Report as of FY2006 for 2005KS45B: "Fate of Nitrate Beneath Fields Irrigated with Treated Wastewater in Ford County, Kansas Using Field Data and Preferential Flow Modeling -- Year 2"

Publications

- Conference Proceedings:
  - Sophocleous Marios, Townsend, M.A., Willson, T., Vocasek, F., 2006. Fate of nitrate beneath fields irrigated with treated wastewater, Ford County, KS. 23rd Annual Water and the Future of Kansas Conference, Oral Abstracts, Topeka, KS, March 16, 2006.
- Other Publications:
  - Sophocleous, Marios, Townsend, Margaret, A., 2006. Fate of nitrate beneath fields irrigated with treated wastewater, Ford County, KS. Hydrogeology-In-Progress seminar, Department of Geology, University of Kansas, Lawrence, KS, March 8, 2006.
  - Sophocleous, Marios, 2006. Preferential flow and transport of nitrate beneath treated wastewater-irrigated fields. Kansas Geological Survey Advisory Council, Lawrence, KS, March 31, 2006.

Report Follows

Treated Wastewater and Nitrate Transport Beneath Irrigated Fields near Dodge City, Kansas

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Keywords: wastewater fertigation; dye tracer; macropores; RZWQM model; sensitivity analysis; nitrogen use efficiency; nitrogen management scenarios

Table of Contents

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1. Problem and Research Objectives

With increasingly limited ground-water resources, reuse of treated wastewater provides an alternative source of water for irrigation of crops and landscaping. In addition, utilization of the nutrients in recycled wastewater as fertilizer results in less application of fertilizer to a plant system.

A long-term irrigation project using treated municipal wastewater has been ongoing south of Dodge City in Ford County since the mid-1980s (Fig. 1). The Dodge City Wastewater Treatment Plant (DCWTP) consists of three covered anaerobic digesters and three aeration basins. The treated water is stored in storage lagoons with a capacity of more than 2800 acre-ft. A pumping system, consisting of several electric, centrifugal pumps distributes the water to irrigate more than 2700 acres of cropland in 25 fields (Fig. 1). The system is managed by Operations Management International (OMI) and the agronomic firm Servi-Tech, Inc., under contracts with the City.

Use of the treated wastewater, which includes inputs from both the municipality of Dodge City and its meat-packing plant, has resulted in relatively high soil nitrate-nitrogen concentrations (10–50 mg/kg) in the soil profile at the sites irrigated with this treated wastewater effluent as well as in nitrate-nitrogen concentrations in ground water from monitoring wells in the area exceeding the safe drinking-water limit of 10 mg/L (Zupancic and Vocasek, 2002). Evaluation of the environmental impact of such land-use strategies needs to be made in order to determine if and when this process may impact usable ground water at depth and what management changes may need to be made to slow the downwards nitrogen (N) migration.

The study area overlies the High Plains aquifer with depth to water in the range of 75 to 150 ft. The overlying soils are predominantly Harney and Ulysses silt loams (Dodge et al., 1965). Although this area has a deep water table and soils with a silty clay component, there is evidence that nitrate is migrating to those depths through the vadose zone. USGS National Water-Quality Assessment and other studies in the central High Plains aquifer region indicate that nitrate from fertilizer sources and animal waste has reached the Ogallala portion of the High Plains aquifer most likely due to increased recharge from irrigation but also because of preferential flow processes (U.S. Geological Survey, 2004).

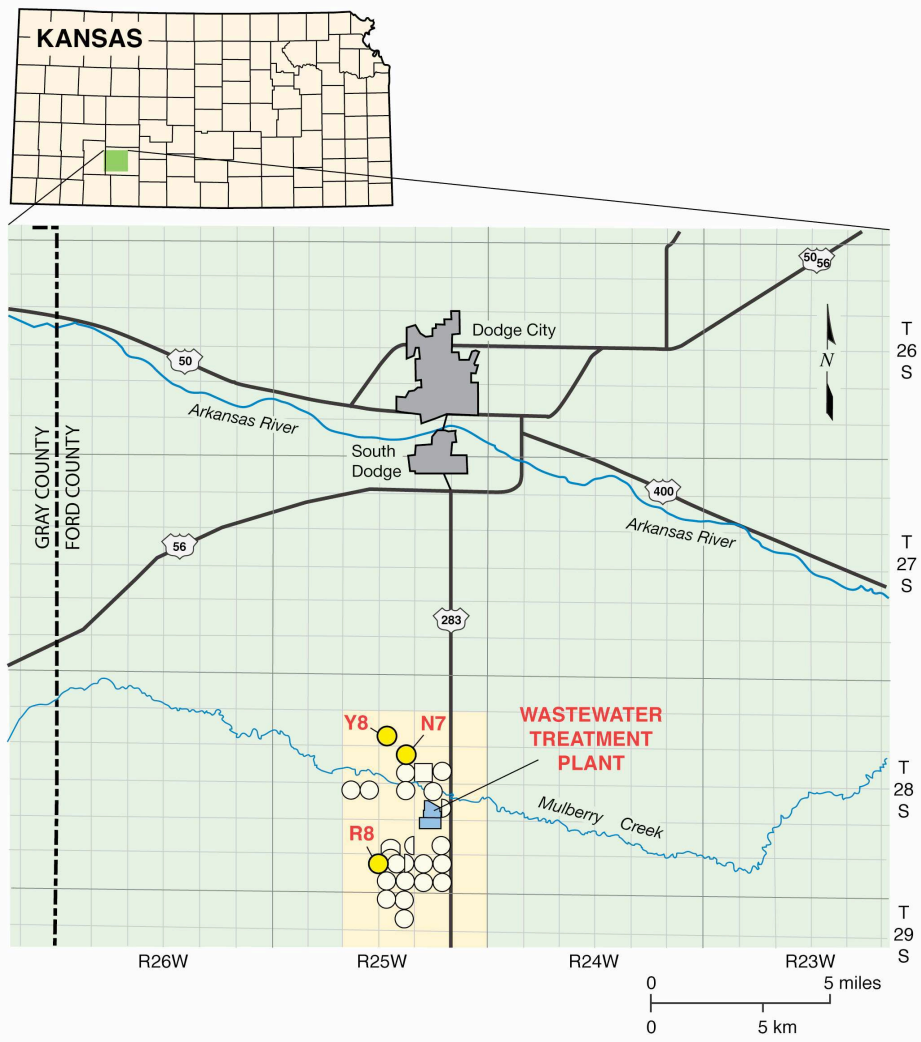


Figure 1. Location of the study area. Circular areas indicate irrigated fields.

It is now generally recognized that preferential flow occurs to some degree in most soils (Shipitalo and Edwards, 1996). In some soils, macropores can serve as important pathways for preferential flow that allow rapid gravitational flow of the free water available at the soil surface or above an impeding soil horizon, thus bypassing the soil matrix. Short-circuiting to ground water through macropores is of serious concern because of the possibilities of rapid transport of a portion of fertilizers, pesticides, and other chemicals applied on the soil surface. As macropore development, preservation, and continuity can be strongly affected by soil management, such concerns have been exacerbated by the growing practice of minimum or no tillage, which (1) allows chemical solutes in surface water applied on the soil to accumulate and to enter macropores at the surface, and (2) leaves plant residues on the surface as well as no tillage also enhancing worm activity and allowing worm holes and other macropore channels to stay open at the surface (Ahuja et al., 1993).

Therefore, the objectives of this project are

1) to conduct field sampling and other analyses to study and document the impact of treated wastewater irrigation in the area south of Dodge City; and

2) to employ sophisticated numerical modeling of N fate and transport that also account for preferential flow to identify key parameters and processes that influence N losses, thus facilitating evaluation of the environmental impact of different land-use practices.

2. Methodology

2.1 Field Monitoring/Field Experiments

To analyze this nitrogen-leaching problem further, we established two main monitoring sites, one in each of the two major loess-derived soil series in the project area, the Harney and the Ulysses soils (Fig. 2; the Harney silt loams are the bluish and greenish colors in the slide, whereas the Ulysses silt loams are the reddish and purplish colors). One of the sites, the R8 in Harney soils, has a long-term treated wastewater irrigation history (since 1986), whereas the other site, N7 in Ulysses soils, has a short-term treated

wastewater irrigation history (since 1998). In addition, a third, control site, Y8, without any wastewater irrigation record, has also been established (Fig. 2). Crop-history records indicate that corn (Zea mays L.) was planted at site N7 each year since 1998, and at site R8 since 2003. From 1997 to 2002, site R8 was planted in alfalfa (Medicago sativa). During 2005, sites N7 and R8 were planted in corn, whereas site Y8 was planted in sorghum (milo). During 2006, all three sites were planted in corn.

We collected several deep cores, down to 15.2 m, from each of the sites for a number of physical and chemical analyses using a truck-mounted Giddings probe. The textural, soil hydraulic, and additional physical and chemical analyses were performed by NRCS personnel at the Lincoln, NE, National Soils Laboratory. Core nitrogen and carbon and related analyses were conducted at the KSU and Servi-Tech Soil Analysis Laboratories. Tables and figures of analyzed values are presented in Sophocleous et al. (2006) and are summarized by model simulation layer in section 2.3.

The soil bulk density down to 15.2 m was determined from collected cores of known diameter by cutting the core in 15.2-cm (6-inch) increments, weighing them in the field, and then oven-drying them in the lab. For a smoother bulk density profile estimation, a three-consecutive 15.2-cm core-sample moving average was obtained down to 15.2 m.

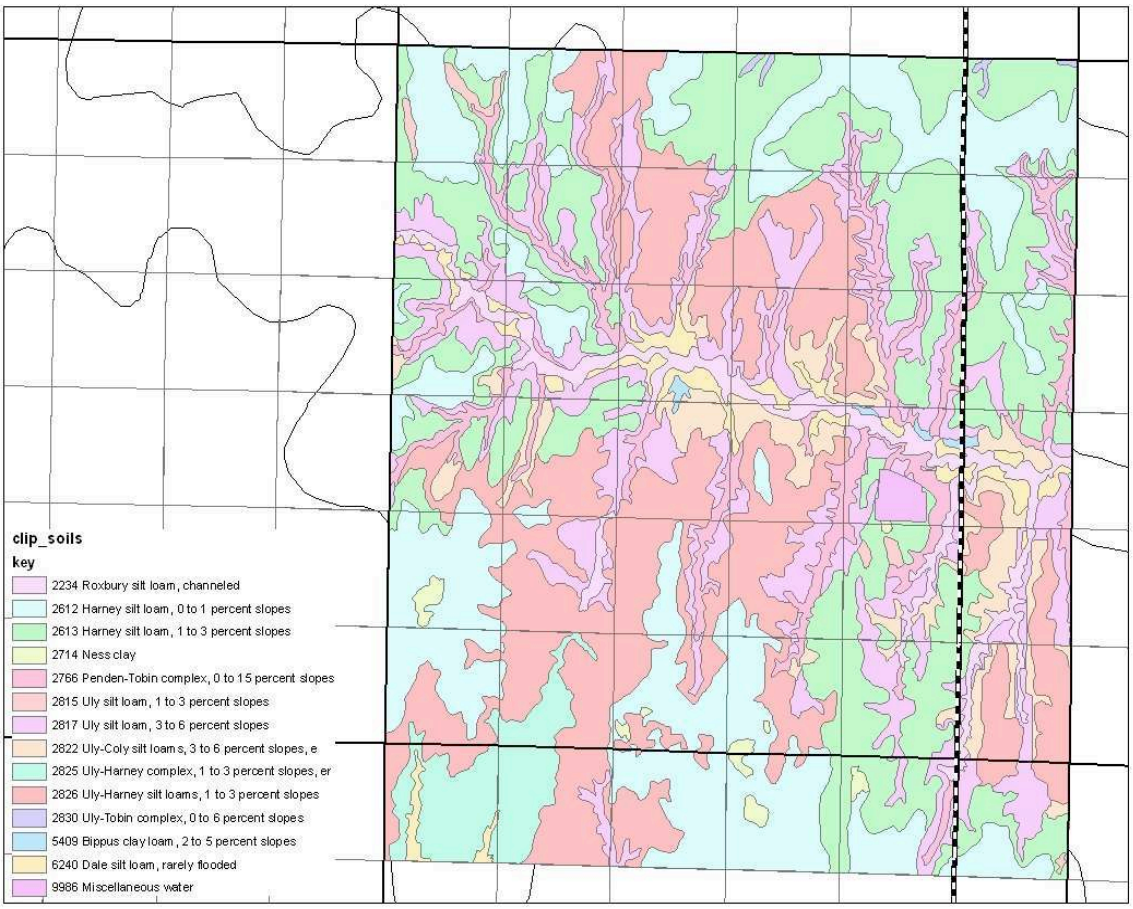


Figure 2. Map of soils in Ford County at study sites (data downloaded from the NRCS Geospatial Data Gateway at http://soildatamart.nrcs.usda.gov).

