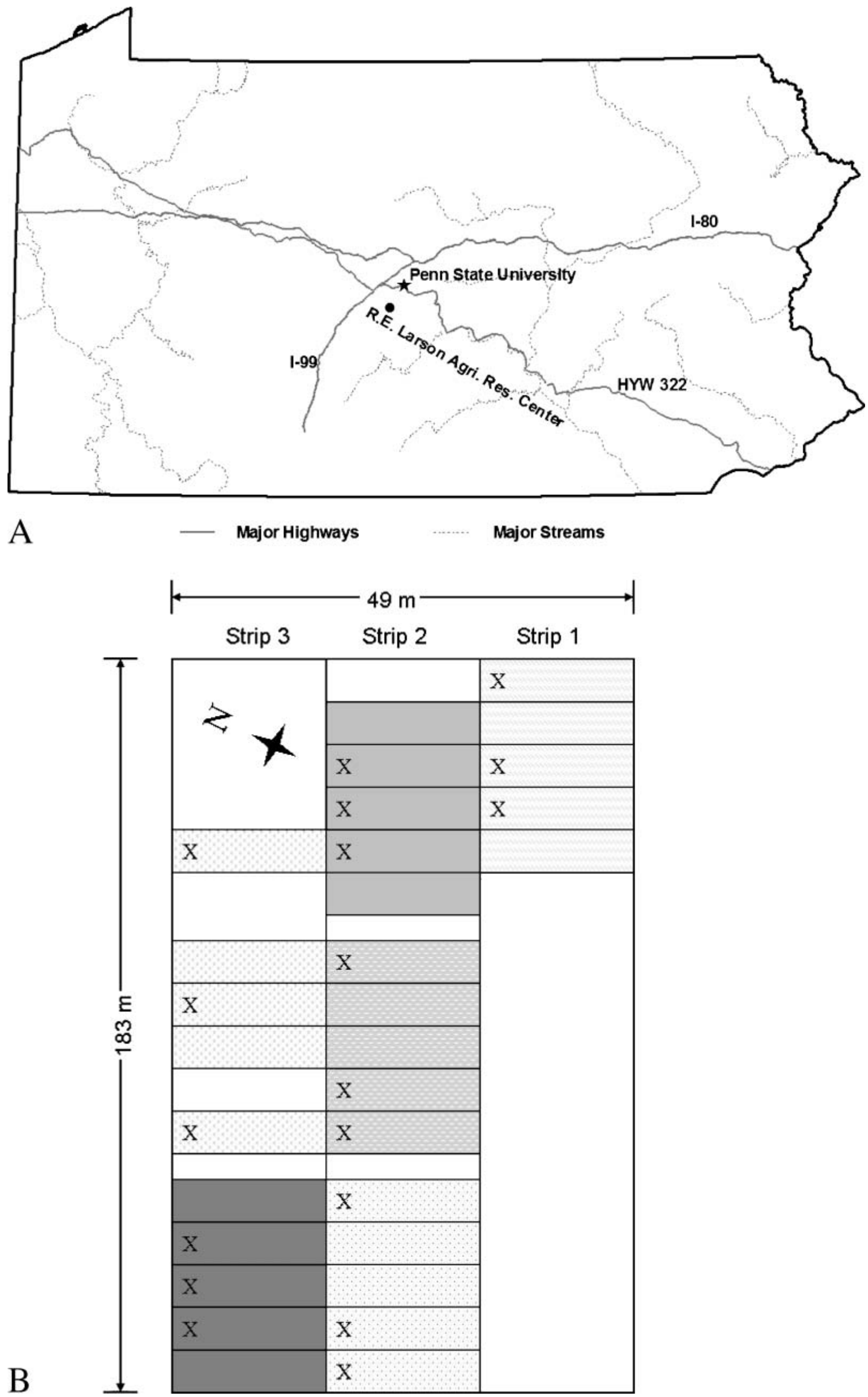

Fig. 1. (A) Geographic location of the experimental site. (B) Layout of the experimental site shows location of lysimeters. Strips 1 and 3, tilled N fertilized corn from 1988 to 1997. Strip 2, tilled N fertilized corn from 1988 to 1990, alfalfa from 1991 to 1993, and post-alfalfa tilled corn in 1994. X indicates the plots that have zero-tension lysimeters installed (adapted from Zhu, 2002).

Table 1. Physical and hydraulic properties of Hagerstown silt loam soil as used in model simulations (Jabro et al., 1996, 1998).