A neutron probe (Campbell Pacific Nuclear (CPN) 503DR Hydroprobe) is used to collect moisture-data profiles to 15.2-m depth. Aluminized steel pipe was used for the neutron probe access tube. The neutron probe was calibrated in the field as follows: a 15.2-m hole was cored with the Giddings probe, and the access tube was snuggly inserted down the hole. The collected core was cut in 15.2-cm increments, weighed in the field, and taken to the Servi-Tech, Inc., soils lab for oven-drying and re-weighing. Following access-tube installation, neutron profile readings were taken in 15.2-cm increments within the root zone (180 cm) and in 30.48-cm increments from the bottom of the root zone to 15.2 m. At each site, two field corner (180- by 180-cm) plots were selected as additional calibration plots in which a 305-cm access was installed in each. One plot was used for the neutron-moisture calibration at the dry end-end of the moisture range, whereas the other plot was periodically wetted by applying measured amounts of water

for neutron probe calibration at the wet end of the moisture range. Periodically, 244-cm-long cores were collected from within the corner, calibration plots were done with the Giddings probe, and moisture content was calculated by oven-drying for comparison with neutron readings. Additional details of neutron access tube installation and probe calibration are presented in Sophocleous et al. (2006). Periodic measurements of neutron probe-based soil water content down to 15.2 m were conducted throughout the growing seasons for 2005 and 2006.

A small number of suction lysimeters were also installed in all sites at various depths, mainly at shallow (152–183 cm) and intermediate depths (518–793 cm) for occasional analyses of pore waters.

We also sampled most of the existing monitoring wells in the area (shown in Fig. 9) to check any impacts on the relatively deep water table, which ranges from about 21 m close to Mulberry Creek to more than 45 m deep as one goes away from the usually dry Mulberry Creek (Fig. 1). Additional water samples from monitoring, domestic, and irrigation wells and wastewater lagoons were periodically collected by OMI and occasionally KGS personnel.

To explain deep occurrences of nitrogen concentrations through possible preferential pathways, we conducted two dye-tracer experiments in each of the two major soil types in the study area in which we established our study sites (site R8 in Harney soil, and site N7 in Ulysses soil). A literature search for a suitable dye tracer (Flury and Fluhler, 1994, 1995; Flury et al., 1994; Petersen et al., 1997; Schwartz et al., 1999; Flury and Wai, 2003) revealed that the brilliant-blue food-coloring dye (FD&C Blue 1, tri-phenyl-methane dye) would be a suitable tracer because of its desirable properties of mobility and distinguishability in soils, and also because of its non-toxicity.

The steps we followed in conducting the dye-tracer tests at sites R8 and N7 are as follows: we rented a 3785-liter (1000-gallon) water tank and filled it with 1514 liters (400 gallons) of water. We then added a carefully pre-weighted total quantity of 6,056.7 grams

of brilliant-blue powder dye (3,028.4 grams per 757 liters {200 gallons} of water) and mixed it well to obtain a dye concentration of 4 g/L (which was also employed in the studies cited above). We prepared two 91.4-cm by 152.4-cm (3-ft by 5-ft) wooden rectangular frames of 91.4-cm height for flooding the sites with the dye solution as shown in Figure 3.

Figure 3. Wooden rectangular frame for flooding the site with dye solution.

2.2 Numerical Model Employed

The USDA-ARS developed a Root Zone Water Quality Model (RZWQM), which is a comprehensive agricultural systems model intended as a research tool to investigate the effects of agricultural management on crop production and environmental quality (Ahuja et al., 2000). The RZWQM is an integrated physical, biological, and chemical process model that simulates plant growth, and the movement and interactions of water, nutrients, and pesticides over and through the root zone at a representative area of an

agricultural cropping system. It is a one-dimensional (vertical into the soil profile) model designed to simulate conditions on a unit-area basis.

The reasons we chose to evaluate the RZWQM model are because, in addition to having been extensively tested nationally and internationally (Ahuja et al., 2000; Abrahamson et al., 2005; Malone et al., in press), it contains special features of interest to this study, such as macropore flow as well as an exchange component between the soil matrix and macropore walls; a wide variety of management effects, such as evaluation of conservation tillage, residue cover and conventional tillage, methods and timing of water applications as well as fertilizer and pesticide applications, and different crop rotations; and a user-friendly interface that can be initially set up with a minimum dataset using readily available data, as well as other features.

The RZWQM consists of six subsystems or processes that define the simulation program: 1) physical processes 2) soil chemical processes 3) nutrient processes 4) pesticides processes 5) plant growth processes and 6) management processes. Information about the RZWQM processes is calculated at daily and sub-hourly time scales as shown in Figure 4.

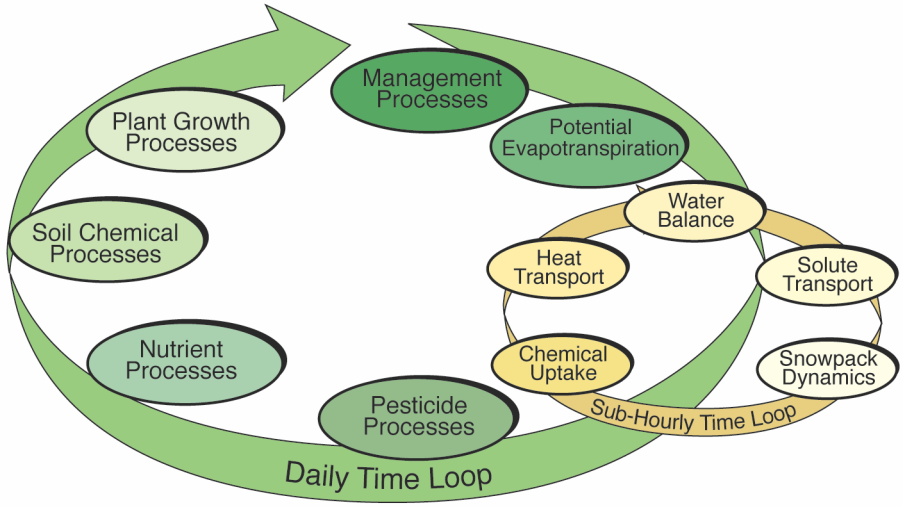


Figure 4. Execution sequence for RZWQM (adapted from Ahuja et al., 2000).

Management effects on the system (such as tillage, addition of chemicals or irrigation water) are calculated first. A daily estimate of potential ET is then determined (based on an extended Shuttleworth-Wallace potential ET module (Farahani and Ahuja, 1996) that considers the effects of surface-crop residue cover on soil evaporation and partitions evaporation into the bare soil and residue-covered fractions) so that the evaporation and transpiration fluxes can be applied to the soil surface and plant roots, respectively.

The sub-hourly time loop is then executed to calculate the transport and fate of the water-controlled processes. These processes include infiltration and runoff, soil water distribution, chemical transport, actual evaporation and transpiration, plant nitrogen uptake, and others.

The water flow processes in the RZWQM are divided into two phases: 1) infiltration into the soil matrix and macropores and macropore-matrix interaction during a rainfall or an irrigation event, modeled by using the Green and Ampt approach; and 2) redistribution of water in the soil matrix following infiltration, estimated by a mass-conservative numerical solution of the Richards' equation. Rainfall or irrigation water in excess of the soil-infiltration capacity (overland flow) is routed into macropores if present. The maximum macropore flow rate and lateral water movement into macropores in the surrounding soil are computed using Poiseuilles' law and the lateral Green-Ampt equation, respectively. Macropore flow in excess of its maximum flow rate or excess infiltration is routed to runoff. In the RZWQM, water can only enter the macropores at the surface. High-intensity rainfalls generally yield greater water flow and chemical transport in macropores than low-intensity rainfalls (Shipitalo and Edwards, 1996), and this is true with the RZWQM as well.

Continuing along the daily loop, pools of carbon and nitrogen are transformed by the nutrient processes (Ma et al., 1998). The soil carbon/nitrogen dynamics module of the RZWQM model (Hanson et al., 1999) contains two surface residue pools (fast and slow decomposition), three soil humus pools (slow, medium, and fast decomposition),

and three soil microbial pools (aerobic heterotrophs, autotrophs, and anaerobic heterotrophs). It simulates N mineralization, nitrification, denitnification, ammonia volatilization, urea hydrolysis, methane production, and microbial population. These processes are functions of soil pH, soil O_2, soil microbial population, soil temperature, soil water content, and soil ion strength. Despite the complexity of this organic matter/N-cycling component, good estimates of initial soil carbon content and nitrogen are generally the only site-specific parameters needed. The required inputs (e.g. fast pool, slow pool) are then usually determined through an initiation wizard and calibration.

Finally, after accounting for all the physical and chemical changes to the system throughout the day, the plant-growth processes determine crop production. The RZWQM has a generic plant-growth component that can be parameterized to simulates different crops. Both individual plant growth through seven phenological growth stages (dormancy, germination, emergence, 4-leaf plant, vegetative growth, reproductive growth, and senescence), and population development (controlled by the Leslie matrix {Hanson, 2000}) are simulated. The RZWQM also provides a second option submodel for simulation of crop growth referred to as the Quickplant model. However, Quickplant is not a detailed growth model, and it is recommended (Ahuja et al., 2000) that it only be used when simulating crop production is not the primary aim of the modeler. Details on all aspects of the model can be found in Ahuja et al. (2000).

As mentioned previously, the RZWQM is a research-grade complex tool that was designed to analyze soil and plant processes only within the root zone. However, for our application, we had to modify and extend the RZWQM to deal with deeper vadose-zone processes, and in discussing this extension with the RZWQM developers in the Agricultural Research Service Systems-Research Unit in Fort Collins, CO, ours may be the first RZQWM application to depths beyond the root zone. Soil-horizon depths are converted to a numerical grid with a maximum thickness of 5 cm and 1 cm for the top soil layer. These numerical layers are used for solving the Richards equation during redistribution. During infiltration, 1-cm soil layers are used for the Green-Ampt equation (Ahuja et al., 2000). This model can simulate a soil profile of up to 30 m. A unit gradient

was assumed for the lower boundary condition at 10.8 m for site N7 and 4.84 m for site R8.

2.3 Outline of Some Model Input Requirements

To simulate the transport of water and chemicals, the soil profile must be well defined in its depth, horizon delineation, physical properties (bulk density, particle density, porosity, and texture), and hydraulic properties. A detailed description of site soil horizons and related physical and chemical properties is presented in Sophocleous et al. (2006). Because of model limitations, we had to combine a number of soil horizons into a maximum of 10 layers. The soil physical properties by layer used as initial conditions for model simulations {based on NRCS National Soils Lab (Lincoln, NE)-analyzed soil-core measurements that were presented in Sophocleous et al. (2006)} are shown in Tables 1 and 2 for sites N7 and R8, respectively.

The hydraulic properties are defined by the soil water characteristic or retention curves, and the unsaturated hydraulic conductivity function. Those relationships are described by functional forms suggested by Brooks and Corey (1964) with slight modifications (Ahuja et al., 2000).

The volumetric soil water content (θ) versus the capillary pressure head or matric suction head (ψ) relationship representing the water retention or characteristic curve is formulated as follows:

$$\theta(\psi) = \theta_s - A_1 | \psi | \text{ for } \psi \leq \psi_a \quad (1)$$

$$\theta(\psi) = \theta_r + B | \psi |^{-\lambda} \text{ for } \psi > \psi_a \quad (2)$$

where θ_s and θ_r are the saturated and residual soil-water contents (cm^3/cm^3), respectively; ψ_a is the air-entry or bubbling suction head (cm); λ is the pore-size distribution index (and represents the logarithmic slope of the water retention curve); A_1 and B are constants, where $B = (\theta_s - \theta_r - A_1\ \psi_a)\ \psi_a^{\lambda}$ and A_1 was set to zero in our case, thus reducing equations (1) and (2) to the Brooks and Corey (1964) model. Figure 5

displays a schematic of a typical soil-water retention curve with a number of the above-mentioned parameters indicated.

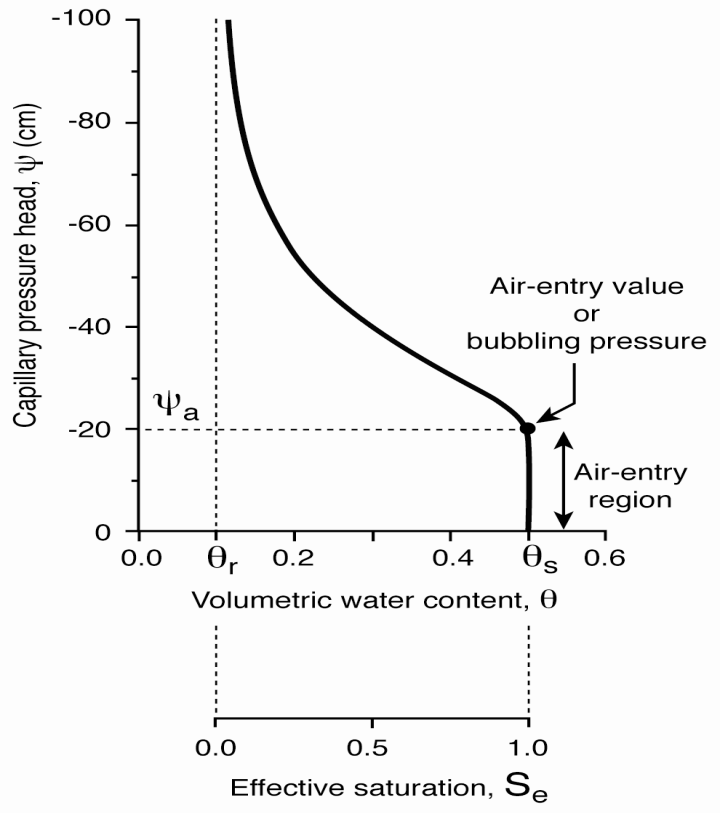


Figure 5. Schematic of a typical soil-water retention curve.