	Depth (m)					
Parameter†	0–0.2	0.2–0.4	0.4–0.6	0.6–0.8	0.8–1	1–1.2
Bulk density, Mg m^{-3}	1.36	1.48	1.53	1.67	1.69	1.70
Particle size, %						
Sand	12.2	11.1	12.3	12.4	12.2	12.8
Silt	59.9	50.1	45.0	43.3	43.3	43.3
Clay	27.9	38.8	42.7	44.3	44.5	43.9
Water content, m^3 m^{-3}, at						
0.01 MPa	0.41	0.37	0.36	0.35	0.35	0.35
0.03 MPa	0.38	0.35	0.35	0.34	0.33	0.33
0.1 MPa	0.34	0.33	0.33	0.32	0.30	0.29
0.5 MPa	0.24	0.29	0.28	0.27	0.26	0.28
1.5 MPa	0.22	0.26	0.25	0.24	0.24	0.26

† Each value is a mean of 18 observations.

Lysimeters Description and Leachate Samples Collection

An array of 18 zero-tension pan lysimeters with size 76 × 61 cm were placed 1.2 m below the soil surface of N fertilized and manured plots to collect leachate (Jemison and Fox, 1992). The soil profile (1.2 m thick) above the pan lysimeter was undisturbed. Corn was planted manually so that one row of corn plants was established above the lysimeters. Drainage water was collected in a 25-L carboy placed at the bottom of each pit (Fig. 2). Following each precipitation event of magnitude sufficient to cause leaching to the 1.2-m depth, the total water volume in the carboy was measured and samples were taken for analyzing NO_3–N using an automated Cd reduction method (USEPA, 1979). The quantities of drained water collected in individual pans were adjusted by the calculated collection efficiencies (Jemison and Fox, 1992). Calculations of individual pan collection efficiencies ranged from 13 to 92% with an overall average of 52% (n = 18, CV = 44%). More discussion regarding the pan lysimeter design, construction, and installation is given in Jemison and Fox (1992) and Jemison et al. (1994).

Water Quality Model Description

LEACHM Model

The LEACHM model consists of five sub-models that describe the one-dimensional storage, transference, and distribution of water and solute within a soil profile (Hutson and Wagenet, 1992). The LEACHM model is a deterministic model that solves the Richards' equation for water flow and the convection-dispersion equation (CDE) for chemical transport and leaching in a one-dimensional, vertical, layered soil profile. The LEACHM numerically solves the Richards' equation to simulate water flow in unsaturated soil and a Campbell's equation to define the relationship between unsaturated conductivity and soil water content using soil-water retention data. The CDE is used to predict the behavior of solutes in the soil solution. Nitrogen transformations are described in terms of fluxes between soil organic N pools (manure, litter, and humus), in addition to urea, NH_4–N, and NO_3–N. A complete description of the LEACHM model, equations and estimation of the parameters, organic N pools, and initial and boundary conditions is given in the LEACHM manual (Hutson and Wagenet, 1992; Hutson, 2003).

Table 2. Initial soil hydraulic and chemical characteristic of Hagerstown silt loam soil as used in model simulations.

Soil characteristic	Depth	Mean
	m	
Infiltration rate†, cm min^{-1}	0–0.3	1.5×10^{-1}
Saturated hydraulic conductivity†, cm min^{-1}	0.3–0.6	4.9×10^{-2}
	0.6–1.2	2.8×10^{-3}
pH	0–0.3	6.6
	0.3–0.6	6.4
Organic carbon, g kg^{-1}	0–0.3	19.1
	0.3–0.6	7.2
	0.6–1.2	2.0
CEC‡, cmol kg^{-1}	0–0.3	10.5
	0.3–0.6	11.3
Total N, g kg^{-1}	0–0.3	2.6
	0.3–0.6	0.5
	0.6–1.2	0.4

† Number of observations = 18.
‡ Cation exchange capacity.

Table 3. Cumulative measured precipitation and pan evapotranspiration (May through April).

Year	Precipitation	Pan evapotranspiration
	mm	
1988–1989	982	797
1989–1990	1162	755
1990–1991	1177	710
1991–1992	800	618
1992–1993†	640	405

† Values are from May through February.

The sensitivity analyses of LEACHM model were previously performed by Hutson and Wagenet (1992), Jemison (1991), Lotse et al. (1992), Toth (1996), and Mahmood et al. (2002). The results of sensitivity analyses indicated that the LEACHM response was affected by slight changes in nitrification, denitrification, and mineralization rate constants. Furthermore, NO_3–N leaching losses and water drainage simulated by LEACHM were also sensitive to changes in the saturated hydraulic conductivity, organic carbon content, initial water content, and Campbell's equation coefficients.