The hydraulic conductivity (K) versus matric suction head (ψ) relationship representing the unsaturated hydraulic conductivity function is formulated as follows:

$$K(\psi) = K_s \, |\psi|^{-N_1} \quad \text{for } \psi \le \psi_a \tag{3}$$

$$K(\psi) = K_2 \, |\psi|^{-N_2} \quad \text{for } \psi > \psi_a \tag{4}$$

where N_1, N_2, and K_2 are constants and $K_2 = K_s \, |\psi_a|^{-N_2}$, $N_2 = 2 + 3\lambda$, and N_1 was set to zero in our case, thus reducing equations (3) and (4) to the Brooks and Corey (1964) model, where the effective saturation, S_e is defined as

$S_e = (\theta - \theta_r)/(\theta_s - \theta_r)$

Table 1. Soil physical properties for site N7 by layer based on measurements by the NRCS National Soils Lab (Lincoln, NE) that are presented in Sophocleous et al. (2006)

Layer	Soil Type	Horizon Depth (cm)	Bulk Density (g/cm^3)	Porosity[a]	Sand fraction	Silt fraction	Clay fraction	K_s[b] (cm/hr)	1/3-bar W.C.[c]	1/10-bar W.C.[c]	15-bar W.C.[c]
1	Silty loam	0-23	1.280	0.517	0.056	0.686	0.258	1.3163	0.2260	0.3637	0.1305
2	Silty clay loam	23-74	1.470	0.445	0.027	0.621	0.352	0.3911	0.2540	0.4037	0.1690
3	Silty clay loam	74-168	1.300	0.509	0.033	0.624	0.343	0.7268	0.2710	0.4037	0.1617
4	Silty clay loam	168-221	1.240	0.532	0.114	0.558	0.328	0.9829	0.2390	0.4037	0.1410
5	Silty clay loam	221-363	1.380	0.479	0.115	0.554	0.331	0.2266	0.2070	0.3742	0.1215
6	Silty clay loam	363-625	1.420	0.464	0.090	0.610	0.300	0.5431	0.2340	0.4037	0.1185
7	Silty loam	625-848	1.350	0.491	0.126	0.631	0.243	0.7048	0.2855	0.3637	0.1070
8	Silty loam	848-889	1.380	0.479	0.141	0.638	0.221	0.6966	0.2855	0.3637	0.1260
9	Silty loam	889-945	1.410	0.468	0.267	0.513	0.220	0.6966	0.2480	0.2961	0.0960
10	Loam	945-1079	1.520	0.426	0.344	0.416	0.240	0.1463	0.2335	0.2961	0.1015

[a] calculated assuming a particle density of 2.65 g/cm^3

[b] saturated hydraulic conductivity (K_s)

[c] soil water content (W.C.)

Table 2. Soil physical properties for site R8 by layer based on measurements by the NRCS National Soils Lab (Lincoln, NE) that are presented in Sophocleous et al. (2006)

Layer	Soil Type	Horizon Depth (cm)	Bulk Density (g/cm3)	Porosity[a]	Sand fraction	Silt fraction	Clay fraction	K_s[b] (cm/hr)	1/3-bar W.C.[c]	1/10-bar W.C.[c]	15-bar W.C.[c]
1	Silty clay loam	0-16	1.420	0.464	0.041	0.643	0.316	0.4480	0.4463	0.4037	0.2107
2	Silty clay loam	16-29	1.490	0.438	0.036	0.659	0.305	0.4452	0.4216	0.4037	0.2107
3	Silty clay loam	29-50	1.280	0.517	0.023	0.599	0.378	0.1553	0.4928	0.4037	0.2107
4	Silty clay	50-68	1.210	0.543	0.017	0.553	0.430	0.0890	0.5182	0.4251	0.2513
5	Silty clay loam	68-90	1.260	0.525	0.021	0.592	0.387	0.2799	0.5002	0.4037	0.2107
6	Silty clay loam	90-140	1.520	0.426	0.030	0.627	0.343	0.8501	0.4280	0.4037	0.2107
7	Silty clay loam	140-260	1.620	0.389	0.152	0.502	0.346	0.3237	0.4049	0.3890	0.2107
8	Silty clay loam	260-300	1.610	0.392	0.194	0.483	0.323	0.1543	0.3806	0.3920	0.2107
9	Clay loam	300-410	1.530	0.423	0.217	0.494	0.289	0.2968	0.4230	0.3742	0.1882
10	Silty clay loam	410-484	1.540	0.419	0.188	0.496	0.316	0.1308	0.4380	0.4037	0.2107

[a] calculated assuming a particle density of 2.65 g/cm^3

[b] saturated hydraulic conductivity (K_s)

[c] soil water content (W.C.)

The RETention Curve (RETC) computer program (van Genuchten et al., 1991) for describing the hydraulic properties of soils as well as the neural network program ROSETTA (Schaap et al., 2001) were employed to fit the parameters for several analytical models such as the Brooks and Corey (1964) and van Genuchten functions (van Genuchten, 1980) to experimentally measure water retention and hydraulic conductivity data for input into the RZWQM. (The correspondence of the van Genuchten parameters α and n to the Brooks and Corey parameters ψ_a and λ is as follows: $\alpha = 1/\psi_a$, and $n = \lambda + 1$.)

The model also requires detailed meteorological data on a daily basis, and rainfall data in breakpoint increments. Hourly precipitation and other meteorological data (except for solar radiation) were obtained from the Dodge City Municipal Airport weather station, some 17 km northeast of the study sites, whereas daily solar radiation data were obtained from the Garden City Agricultural Experiment Station some 80 km west-northwest of Dodge City, operated by Kansas State University. The model also requires specification of land-use practices such as planting and harvesting dates, specification of irrigation and fertilization events, as well as the chemical quality of irrigation. The daily precipitation and irrigation events during the 2005 irrigation season for site N7 are shown in Figure 6.

The physically based nature of RZWQM necessitates a good deal of data from the user to adequately parameterize and initialize the model. From experience, users do not have enough data to completely describe the state of an agricultural cropping system. To facilitate use of the model, the RZWQM allows for input options where certain parameters are estimated from easily determined soil properties (e.g., soil texture) or obtained from default value tables if measured data are not available.

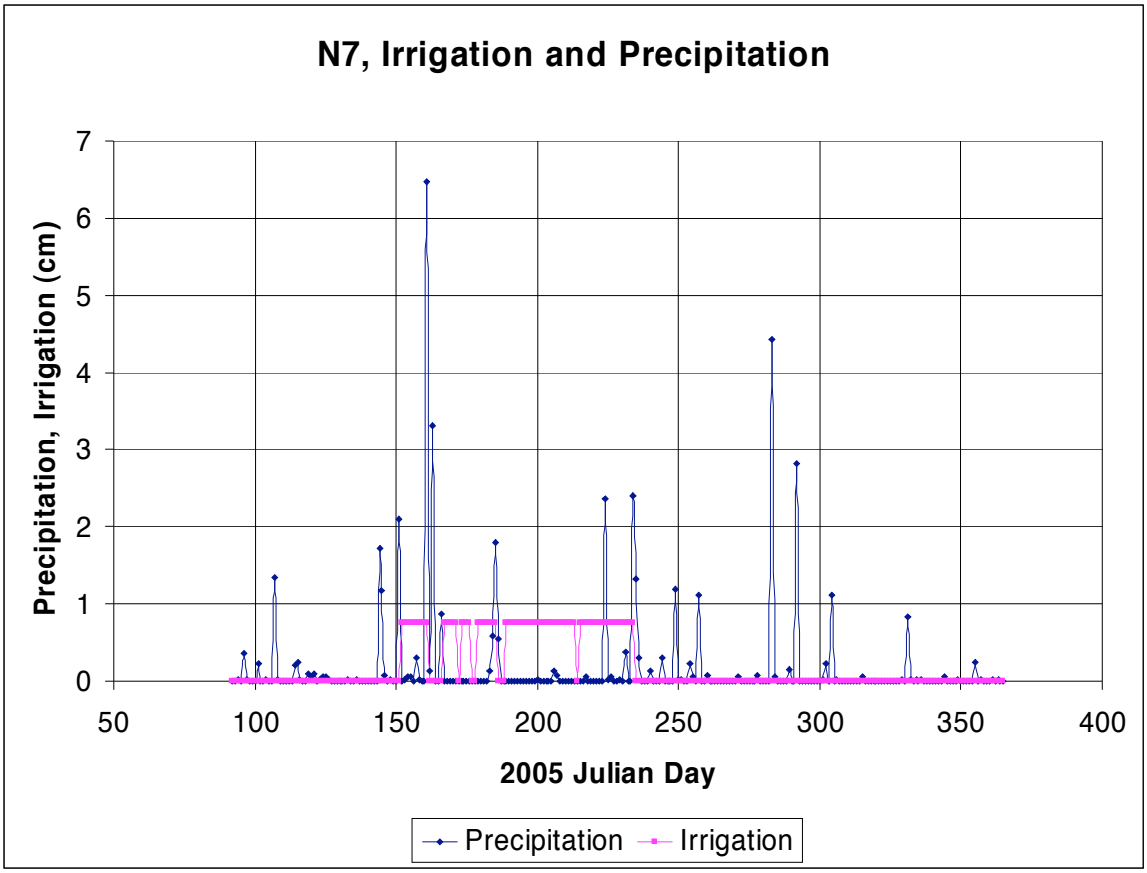


Figure 6. Daily precipitation and irrigation events during the 2005 irrigation season at site N7.

2.4 Model Calibration Procedures

2.4a General Procedures

For accurate simulations, RZWQM must be calibrated for soil hydraulic properties, nutrient properties, and plant-growth parameters for the site and crops being simulated (Hanson et. al., 1999), as there are significant interactions among the different model components. The number of parameters and processes in the RZWQM are so numerous that it is exceedingly difficult to decide which ones to optimize and what optimization scheme might be appropriate, if at all feasible. As a result, such agricultural system models as the RZWQM are usually parameterized by trial-and-error or iterative processes (Ahuja and Ma, 2002). In this report, we followed the detailed procedures for calibrating the RZWQM as laid out by Hanson et al. (1999) and Ahuja and Ma (2002).

The model requires establishment of initial C/N pool sizes for the fast and slow decomposition residue pools; slow, medium, and fast decomposition humus pools; and the three microbial pools (aerobic heterotrophs, autotrophs, and anaerobic heterotrophs) (Hanson et al., 1999). No laboratory procedures were known to effectively determine the sizes of these pools (Ahuja and Ma, 2002). Therefore, because previous management at a site determines the initial state of a soil in terms of its organic matter and microbial populations, simulations with previous management practices will usually create a better initial condition for these parameters (Ma et al., 1998). After entering all the model inputs and parameters, we began by estimating the three humus organic-matter pool sizes (based on measured organic-carbon depth profiles) at 5, 10, and 85%, respectively, for fast, medium, and slow pools and set the microbial pools at 50,000, 500, and 5000 organisms per gram of soil, respectively, for aerobic heterotrophs, autrotrophs, and facultative heterotrophs, as recommended by Ahuja and Ma (2002). RZWQM was initialized for the organic-matter pools by running the model for 12 years prior to the 2005-06 actual simulation periods. A 12-year initialization run was suggested by Ma et al. (1998) to obtain steady-state conditions for the faster soil organic pools. The only parameters that we adjusted after the initialization procedure were the soil nitrate and soil ammonium nitrate for the analysis period (2005-06) as we had available measured values of those quantities from the sites before corn was planted in the spring of 2005.

2.4b Sensitivity Analysis

To identify key model parameters and sources of simulation errors resulting from parameter uncertainty, we conducted extensive sensitivity analysis. A sensitivity analysis is usually done by varying (perturbing) model parameter values around their base values independently. The range of the perturbation may be a specific percentage around a base value (Walker et al., 2000; Ma et al., 2000).

Different sets of model input parameter groups were perturbed, such as 1) hydraulic properties 2) organic matter/nitrogen cycling parameters 3) plant-growth parameters, and 4) irrigation water and fertilization rates. The purpose is to identify key

(sensitive) model input parameters under western Kansas conditions in terms of corn production and NO_3-N leaching, so as to guide calibration and measurement efforts.

2.4c Calibration Strategy

Following the sensitivity analysis, which identified the most sensitive or critical parameters affecting model output, the model calibration strategy we adopted was as follows: the RZWQM was first calibrated for soil hydraulic properties by adjusting one or more of the most sensitive hydraulic parameters from the sensitivity analysis, then for the N-nutrient properties as outlined in the "General Procedures" section, and finally for the plant-growth parameters for the site and crops being simulated. Because plant production was part of the N balance and tightly coupled to the other processes, we followed the procedure for calibrating plant growth recommended for the model by Hanson (2000) when using the generic plant-growth submodel. This procedure is based on adjustments to five relatively sensitive plant parameters (see also section 3.4 on sensitivity analysis results further on for additional explanations) including active N uptake rate (μ_l), the proportion of daily respiration as a function of photosynthesis (Φ), the specific leaf density, i.e., the biomass to leaf area conversion coefficient (C_{LA}), and the age effect for plants during the propagule stage and the seed-development stage (A_p and A_s). We based adjustments of these parameters for corn within the range of values used for calibration of the Management Systems Evaluation Areas (MSEA) sites in the midwestern USA (Hanson, 2000). Because the nitrogen-related and plant-growth parameters are difficult to measure with independent experiments, an accurate description of the water-related processes is required to minimize N-simulation errors.