NCSWAP Model

The NCSWAP model (revised version 46) was developed by Molina and Richards (1984). The NCSWAP model is a comprehensive, deterministic, research-type simulation model that predicts seasonal N and C cycles in the soil-water-plant system

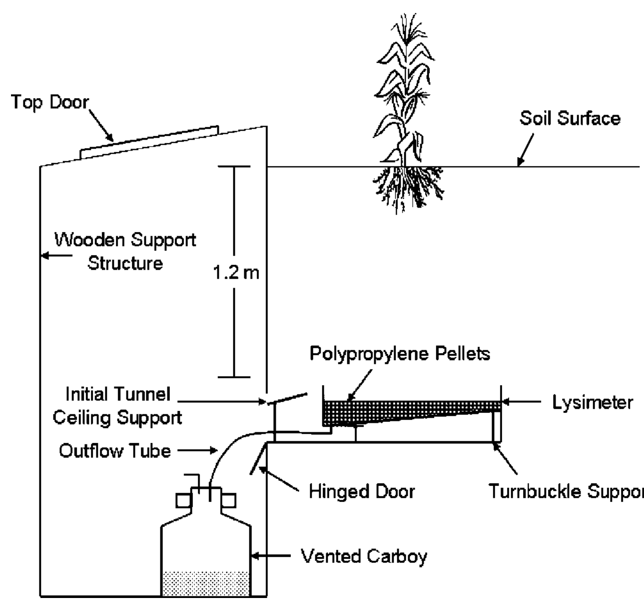

Fig. 2. Schematic diagram of pan lysimeter and its structural support (adapted from Jemison, 1991).

as affected by water flow, crop growth, N transformations, tillage and residue effects, temperature, and solute transport. The NCSWAP model is comprised of four major sub-models: the C and N cycling portion of the model (NCSOIL), the two water flow portions of the model (INFIL and REDIS), and the crop growth sub-model (Clay et al., 1985a, 1985b). The NCSOIL model simulates C and N flow through three active soil organic matter pools (plant residues or litter, microbial biomass [Pool I], and humads or relatively simple humic compounds [Pool II]) (Molina et al., 1983). The plant residues, Pools I and II, are partitioned into more resistant (recalcitrant) or less resistant (labile) to microbial utilization, each with a corresponding rate constant (Clay et al., 1985a; Molina et al., 1983, 1987). The NCSWAP model simulates water flow processes in the vertical dimension using the Green and Ampt equation and water redistribution system (Clay et al., 1985a). The initial NCSWAP evaluation by its developers with data collected from a field experiment reported successful simulation of soil inorganic N dynamics, nitrate leaching, and corn N uptake (Clay et al., 1985a, 1985b, 1989).

The results of prior sensitivity analyses indicate that output was slightly sensitive to saturated hydraulic conductivity, but sensitive to initial soil water potential, soil water retention data, bulk density (porosity), and particle size distribution. On the other hand, the NCSWAP model was insensitive to nitrification rates, but highly sensitive to the N content of the active organic matter pools, N mineralization, and solute flow factor. Furthermore, the NO_3–N leaching losses were strongly affected by the C to N ratio of the added organic matter as well as by the distribution of C between labile and recalcitrant fractions and by solute flow factor (Molina et al., 1983; Deans et al., 1986; Hadas et al., 1987; Dou, 1993; Lengnick, 1992; Dou and Fox, 1993; Lengnick and Fox, 1994; Toth, 1996). Additional details regarding the NCSWAP sensitivity analyses are given in the aforementioned literature.

SOILN Model

The SOIL and SOILN models are coupled models used to simulate water and heat transport, N dynamics, and biomass production in a layered soil (Johnsson et al., 1987; Eckersten and Jansson, 1991; Jansson, 1991). The SOIL model has a one-dimensional vertical layered structure, and is based on two coupled partial differential equations describing water and heat transport derived from Darcy's law and Fourier's equation, respectively (Eckersten and Jansson, 1991). Standard weather data, soil physical and hydraulic properties, and plant characteristics are used as driving variables and inputs for the SOIL model. Soil hydraulic properties are described by the water retention characteristics curve in the form proposed by Brooks and Corey (1964), and the unsaturated hydraulic conductivity function based on Maulem's equation (Mualem, 1976). The SOIL model provides infiltration, surface runoff, vertical water flow, drainage, soil moisture, and temperature driving variables for the soil nitrogen model (SOILN). The SOILN model is a model simulating the daily N and C drainage fluxes in agricultural systems, including plant growth and N uptake. The SOILN model simulates N transformations as functions of soil water content and temperature, N leaching, and plant N uptake. The soil profile is divided into layers, each of which includes inorganic and organic N pools. The inorganic N pools are nitrate and ammonium. The organic N pools are divided into a litter pool consisting of undecomposed materials, a humus pool consisting of stabilized decomposed material, and a manure-derived feces pool. The N dynamics of litter and feces depend on C dynamics of the pools (Johnsson et al., 1987; Eckersten and Jansson, 1991).