Calibration targets were the measured-profile soil water contents using the neutron probe and the core-sampled nitrate profiles. Field measurement errors are typically >10%; therefore, it is unrealistic to match the observed data any more closely (Hanson et al., 1999). Both qualitative and quantitative methods were used to evaluate the model. Three statistics were used to evaluate the simulation results: (i) root mean squared error (RMSE) between simulated and observed values, eq. (5); (ii) relative root

mean square error (RRMSE), i.e., RMSE relative to the mean of the observed values, eq. (6); and (iii) mean relative error (MRE) or bias, eq. (7).

$$\text{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(S_i - O_i)^2} \quad (5)$$

$$\text{RRMSE} = \text{RMSE} \times \frac{100\%}{O_{avg}} \quad (6)$$

$$\text{MRE} = \frac{1}{n}\sum_{i=1}^{n}\frac{(S_i - O_i)}{O_i} \times 100\% \quad (7)$$

where S_i is the ith simulated value, O_i is the ith observed vale, O_{avg} is the average of observed values, and n is the number of data pairs.

The RMSE reflects the magnitude of the mean difference between simulated and experimental results, whereas the RRMSE standardizes the RMSE and expresses it as a percentage that represents the standard variation of the estimator (Abrahamson et al., 2005). The MRE indicates if there is a systematic bias in the simulation. A positive value indicates an overprediction and a negative value an underprediction.

3. Significant Findings

3.1 Soil Nitrate Profiles

Our coring at the sites indicated relatively high nitrate-N concentrations in the soil profile at all sites sampled as seen in Figure 7 for sites N7, R8, and Y8, respectively. Each curve represents a different soil core analyzed that was collected at the time indicated in the figures.

For site R8 (with a long-term wastewater irrigation history—since 1986) we see (Fig. 7a) a high nitrate peak of about 40 mg/kg around 60 cm, which decreases sharply in the depth interval of 380 to 580 cm, possibly due to previously planted alfalfa roots consuming the nitrate at those depths, as the R8 site was under alfalfa cultivation from 1997 to 2002. The nitrate increases again reaching a secondary maximum near the depth

of 880 cm, then following a decrease near the 940-cm level, it progressively increases with depth down to more than 1500 cm. It seems that a previous nitrate front has reached down to 1500 cm, with yet older fronts reaching even deeper, indicating that nitrate may had already penetrated down to those depths.

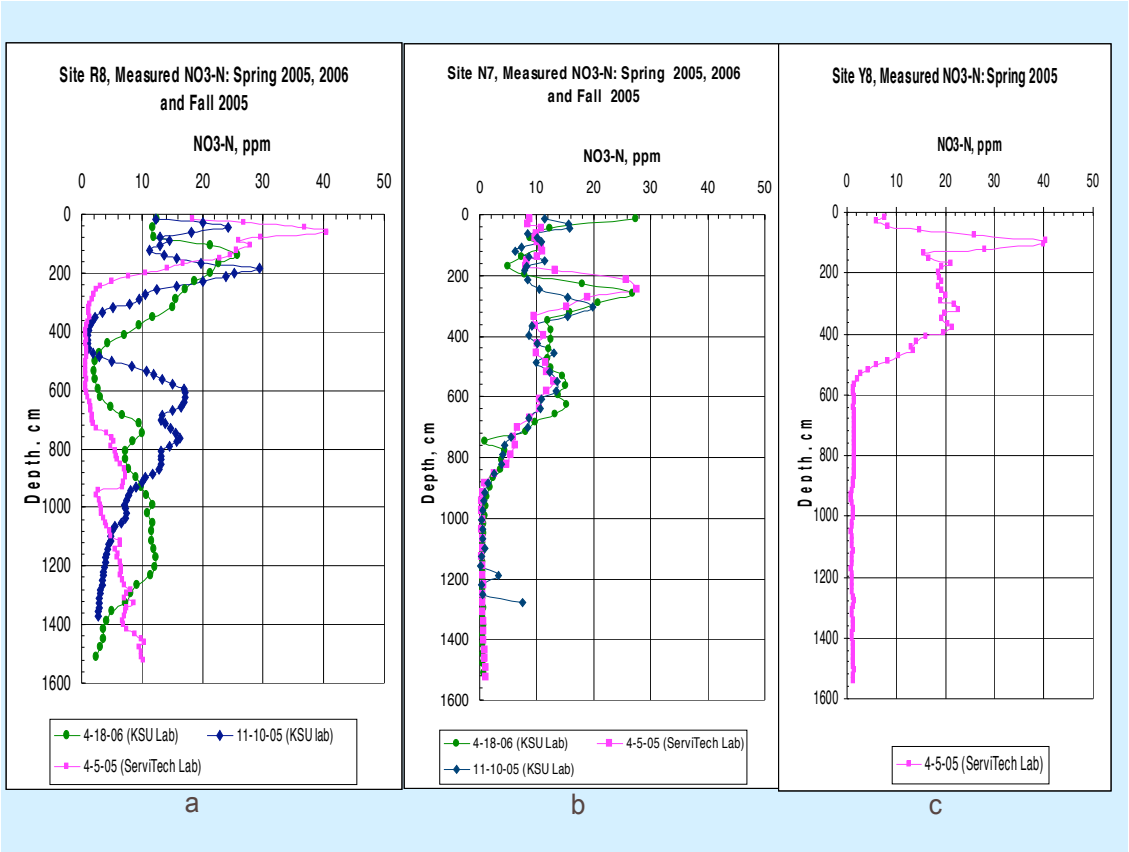


Figure 7. Measured soil profile Nitrate-Nitrogen during Spring 2005 for all study sites (a –R8, b – N7, and c –Y8), and during Fall 2005 and Spring 2006 for sites R8 and N7.

For site N7 (with wastewater irrigation history since 1998) we see (Fig. 7b) a deeper nitrate peak (of less than 28 mg/kg, i.e., not as high as that at site R8) around the 240-cm-depth level. Then, the nitrate distribution progressively decreases to a minimal background level by the time we reach near 900 cm, indicating that nitrate penetrated down to near 900 cm but no further.

Finally, for site Y8 (without any wastewater irrigation), we see (Fig. 7c) a high nitrate peak near the 100-cm level, but by the time we reach the 550-cm depth level, nitrate goes back to minimal background level.

3.2 Wastewater and Ground-water Quality

The sites were periodically LEPA-sprinkle irrigated from mid-May until the latter part of August during 2005 and 2006. The general quality of the treated wastewater effluent applied at the sites during 2005 and 2006 is shown in Figure 8. The chloride concentrations (in green) were around the 300 mg/L level but further increased during the second half of the 2006 year, and the Total Kjeldahl Nitrogen concentrations (TKN, in blue) were generally above the 80 mg/L level. The treated wastewater effluent was analyzed by both the OMI and Servi-Tech labs, and the chemical analysis results are presented in Appendix A (Tables A1 and A2, respectively). Noticeable differences are evident in the resulting wastewater constituents from the two labs.

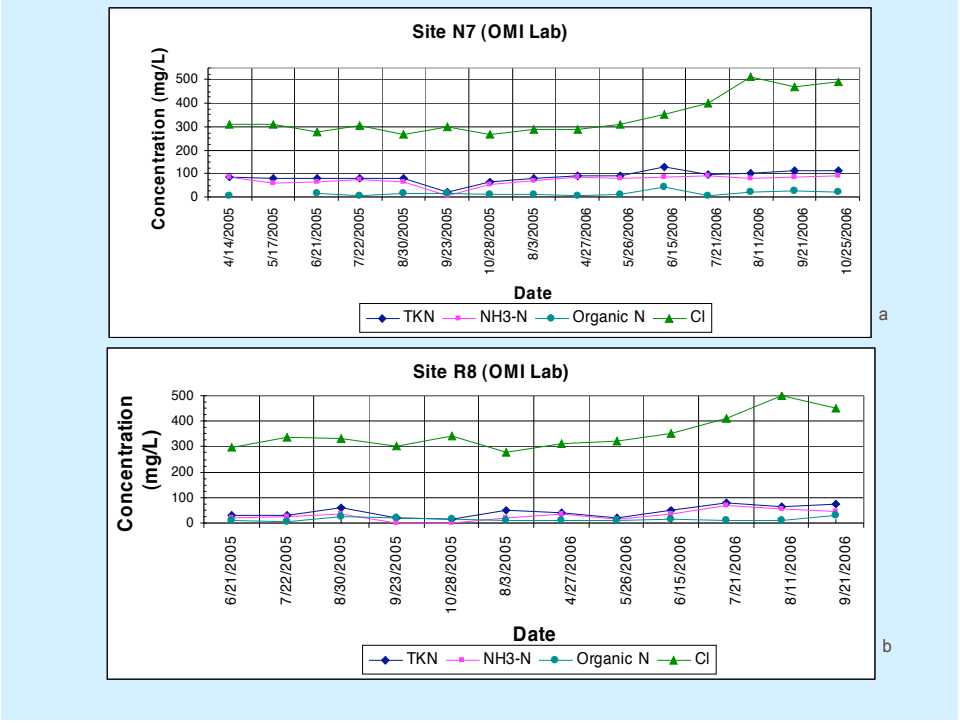


Figure 8. Treated effluent irrigation water chloride, total Kjeldahl nitrogen, and nitrate-nitrogen concentration time series applied to sites N7 (a) and R8 (b) during 2005 and 2006.

Figure 9 shows the ground-water nitrate-N concentrations from the November 2005 survey sampling, where wells shown in red exceed the safe drinking-water limit for nitrate-N of 10 mg/L. Notice that most of the wells have more than 2 mg/L nitrate-N in the ground water. This indicates (Mueller and Helsel, 1996) that anthropogenic sources have begun to impact the ground water in the area.

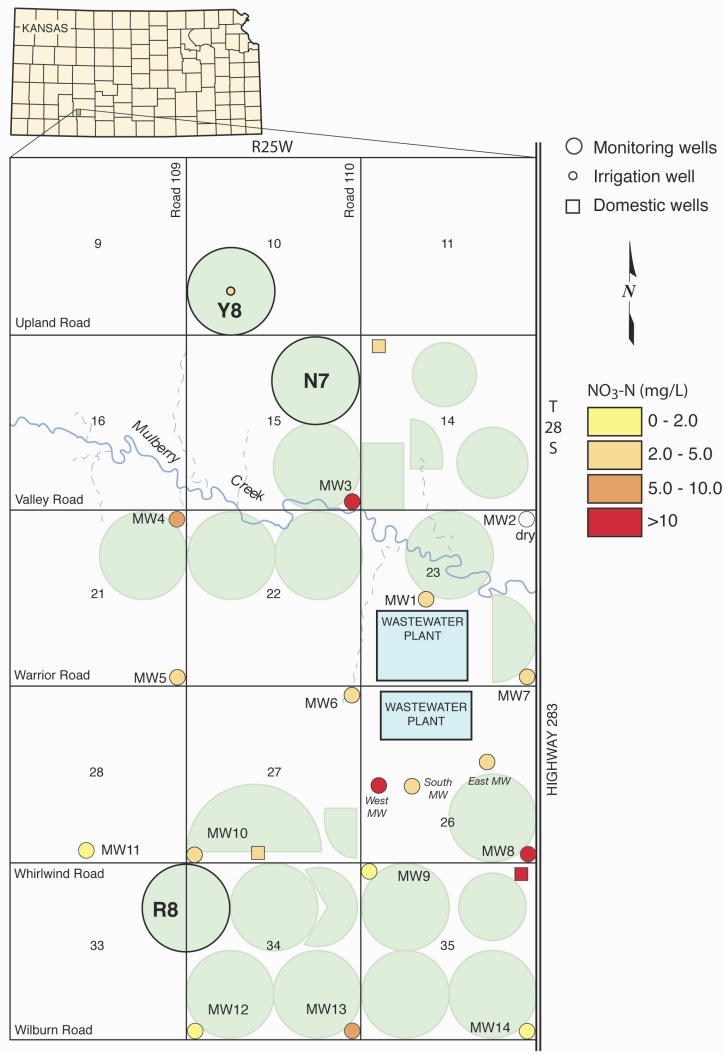


Figure 9. Ground-water nitrate-nitrogen concentrations during November 2005. Numbers at the center of square blocks are Section numbers in the Township and Range system of land classification. Green circles/semicircles are irrigated fields.

Figure 10 displays a trilinear diagram showing the average water quality of the irrigation water applied in both R8 and N7 sites marked as the A circle, the shallow- and intermediate-depth suction lysimeter-sampled pore water from both sites marked as the B

circle, as well as sampled domestic, monitoring, and irrigation wells in the area. The sampled populations of applied wastewater, pore water from suction lysimeters, and monitoring and domestic wells form distinct groups in the trilinear diagram.

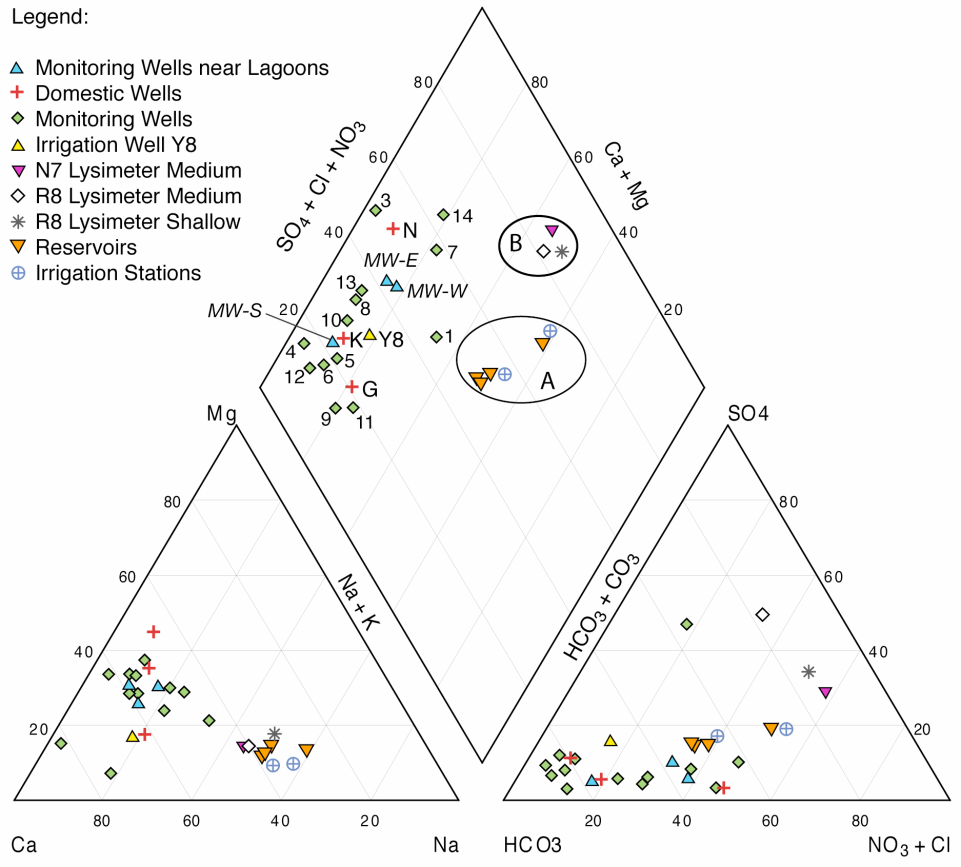


Figure 10. Trilinear diagram showing the average 2005 water quality of irrigation water applied in sites R8 and N7 (circle A), the shallow and intermediate-depth suction lysimeter-sampled pore water from sites R8 and N7 (circle B), and the domestic, monitoring, and irrigation wells sampled in the area.

3.3 Dye-tracer Experiment Results

We observed numerous macropores in the cores collected during sampling, not only in the upper soil profile but also at depths down to more than 9 m. Figure 11 displays a small sampling of the observed macropores from the sites. Because of the occurrence of such macropores and of the relatively high nitrate concentrations observed at the various wells sampled in the area, we run the two brilliant-blue dye experiments at the sites that were briefly described in section 2.1.

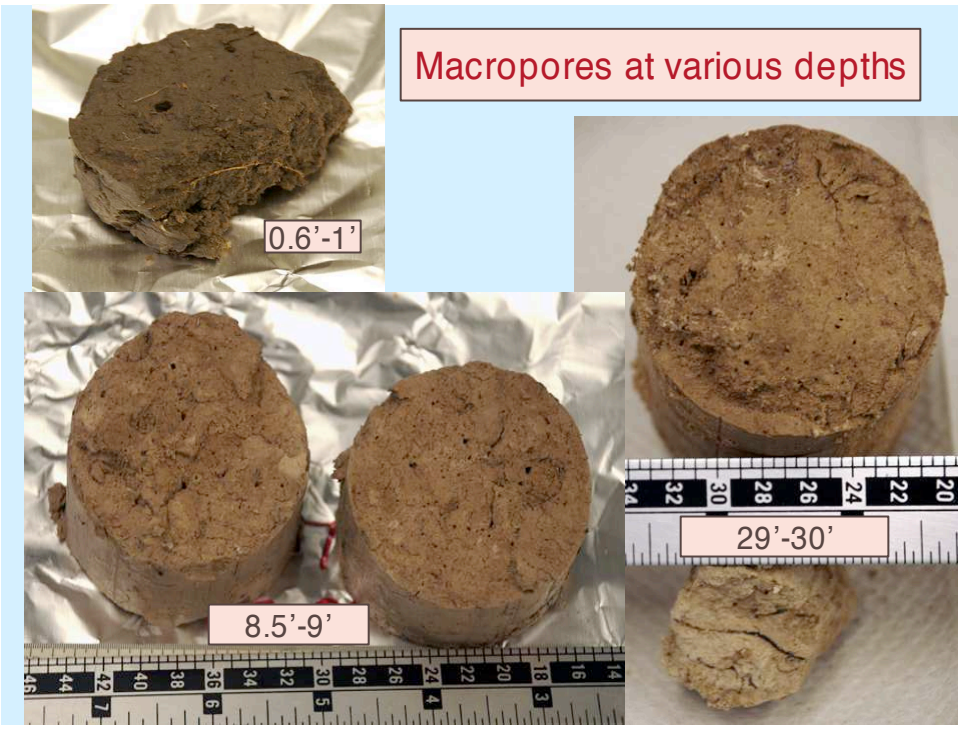


Figure 11. Soil cores at various depths from the study sites showing macropores. Numbers indicate depth in feet.

For the site R8 in Harney soil, the dye solution penetrated down to approximately 200 cm and formed a more-or-less uniform "finger front" at the bottom as shown in Figure 12. The right-hand-side picture in Figure 12 shows a closer-up view of the dye-tracer movement through the blocky-structure soil layers of the Bt horizons (at approximately the 50- to 100-cm depth interval) where the tracer dye moved along the spaces between the blocky soil aggregates and concentrated in numerous fingers in the lower soil layer that did not exhibit the heavy blocky structure of the Bt horizons above.

Figure 12. Uniform finger front from brilliant-blue dye-tracer experiment at site R8. The right-hand-side image shows in more detail the dye moving through the inter-soil block structure spaces of the Bt horizon and accumulating below that blocky layer into numerous fingers.

For site N7 in Ulysses soil, the dye pattern was different, forming a giant funnel front ending in a big finger down to approximately 200 cm, as shown in Figure 13. Closer examination of a side finger, indicated in Figure 13, showed that the dye finger formed along a decaying root channel, as did other fingers examined in both sites.

The observed macropores at depth are probably due to the existence of deep-rooted prairie grasses that dominated the landscape prior to agricultural development. The currently practiced no-till land-use treatment further enhances worm activity near the soil surface, thus maintaining macropores open at the soil surface. Because of the existence of such preferential-flow pathways, the macropore option of the RZWQM was employed. As a result of the observed macropores throughout the soil profile in both sites, macropores were uniformly distributed through all simulated layers using an average estimated pore radius of 0.1 cm and a percentage of macropores of 0.1%.

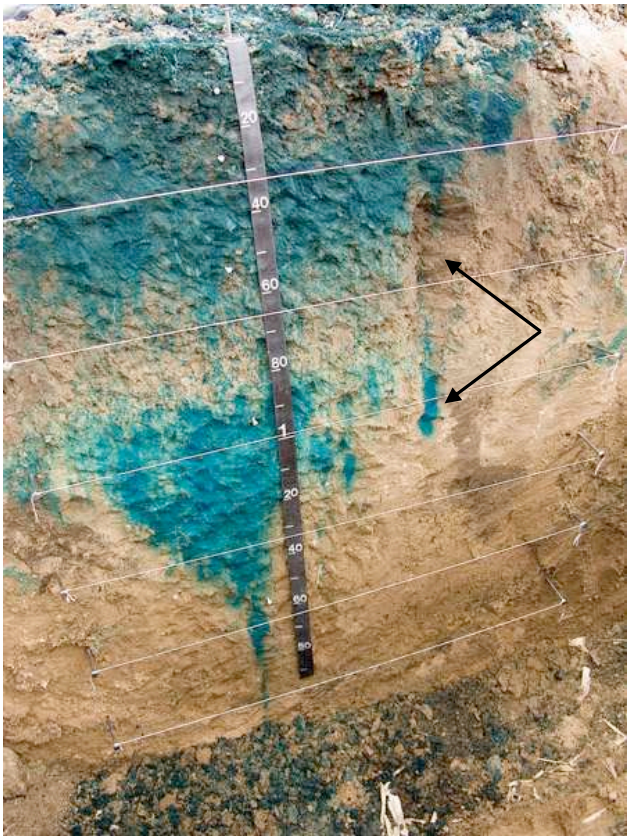


Figure 13. Funnel front pattern from brilliant-blue dye-tracer experiment at site N7 and side finger formed along a decaying root channel (indicated by the two arrows).

3.4 Sensitivity Analysis Results

A sampling of the hydraulic and crop-parameter sensitivities is shown in Figures 14 and 15, respectively. For the sensitivity analysis of hydraulic properties, the response variable considered was the soil-water content, whereas for the sensitivity analysis of crop parameters, the response variable considered was the soil nitrate-nitrogen.

For hydraulic parameters, bulk density, saturation water content (θ_s), and the Brooks and Corey parameters λ and ψ_a were the most sensitive, whereas saturated hydraulic conductivity (Ksat) and residual water content (θ_r) were the least sensitive.

For the macropore parameters, the total macroporosity fraction and the average size of pore radii were the most sensitive (Fig. 16). Macroporosity had minimal effect on soil water content, but had appreciable effect on nitrogen distribution. Macropore flow is generated only during heavy rainfall events in the model. The major hydrologic effect of introducing macropores in the model is to reduce surface runoff.

Ahuja and Williams (1991) and Williams and Ahuja (2003) found that the soil water retention curves as described by the Brooks and Corey equations could be simply described by the pore size distribution index, λ. The importance of λ was used for scaling water infiltration and redistribution (Kozak and Ahuja, 2005) and for scaling evaporation and transpiration across soil textures (Kozak et al., 2005). Because of the relatively high sensitivity of parameters θ_s and λ , both of which are fitted (as opposed to experimentally measured) parameters, we decided to use primarily the λ-parameter and secondarily the θ_s parameter to calibrate our model.

For the plant-growth parameters, the specific leaf density, C_{LA} (i.e., the amount of biomass needed to obtain a leaf area index, LAI = 1), the proportion of daily respiration as a function of photosynthesis, Φ (that maintains N uptake while decreasing biomass accumulation), the propagule age effect, A_p (that may result in increased photosynthesis efficiency during propagule development and thus increased yield, while above-ground biomass is kept constant), the luxurious nitrogen uptake factor (that starts 100 days after corn planting and allows the crop to take up exactly as much N or more or less than it needs), and the maximum depth of roots were the most sensitive. The seed-age effect (same as propagule-age effect but affects photosynthesis later in growing season), minimum leaf stomatal resistance (that is resistance to movement of water through leaf stomata), and the nitrogen sufficiency index (i.e., the fraction of the difference between the ideal and minimum N content of the crop) were the least sensitive.

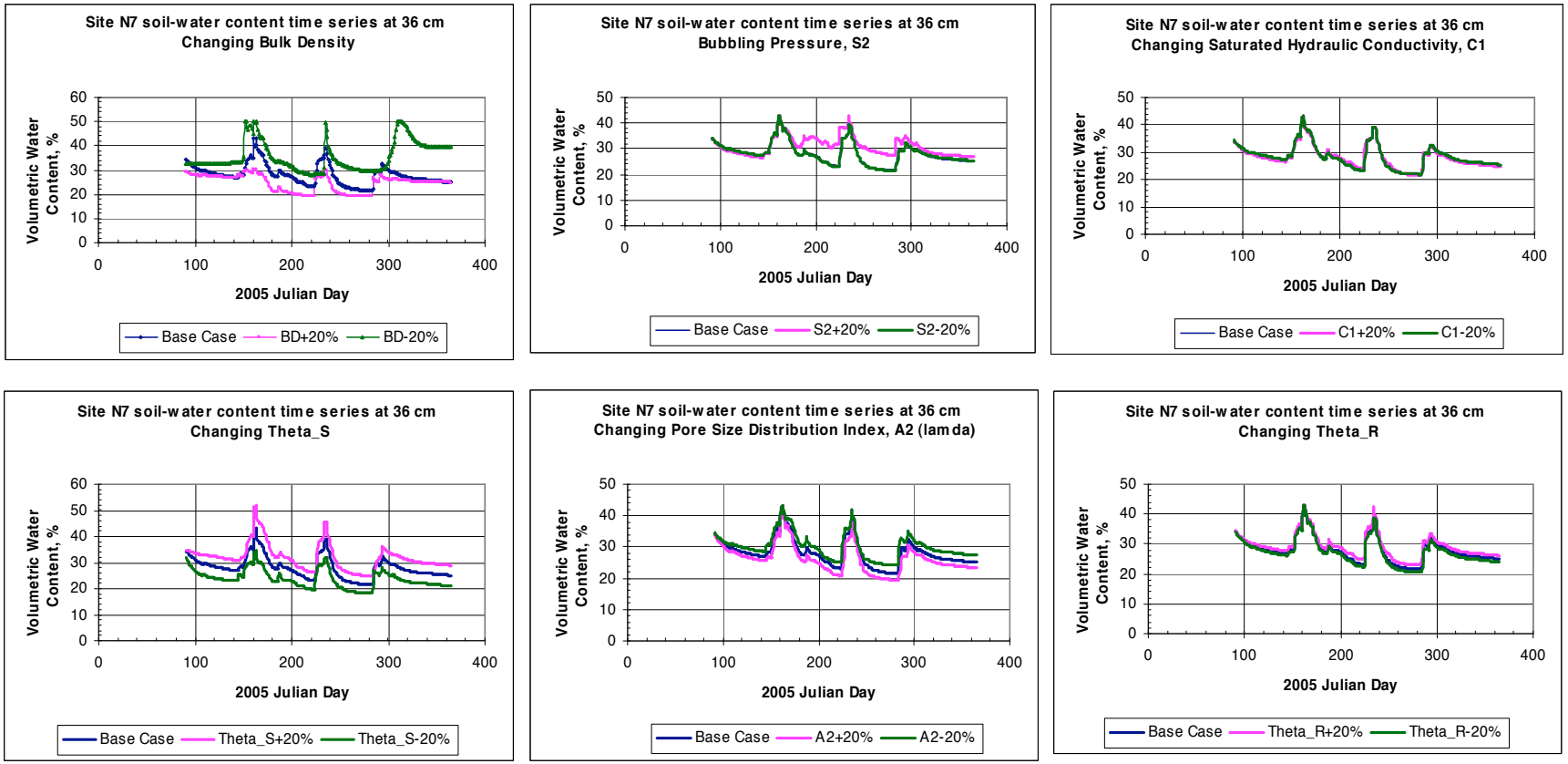


Figure 14. Sensitivity analysis of selected hydraulic parameters as exemplified for a random root-zone depth of 36 cm for site N7. Each variable was increased or decreased by 20% around a base (measured or estimated) initial value.