We performed sensitivity analyses of SOIL-SOILN to identify the effect on the model output of changing the value of selected input parameters controlling the NO_3–N leaching and water drainage beyond the root zone. The SOIL model response was highly sensitive to saturated hydraulic conductivity and less sensitive to coefficients of Brooks-Corey's equation, air entry value, and residual water content. On the other hand, the SOILN was highly affected by humus specific mineralization rate, specific nitrification rate constant, and efficiency of internal synthesis of microbial biomass and metabolites parameters. The response of SOILN in terms of NO_3–N leaching was less affected by other remaining parameters. During model calibration and sensitivity analyses processes, several personal communications were made with Dr. Per-Erick Jansson, developer of SOIL-SOILN. Other details regarding the SOIL-SOILN model, equations, and estimation of the parameters, calibration, and sensitivity analyses are given in Johnsson et al. (1987), Eckersten and Jansson (1991), and Jansson (1991).

Model Evaluation Process

LEACHM, NCSWAP, and SOILN require a variety of input data, which include soil properties for each layer (initial water contents and soil water potentials, hydrological constants for water retentivity curve, chemical contents, and soil physical and chemical properties); soil surface boundary conditions (irrigation and rainfall amounts and rates of application); soil N transformation rate constants; environmental, hydrological, and weather data; and management information for the simulation site for each year. A lysimeter option was assigned for soil lower boundary conditions.

The input parameters used by the models were either measured, estimated, obtained from literature sources, or suggested by the models' developers (Hutson and Wagenet, 1992; Hutson, 2003; Molina and Richards, 1984; Clay et al., 1985a, 1985b; Molina et al., 1987; Johnsson et al., 1987; Eckersten and Jansson, 1991; Jansson, 1991; personal communications).

The LEACHM, NCSWAP, and SOILN models were run with the simulation period beginning in May of one year and continuing through April of the following year. An exception was 1992–1993 when the three models were executed with the simulation period beginning in May 1992 and ending in February 1993. Water drainage data were not collected in March and April 1993 due to flooded lysimeters resulting from melting of a heavy snowpack (Toth, 1996).

Model calibration was performed in terms of the simulative ability of the model to approximate the measured field values. The three models were calibrated to the field site conditions for each treatment using 1989–1990 data. The 1989–1990 data set was chosen for calibration because the environmental and weather conditions in 1989–1990 were normal and less extreme than the dry 1988 season in the 1988–1989 (Jabro et al., 1995). Model calibration is the process of adjusting model input parameters within expected values to minimize the difference between simulated and measured values. The first phase of calibration focused on small changes to the soil water flow parameters in the models. Calibration then focused on the input parameters controlling soil N transformation processes and rate constants in each of the three models (Tables 4, 5, 6, and 7). The input parameters given in Tables 4, 5, 6, and 7 determined through the calibration process were applied to the models. Each of the three models was then validated for its simulative capability and accuracy using 1988–1989, 1990–1991, 1991–1992, and 1992–1993 NO_3–N data by comparing model simulated NO_3–N leaching results against the mean of three replicated field measurements. The water drainage flux

Table 4. Input parameter values used in the LEACHM model during calibration.

N parameter†	Input value
Partition coefficient, NH_4–N, L kg^{-1}	3.0
Partition coefficient, NO_3–N, L kg^{-1}	0.0
Nitrification rate constant, d^{-1}	0.2–0.4
Denitrification rate constant, d^{-1}	0.02–0.08
Litter mineralization rate constant, d^{-1}	0.01
Manure mineralization rate constant, d^{-1}	0.02
Humus mineralization constant, 10^{-4} d^{-1}	0.3
Ammonia volatilization rate constant, d^{-1}	0–0.4
C to N ratio for biomass and humus	10
Q_{10} factor	2.0
Soil parameter‡	
Saturated hydraulic conductivity, mm d^{-1}	2184–40
Water potential, kPa	35–10
Retentivity parameters, Campbell's equation:	
Air-entry value, kPa	0.3–3
β parameter, kPa	7.8–18.7

† Values are within the range suggested by Hutson and Wagenet (1992) and Lotse et al. (1992).
‡ Represent the range of values within soil profile.

data are not included in this paper because it has been proved that the three models are capable of simulating annual water drainage fluxes below the 1.2-m depth from the continuous corn cropping system and has been published elsewhere (Jabro et al., 1998).

Model Accuracy and Performance

Several statistical methods were used to quantify how closely each of the three models' simulations matched the measured NO_3–N loss results (Smith et al., 1996). Linear regression equations were generated for the simulated and measured annual NO_3–N leaching values. The correlation coefficient (r) and comparison of the estimated intercept and slope with zero and one, respectively, were used as measures of the degree of association and coincidence between simulated and measured NO_3–N values. The null hypothesis of an intercept of zero and a slope of one was evaluated using a t test at the 0.05 probability level (Smith et al., 1996). The root mean square error (RMSE, Eq. [1]) provides a percentage for the total difference between simulated and measured values proportioned against the mean observed values (Smith et al., 1996). The lower limit for RMSE is zero, which denotes no difference between measured and simulated values. The RMSE can be used directly to compare the error in the simulations of different models (Smith et al., 1996). A smaller RMSE indicates a more accurate simulation. The modeling efficiency (ME, [Eq. 2]) is a measure for assessing the accuracy of simulations. The maximum value for ME is one, which occurs when the simulated values perfectly match the measured values (Smith et al., 1996). The mean difference (MD, [Eq. 3]) is a measure of the average difference between the simulated and the measured values for each year (Addiscott and Whitmore, 1987). A small, nonsignificant MD (H_0: MD = 0, $p > 0.05$) verifies statistically the accuracy of the model simulation. The MD can be positive or negative, the positive and negative signs indicate whether the model tends to overestimate or underestimate the measured values. A t test was used to check the null hypothesis that MD = 0 (Addiscott and Whitmore, 1987; Smith et al., 1996). These statistical measures were defined as:

$$\mathrm{RMSE} = \left[\frac{1}{n}\sum_{i=1}^{n}(M_i - S_i)^2\right]^{0.5} \times \left(\frac{100}{\overline{M}}\right) \qquad [1]$$

$$\mathrm{ME} = \frac{\sum_{i=1}^{n}(M_i - \overline{M})^2 - \sum_{i=1}^{n}(M_i - S_i)^2}{\sum_{i=1}^{n}(M_i - \overline{M})^2} \qquad [2]$$

$$\mathrm{MD} = \frac{\sum_{i=1}^{n}(S_i - M_i)}{n} \qquad [3]$$

where S is the model simulated value, M is the corresponding measured value, n is the number of measurements, MD is a

Table 5. Selected C and N input values used during calibration of the NCSWAP model for the surface soil horizon.

	Pool I	Pool II	Plant residue	Manure
	C to N ratio			
	6	6	40	20
Parameter description	N		C	
	mg kg^{-1}		kg ha^{-1}	
Initial content	12.5	60	1800–3200	1000–1500
Labile fraction	0.05	0.02	0.24	0.52
	Decomposition rate			
	d^{-1}			
Labile	0.33	0.04	0.045	0.30
Recalcitrant	0.16	0.007	0.001	0.04

Table 6. Water flow input parameters used during NCSWAP calibration.

Input parameter	Input value†
Saturated hydraulic conductivity, cm d^{-1}	21–4
Gravimetric water content, kg kg^{-1}, at:	
Saturation	0.44–0.31
Field capacity	0.21–0.29
Wilting point	0.18–0.13
Sand %	20–8
Clay %	21–40
Solute flow factor	0.8–1.0

† Represents the range of values within soil profile.

Table 7. Input parameter values used in the SOIL-SOILN model during calibration.

Parameter description	Input value
SOIL model†	
Saturated hydraulic conductivity, cm min^{-1}	0.15–0.0028‡
Pore size distribution index (Brooks–Corey equation)	0.19–12
Air-entry pressure, cm	20–3
Residual water content, m^3 m^{-3}	0.03–0.027
SOILN model	
Humus-specific mineralization rate, 10^{-4} d^{-1}	2–8‡
Litter-specific decomposition rate, d^{-1}	0.04
Manure-specific decomposition rate, d^{-1}	0.04
Litter carbon humification fraction, d^{-1}	0.12
C to N ratio of decomposer biomass	10
C to N ratio of humified products	10
Specific nitrification rate constant, d^{-1}	0.3–0.5‡
Q_{10}	2.0
C to N ratio of above ground residues	50
C to N ratios of roots	25
Denitrification potential rate, g N m^{-2} d^{-1}	0.06–0.1
Half saturation constant, mg L^{-1}	10
C to N ratio of manure	20
Fertilizer specific dissolution rate, d^{-1}	0.3
Efficiency of internal synthesis of microbial biomass and metabolites in manure	0.5‡

† Represents range values within soil profile.
‡ Parameters adjusted during calibration process. Model's output was highly sensitive to these parameters.

mean difference, and M is the mean of the measured data defined as:

$$\overline{M} = \frac{1}{n} \sum_{i=1}^{n} M_i \qquad [4]$$

In addition to the above statistical measures, model simulations were also assumed to be accurate if the predicted NO_3–N leached values fell within the 95% confidence intervals of the measured data (approximately ±2 standard error). Smith et al. (1996) have suggested that these statistical analyses are efficient for assessing model performance and accuracy, and for comparison among models.

RESULTS AND DISCUSSION

Model Accuracy Assessment

The LEACHM, NCSWAP, and SOILN simulations of NO_3–N leaching losses were compared with the mean of the lysimeter field measured values for each year. Each measured mean value of NO_3–N was calculated from three replications for each treatment.

Since the lysimeter measured NO_3–N leaching data were replicated, modeled annual NO_3–N values were compared to the 95% confidence interval (approximately ±2 standard error) of the annual field-measured data.