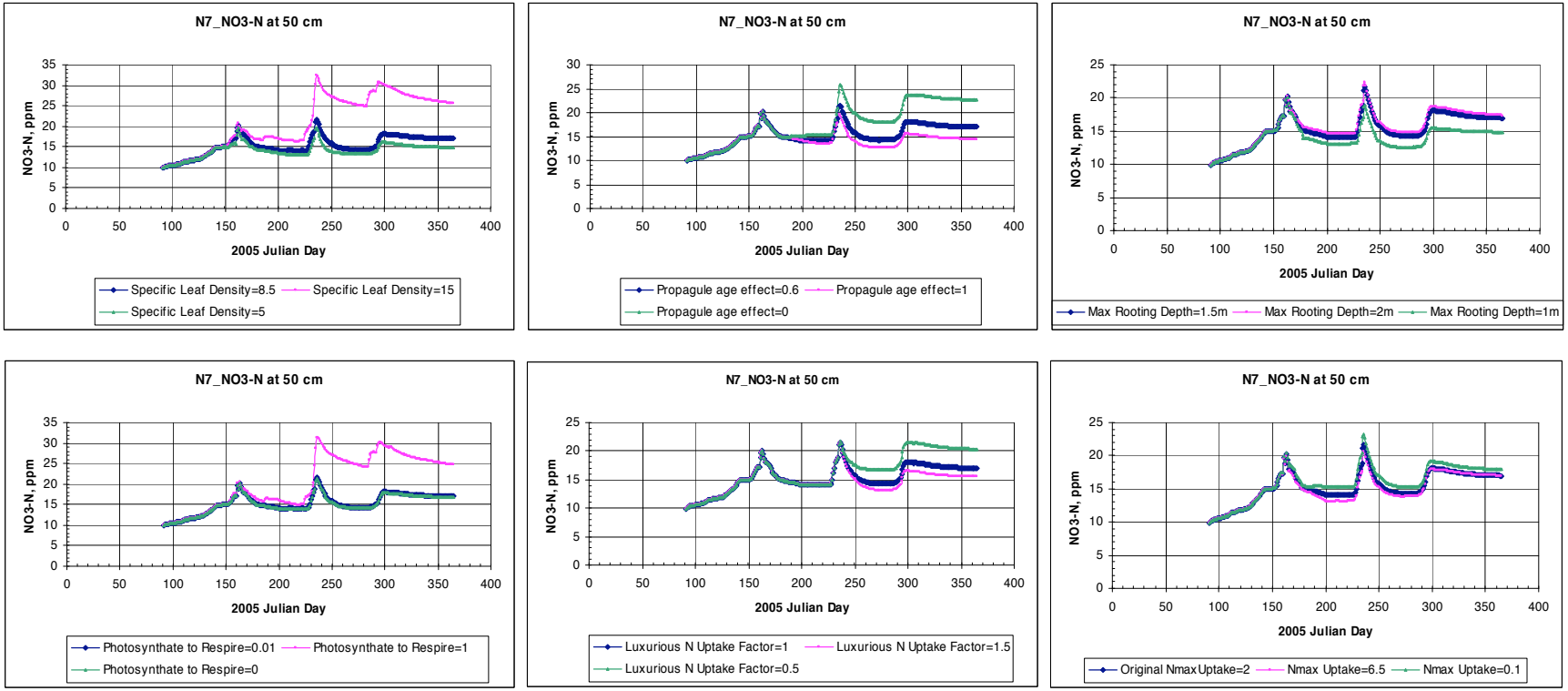


Figure 15. Sensitivity analysis of selected crop-growth parameters as exemplified for a random root-zone depth of 50 cm for site N7. Each variable was increased or decreased by a certain amount around an estimated base or initial value.

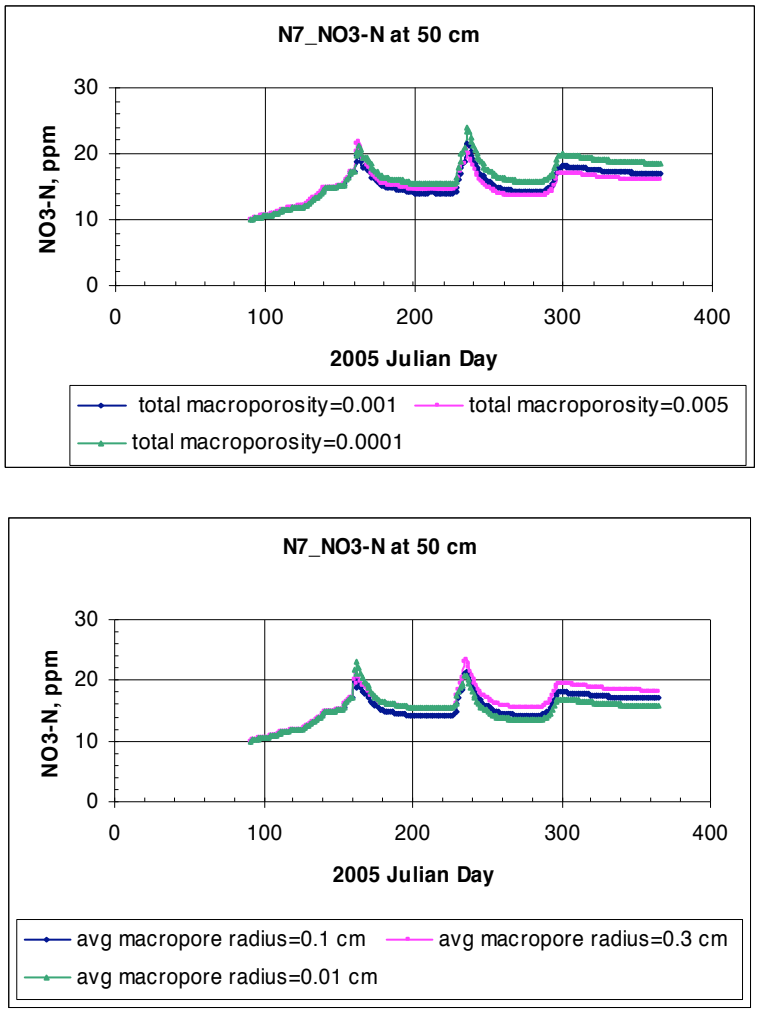
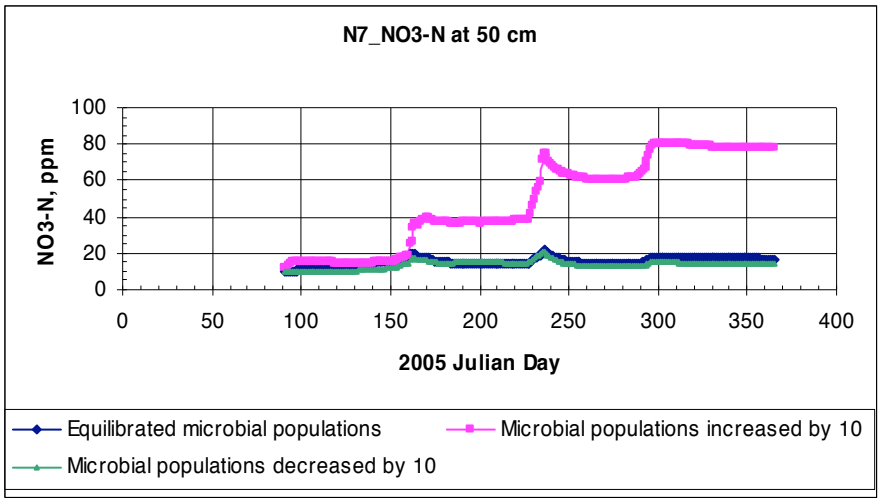
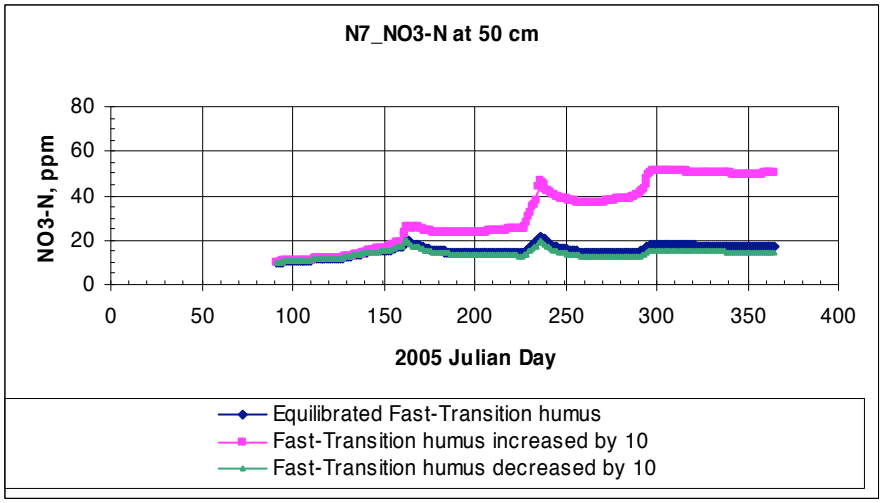


Figure 16. Macropore sensitivity analysis as exemplified for a random root-zone depth of 50 cm for site N7.

For the organic matter/nitrogen-cycling parameters, the aerobic heterotroph microbial population (that is, organisms capable of deriving carbon and energy from organic compounds, and growing only in the presence of molecular oxygen) and the transition and fast humus were the most sensitive parameters, as shown in Figure 17.

Of course, the irrigation and fertilization rates were very sensitive inputs.





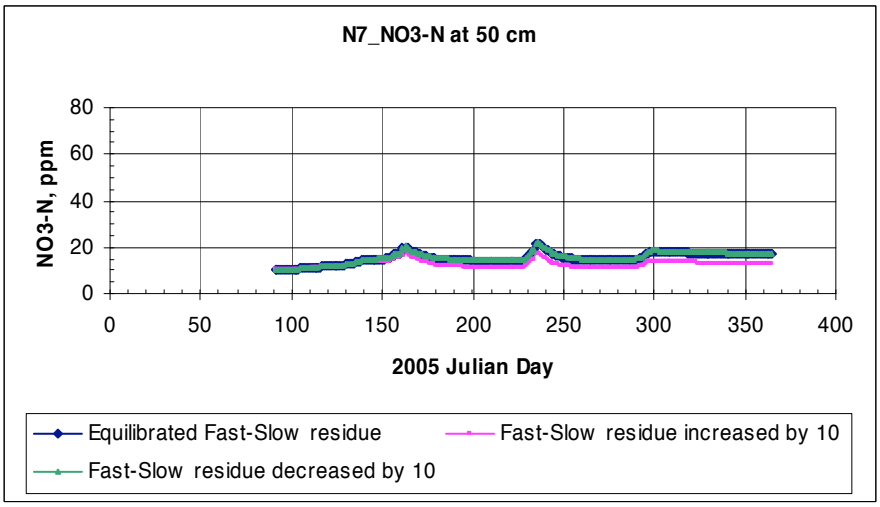


Figure 17. Sensitivity analysis of organic matter pools as exemplified for a random root-zone depth of 50 cm for site N7. The size of each pool was increased or decreased by one order of magnitude around the equilibrium base value.

3.5 Model Calibration and Simulation Results

The simulated and observed moistures for the various individual layers are shown in Figures 18 and 19, for sites N7 and R8, respectively. Although for the upper layers of the soil in both sites the RRMSE and other error measures were relatively high, they much improved at increasing depths, as shown in the figures for the deeper layers. In addition, the simulation results, especially for site R8, show a slight negative bias or underprediction, as indicated by the negative value of the MRE statistic. In order to economize space from here onwards, we present simulation results from site N7 in more detail (for which we have relatively more detailed hydraulic-property data, resulting in generally and relatively somewhat better simulation results than for site R8).

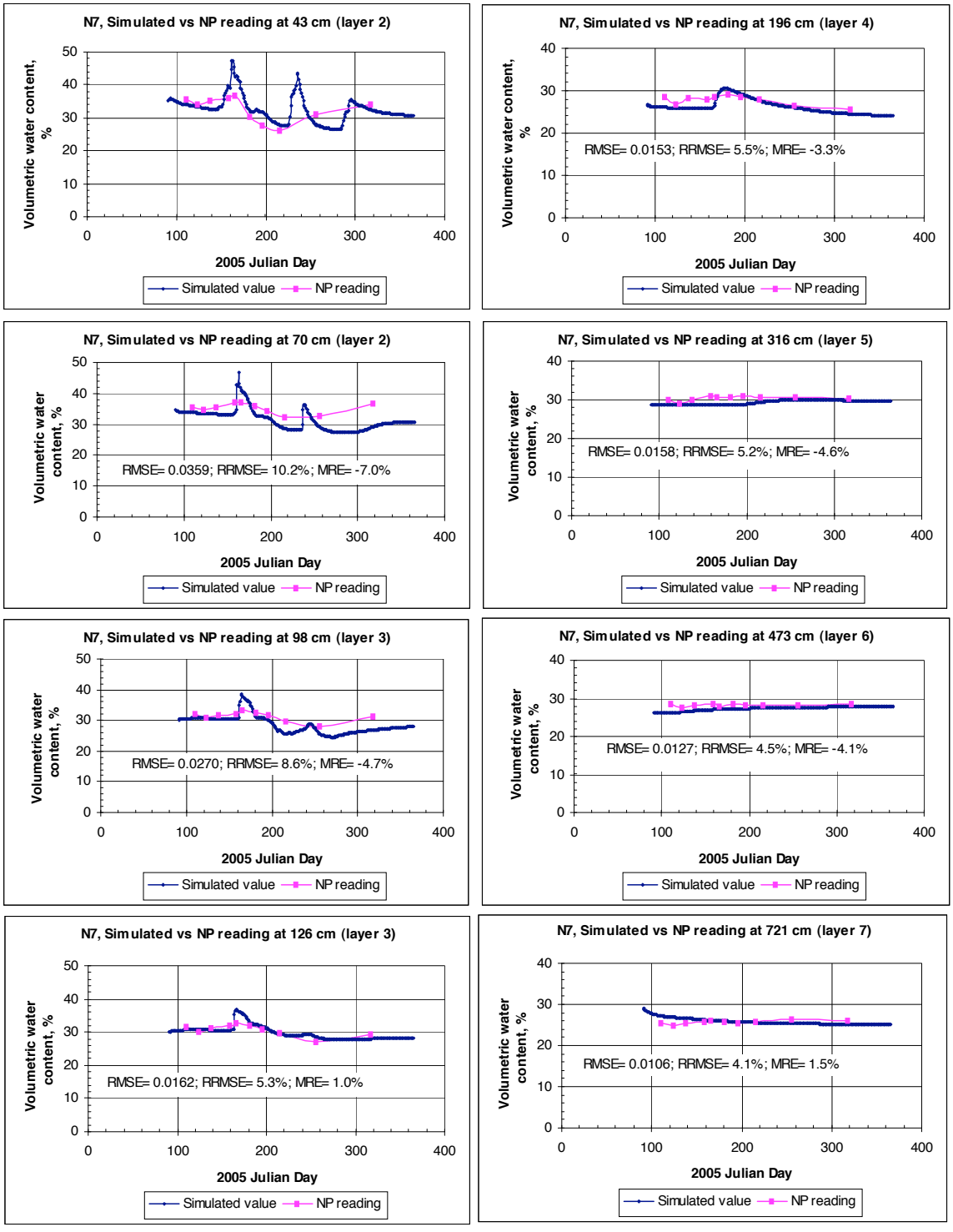


Figure 18. Comparison of model-simulated and field-measured soil water contents at various soil depths for site N7. Three statistical indices, root mean square error (RMSE), relative RMSE (RRMSE), and mean relative error (MRE), all defined in the text, are used to quantify the goodness of fit of model parameterization.

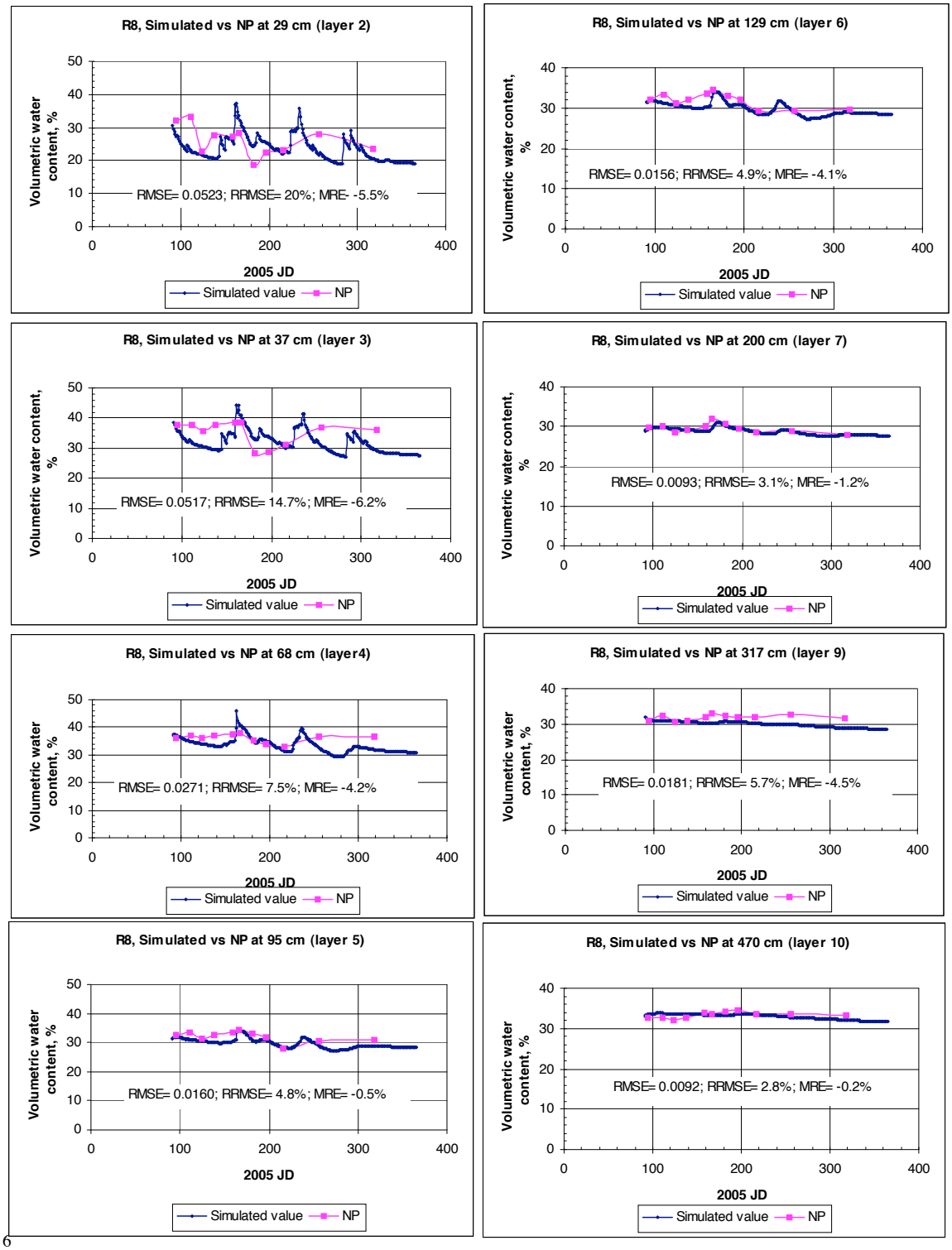


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Figure 19. Comparison of model-simulated and field-measured soil water contents at various soil depths for site R8. Three statistical indices, root mean square error (RMSE), relative RMSE (RRMSE), and mean relative error (MRE), all defined in the text, are used to quantify the goodness of fit of model parameterization.

The simulated cumulative water budget components for the 2005 growing season are shown in Figure 20, where you notice that the runoff component is negligible during 2005.

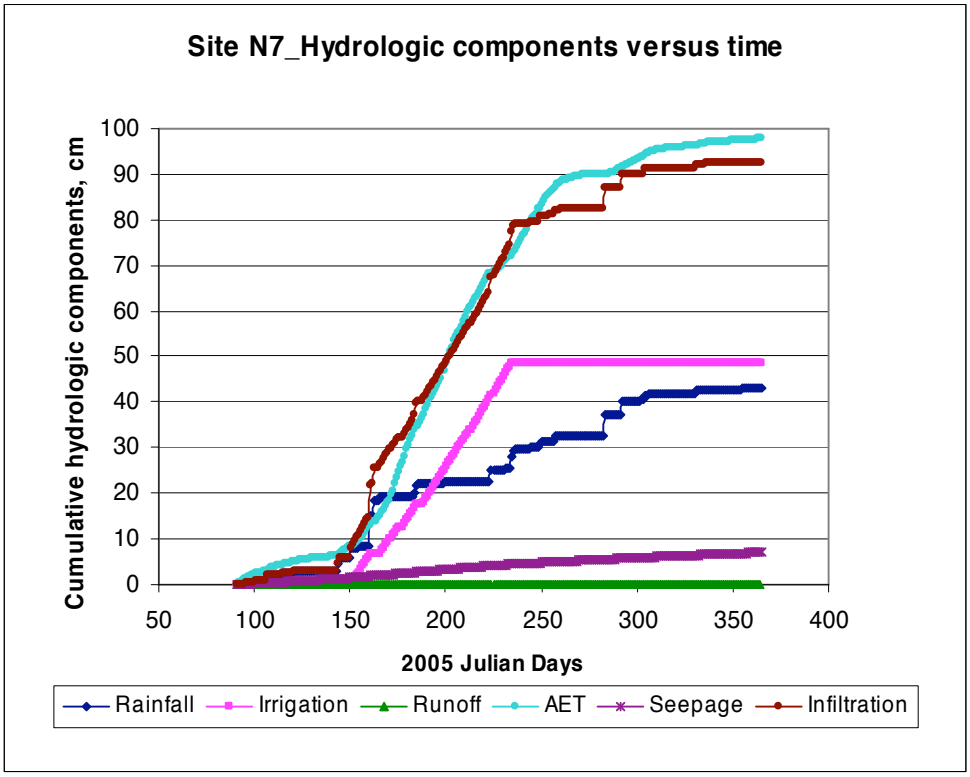

Figure 20. Simulated cumulative hydrologic components for site N7 during the 2005 growing season.

The simulated and measured soil nitrate profiles in the fall of 2005 in sites N7 and R8, both of which were planted in corn in April and harvested at the end of September are shown in Figure 21. For the case of site N7, the model approximated the main patterns of the nitrate depth profile fairly well, but not the observed detailed patterns. The results for site R8 were not as good as those for site N7, although they may be considered acceptable. As mentioned previously, we did not have hydraulic property data for the deeper R8 soil profile (only down to ~4.8 m), and as explained in the section on water-retention parameters in Sophocleous et al. (2006), some outside lab-determined hydraulic property data for that site were questionable.

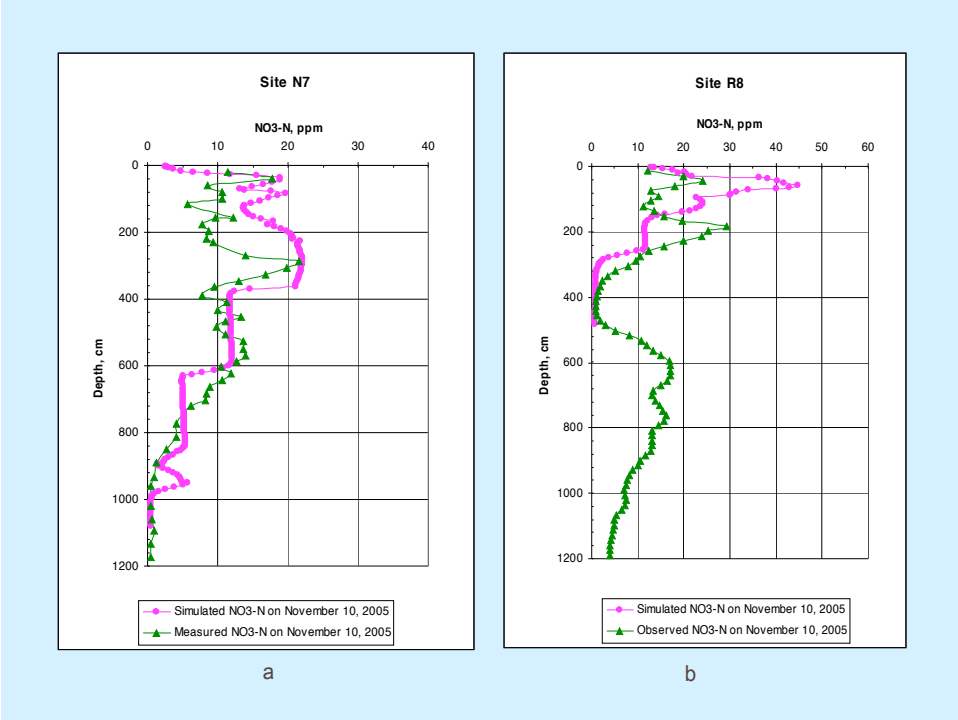

Figure 21. Measured and simulated soil nitrate-nitrogen profiles at (a) site N7 (simulated depth 1080 cm) and (b) site R8 (simulated depth 484 cm) during the soil-sampling date of November 10, 2005, following corn harvest.

The simulated temporal distribution of nitrogen losses are shown in Figure 22, whereas the simulated spatial and temporal nitrogen uptake are shown in Figure 23.