In the validation years (1988–1989, 1990–1991, 1991–1992, and 1992–1993), LEACHM accurately simulated NO_3–N leached below the 1.2-m depth for 8 of 10 cases (Table 8). The LEACHM annual simulated NO_3–N leaching losses fell within the 95% confidence interval of the measured values for these treatments (Table 8). However, the model inaccurately simulated the annual NO_3–N leached for the two control treatments in 1990–1991 and 1991–1992, indicating an inadequacy of LEACHM model for simulating these two treatments (Table 8).

The NCSWAP model provided good simulations of the annually measured NO_3–N leached below the 1.2-m depth under a continuous corn cropping system for all treatments in the validation years except for the control treatment in 1990–1991 (Table 8). The fact that NCSWAP annual simulated NO_3–N leaching losses fell within the 95% confidence interval of the measured values for 9 of 10 cases demonstrated a very satisfactory fit of the NCSWAP model predictions (Table 8).

The LEACHM and the NCSWAP models overestimated mass of NO_3–N leached for three control treatments in the validation years (Table 8). The simulation error in these treatments in 1990–1991 and 1991–1992 appeared to be related to the N-mineralization process in N submodels of LEACHM and NCSWAP models. Prior sensitivity analyses results showed that both models were sensitive to the N mineralization rate constant (Molina et al., 1983; Hutson and Wagenet, 1992; Lotse et al., 1992; Dou and Fox, 1995; Lengnick and Fox, 1994; Toth, 1996; Mahmood et al., 2002).

The SOILN model accurately simulated NO_3–N leaching masses for 7 of 10 cases (Table 8). The SOILN annual simulated NO_3–N leaching losses fell within 95% confidence interval of the measured values for these seven treatments (Table 8). However, the model appears to underestimate the annual mass of NO_3–N leached for the control and manure treatments in 1988–1989 and the control treatment in 1990–1991, demonstrating an inadequate fit of the SOILN simulations (Table 8). The cause of the simulation inaccuracy for the control and manure treatments in 1988–1989 and the control treatment in 1990–1991 could have resulted from using N mineralization rate constants determined during the calibration process. The humus-specific mineralization rate parameter might have affected the production of N and the amount of NO_3–N leached in all treatments. This is particularly true for treatments where amendments such as manure and organic materials are applied. The other input parameters that might have been the most sensitive for the manure treatment were the specific nitrification rate and efficiency of the internal synthesis of microbial biomass and metabolites.

Furthermore, it is surprising that the three models failed to produce accurate simulations of annual NO_3–N leaching losses beyond the corn root zone for the control treatment in 1990–1991 (Table 8). We have no obvious explanation for this unexpected modeling situation.

Despite discrepancies in the results of some treatments, the three water quality models were able to provide accurate simulations of annual NO_3–N leaching losses below the 1.2-m depth under corn for most treatments (7–9 cases of 10) in the validations years.

Table 8. Measured and simulated mass values of cumulative nitrate leached below the 1.2-m soil depth.

Year	Treatment†	Cumulative mass of NO_3–N leached: Measured (mean ± 95% CI)	Simulated: LEACHM	NCSWAP	SOILN
		kg ha^{-1}			
1988–1989	control	49.3 ± 10.7	42.2	54.9	28.1‡
	fertilizer	107.7 ± 44.2	87.2	94.9	80.5
	manure	70.6 ± 26	56.1	65.7	23.1‡
1989–1990	control	37.7 ± 20.1	42.5	46.3	38.4
	fertilizer	89 ± 38.1	95	82.8	89.1
	manure	60.3 ± 17.4	60.8	51.1	54.8
1990–1991	control	24 ± 6.8	47‡	43.6‡	13.1‡
	fertilizer	111.8 ± 47.4	120.3	100.9	71.3
	manure	41.8 ± 22.4	51.2	52.07	26.7
1991–1992	control	11 ± 2.9	14.1‡	12.1	9.2
	fertilizer	81.9 ± 13.8	77.8	93.2	74.9
1992–1993	control	4.3 ± 2.8	4.9	4.6	3.4
	fertilizer	25.8 ± 8.2	31.1	29.7	20.8

† Control = 0 kg N ha^{-1}, fertilizer = 200 kg N ha^{-1} as NH_4NO_3, manure = N supplied as dairy manure slurry containing 264, 132, and 158 kg total N ha^{-1} in 1988, 1989, and 1990, respectively.

‡ Simulated values are not within the 95% CI of the measured values.

Overall Performance and Comparison

Several statistical measures were used to assess and compare the overall performance and accuracy of NCSWAP, LEACHM, and SOILN models. The statistical measures (RMSE, ME, and MD) were computed between the overall measured and simulated NO_3–N leached for all 13 treatments and five years. The RMSE values were 10.7, 9.5, and 20.7 kg ha^{-1} and ME values were 0.90, 0.93, and 0.63 for LEACHM, NCSWAP, and SOILN, respectively. The RMSE values were small and ME values were somewhat large for all three models

Table 9. Overall performance and comparison statistics for three model simulations of NO_3–N losses (kg ha^{-1}).

Statistic†	LEACHM	NCSWAP	SOILN	Perfect‡ simulation
r	0.95	0.97	0.90	1
a	−3.19	−7.69	10.96	0
b	1.04	1.11	1.07	1
RMSE	10.7	9.5	20.7	0
ME	0.90	0.93	0.63	1
MD	−1.14	−1.29	−13.98*	0
	$t = -0.37$	$t = -0.47$	$t = 3.19$	
	$p = 0.72$	$p = 0.65$	$p = 0.0078$	

* MD is significantly different from zero.
† *r* = correlation coefficient, *a* = intercept, *b* = slope, RMSE = root mean square error, ME = modeling efficiency, MD = mean difference.
‡ Theoretical values when simulated results are the same as the measured.

(Table 9). Furthermore, the mean difference (MD) values between overall simulated and measured NO_3–N leached for LEACHM (MD = −1.14 kg ha^{-1}, $t = 0.37$, $p > 0.7156$) and NCSWAP (MD = −1.29 kg ha^{-1}, $t = 0.47$, $p > 0.6440$) were small, negative, and not significantly different from zero for these two models. However, the MD value for the SOILN model (MD = −13.98 kg ha^{-1}, $t = 3.19$, $p < 0.0078$) was larger, negative, and significantly different from zero compared to both LEACHM and NCSWAP models (Table 9). The overall accuracy and performance of SOILN was worse than the LEACHM and NCSWAP models.

Linear equations (Fig. 3, 4, and 5, and Table 9) were generated from the regression analysis of overall simulated NO_3–N leached obtained from the three models and measured values (SAS Institute, 2003). A high degree of association and coincidence between annual model simulated and measured NO_3–N leaching values is indicated by a high correlation coefficient, an intercept not significantly different from zero, and a slope not significantly different from one. Regression analysis indicated that slopes and intercepts of the three linear equations for LEACHM, NCSWAP, and SOILN models were not significantly different from one and zero, respectively, at $p > 0.05$ using a *t* test (Table 9). The correlation coefficients between overall models' simulated and measured values of NO_3–N leached were high and significant (Table 9).

Overall, the statistical results showed that LEACHM, NCSWAP, and SOILN have the potential to simulate annual NO_3–N leaching losses through a soil profile to a 1.2-m depth under corn. However, the statistical param-

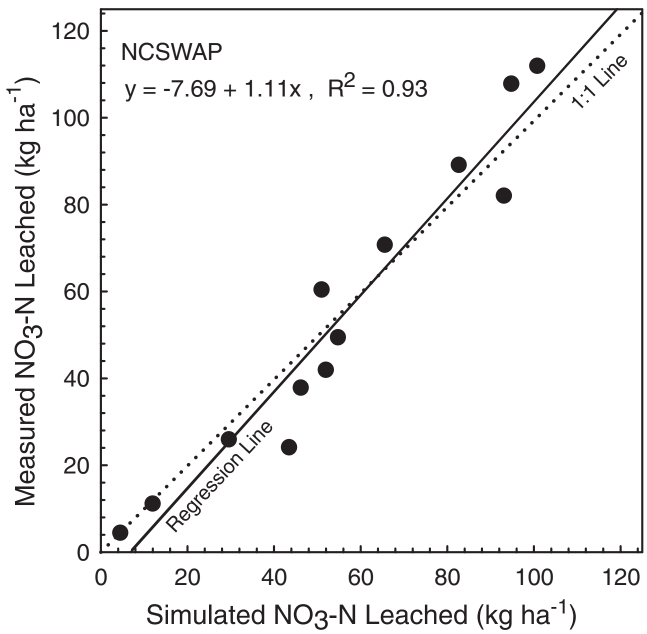

Fig. 4. Relationship between the overall measured and the models' simulated NO_3–N masses leached below 1.2 m for all five years and 13 treatments of NCSWAP.

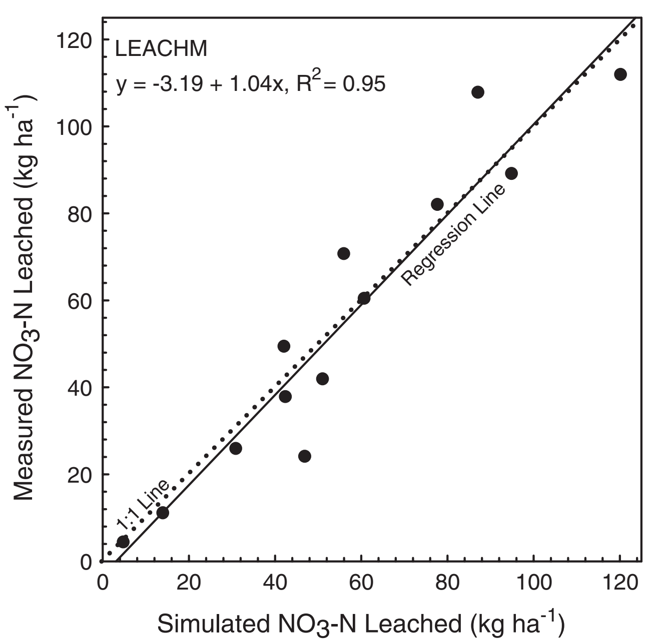

Fig. 3. Relationship between the overall measured and the models' simulated NO_3–N masses leached below 1.2 m for all five years and 13 treatments of LEACHM.

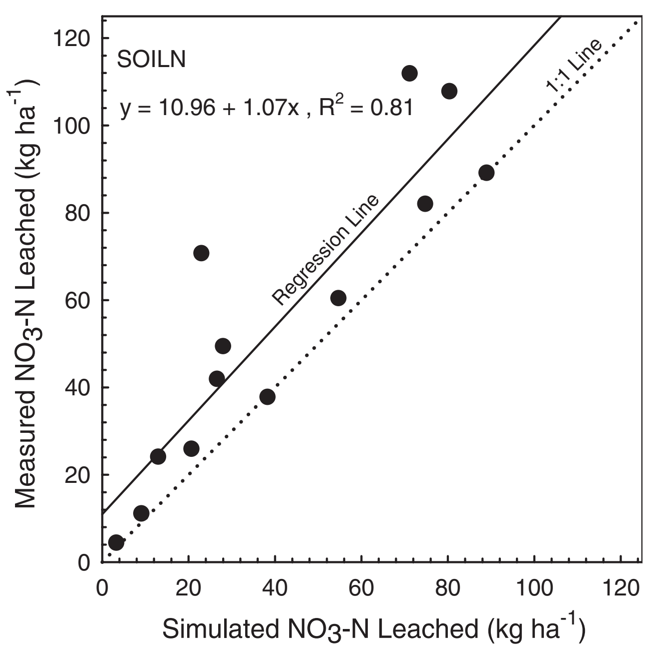

Fig. 5. Relationship between the overall measured and the models' simulated NO_3–N masses leached below 1.2 m for all five years and 13 treatments of SOILN.

eters (RMSE, ME, and MD) indicated that differences existed among these models in terms of their performances and abilities to produce accurate simulations of NO_3–N leaching. Both NCSWAP and LEACHM performed better than SOILN, based on measured versus simulated nitrate mass (Table 8) and statistical criteria (Table 9). Additionally, NCSWAP performed somewhat better than LEACHM, because it accurately simulated 9 out of 10 cases, compared with 8 out of 10 for LEACHM (Table 8).

The reason for the discrepancy among these models may be related, in part, to the simulations of N and C transformation and pools incorporated in the code of the models. Each of these three models uses different equations that govern water flow, N and C pools, cycling, and transformations in the soil, water, and plant system.

CONCLUSIONS

The capabilities of three water quality computer models LEACHM, NCSWAP, and SOILN to simulate NO_3–N leaching past 1.2 m from N-fertilized and manured corn were evaluated and compared. The annual, cumulative NO_3–N leaching losses were compared with the mean of the zero-tension pan lysimeter field-measured values for each year. Statistical analyses suggest that LEACHM, NCSWAP, and SOILN models were able to provide accurate simulations of total annual NO_3–N leached below the corn rootzone for 8, 9, and 7 of 10 cases, respectively, in the validation years. The overall performance and accuracy of SOILN model was worse than the LEACHM and NCSWAP models, as reflected by statistical results used in this study. The reason for the differences in modeling accuracy among the three models may be related, in part, to the simulations of N and C cycling and transformation incorporated in the code of the models.

Based on these modeling results, the three models were able to successfully simulate predictions of annual NO_3–N leaching losses below the 1.2-m depth under corn in the validation years without the need for model calibration from year to year.

Further field evaluation is needed using data from various soils, crops, weather, and management conditions to verify each of these models' application to real field conditions. If one of these models is validated with respect to its predictive capability, the model would be extremely helpful for decision makers who are responsible for managing and protecting our ground water and public health. The model may also be used as a means for evaluating water resources contamination threats and identifying management practices that reduce future losses of nitrate from agricultural lands to the ground water.

ACKNOWLEDGMENTS

The authors wish to acknowledge Dr. John Huston, Dr. J.A.E. Molina, Dr. Per-Erick Jansson, and Dr. H. Eckersten for providing the LEACHM, NCSWAP, and SOIL-SOILN program codes and manuals. We also thank the models' developers for their indispensable assistance and feedback during the models' simulation and calibration processes. The helpful suggestions of the Associate Editor, Dr. Thomas Nolan, the Technical Editor, Dr. Dennis Corwin, and three anonymous reviewers are appreciated.

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