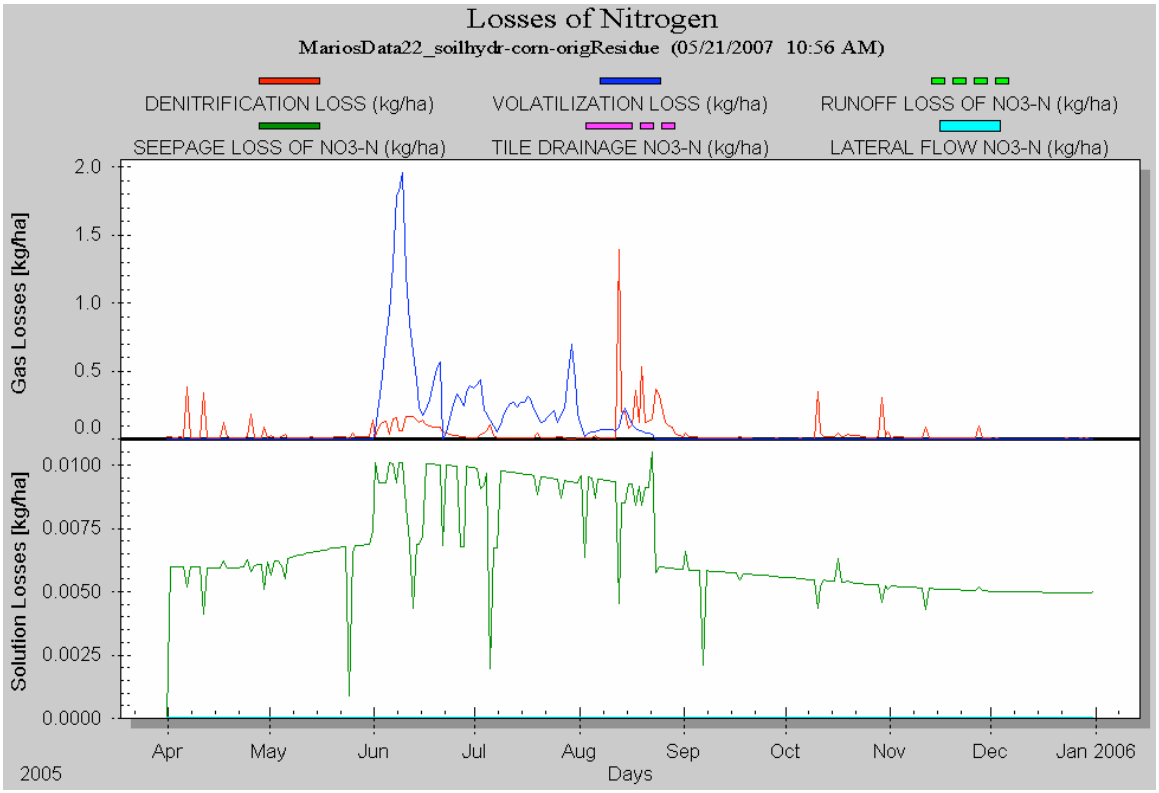

Figure 22. Simulated temporal distribution of nitrogen losses (volatilization, denitrification, deep seepage) at site N7 during the 2005 corn-growing season.

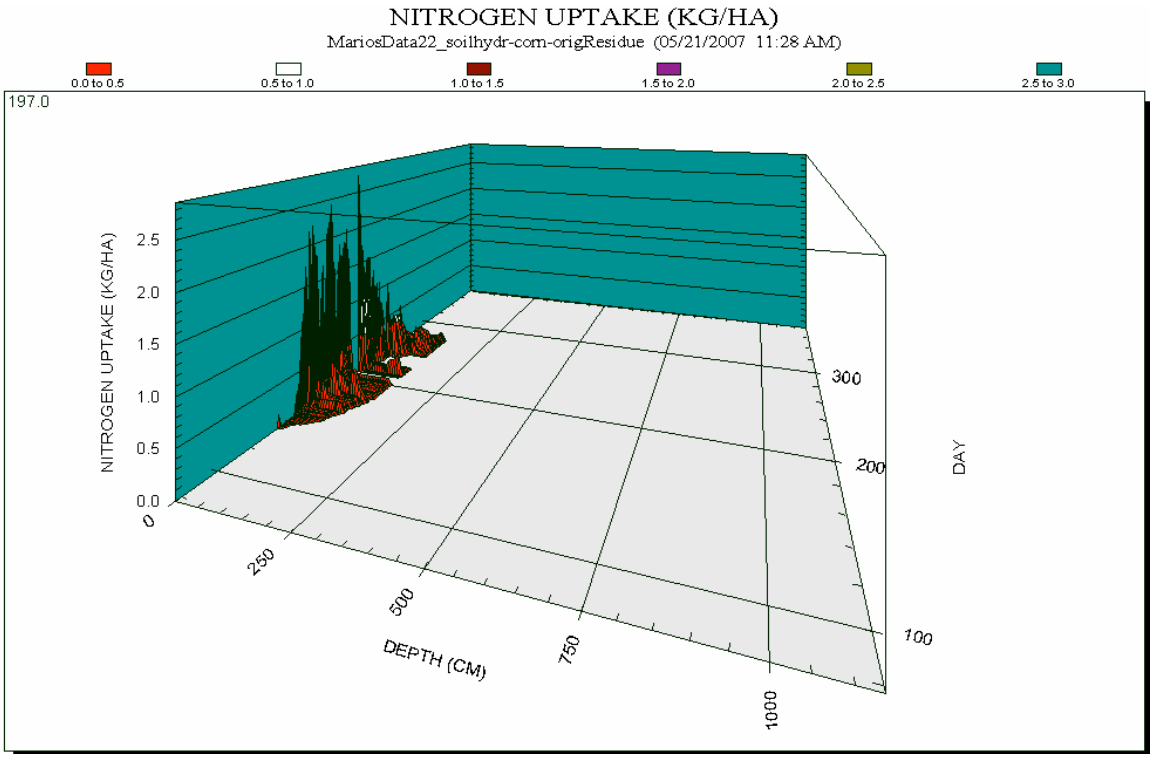

Figure 23. Three-dimensional diagram indicating the simulated spatial and temporal distribution of nitrogen uptake.

The model-estimated soil nitrogen balance is shown in Figure 24. The major source of nitrogen is the applied wastewater effluent that added more than 312 kg/ha during 2005 at site N7. The major nitrogen losses are from plant uptake, and secondarily from volatilization and deep seepage. Mineralization (that is, conversion of organic nitrogen that is present in soil organic matter, crop residues, and applied effluent to inorganic nitrogen, such as ammonium nitrogen, as a result of microbial decomposition) is the major transformation of nitrogen. However, large amounts of nitrate exist in the unsaturated soil profile as can be seen from Figure 7. The model-estimated storage of nitrate-nitrogen in the 10.8-m-deep soil profile analyzed in this model was more than 1500 kg/ha.

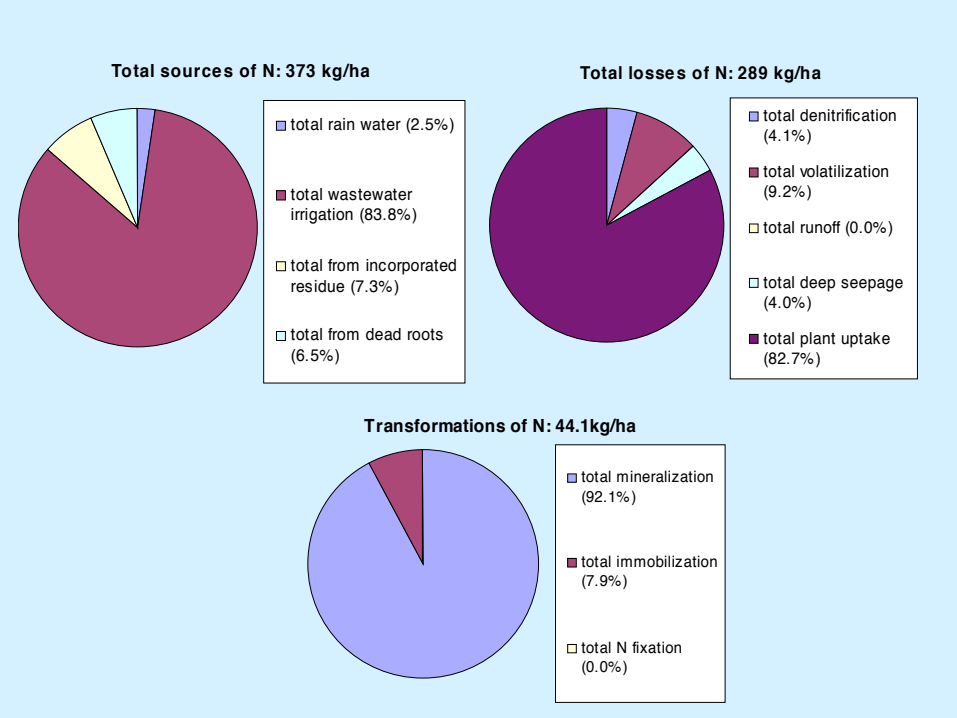

Figure 24. Simulated soil nitrogen balance components for site N7 during the 2005 growing season.

3.6 Management Scenarios Results

Once an agricultural system is adequately calibrated and tested, it has the potential for use in evaluation of alternative crop-soil management practices for the location of interest in terms of their production potential and impact on the environment (Hu et al., 2006). Because of the limited data we had available for calibrating and checking the RZWQM model, the results presented here should be considered preliminary.

Historical and current sampling of nitrogen in the soil at the wastewater-irrigated sites shows increased accumulation of inorganic nitrogen in the soil profile with time (see also Fig. 7), which indicates that the inorganic nitrogen left in the soil at harvest is not taken up completely by the subsequent crop. This residual nitrogen is subject to leaching to ground water when rainfall, especially of high intensity that enhances macropore flow, occurs between crop seasons. Numerical simulations indicated consistent increases in

nitrogen losses due to volatilization (primarily) and deep seepage and denitrification (secondarily) with increased nitrogen application rates (see also Figs. 22-24).

Nitrogen Use Efficiency (NUE) is a term used to indicate the relative balance between the amount of fertilizer N taken up and used by the crop versus the amount of fertilizer N "lost." Nitrogen Use Efficiency in this report is defined as follows (Hu et al., 2006):

$$\text{NUE} = \frac{\text{(Plant N uptake under a particular N treatment) - (Plant N uptake under no N fertilization)}}{\text{(amount of N applied)}} \quad (8)$$

The RZWQM model was run with a zero-N treatment, and the results were used in the NUE computations.

Differences in predicted grain yields, plant N uptake, residual soil profile N, volatilization, and other N losses with different irrigation and fertilization treatments were analyzed using the RZWQM model and are summarized in Table 3. There is some uncertainty as to the total amount of fertilization applied in the fields. According to OMI lab analyses (see also Fig. 8 and Appendix A), the total N applied during the 2005 irrigation season was 434.5 kg/ha. According to Servi-Tech lab analyses (Appendix A, F. Vocasek, March 2007 written communication), the total was 312.4 kg/ha. To somewhat resolve this discrepancy, we adopted the Servi-Tech total but employed the OMI lab proportions of NO_3, NH_3, and organic nitrogen constituents of treated wastewater applied for irrigation (fertigation). The N balance components and NUE for both of the totals mentioned above are shown in Table 3. In addition, several management scenarios were simulated using reduced fertilization treatments of 50% of those OMI- and Servi-Tech-based wastewater-N totals mentioned above, as well as 75% and 50% reduced irrigation totals while maintaining the same irrigation scheduling.

We see that reducing fertilization by 50% using the same 2005 irrigation scheduling increases NUE while keeping relative crop yield nearly constant with a decrease of only 1% of maximum simulated yield (see Table 3, items 2, 5, 8, 11, and 14). Lowering fertigation from 435 kg/ha (Table 3, item 10) to 312 kg/ha (Table 3, item 1), to

217 kg/ha (Table 3, item 11), to 157 kg/ha (Table 3, item 2) consistently increased NUE (10.5%, 17.1%, 31.9%, 42.2%, respectively). Reducing irrigation total amount while keeping fertilization levels at 157 kg/ha further increases NUE from 42.2% (at full irrigation amount—Table 3, item 2) to 48.1% (at 75% of full irrigation amount—Table 3, item 5) to only 48.2% (at 50% of full irrigation amount—Table 3, item 8). This last result indicates that such a drastic irrigation reduction (50%) may not be necessary, as nearly the same NUE is obtained with 75% irrigation reduction.

It seems that reducing the fertilization levels at the study sites to around 150 kg/ha increases the NUE significantly. Such lower fertilization rates can be achieved by blending treated wastewater effluent with freshwater from the underlying High Plains aquifer. In addition, decreasing the amount of irrigation water applied by approximately 25%, while using reduced fertilization rates, further increases NUE.

Table 3. Nitrogen inputs and losses predicted by RZWQM for the 2005 crop season for site N7 for current irrigation, 75% irrigation, and 50% irrigation, and various levels of nitrogen fertilization through the irrigation LEPA system.

Description of method			Total N Input (kg/ha)					Total N losses (kg/ha)								NUE[c]%
	Crop yield (kg/ha)	Percent change in crop yield	Storage (10.8m-profile)	Rain	Ferti-gation[b]	Mineral-ization	Percent change in mineral-ization	Plant uptake	Percent change in plant uptake	Deep seep-age	Percent change in deep seepage	Denitri-fication	Percent change in denitri-fication	Volatili-zation	Percent change in volatili-zation	
1. Full rate irrigation[a], full rate fertilization[b]	6030.3	--------	1518.5	9.4	312.4	40.6	--------	239.0	--------	11.6	------	11.9	--------	26.5	--------	17.12
2. Full rate irrigation, 50% fertilization	5961.8	-1.14	1465.8	9.4	156.9	40.9	0.73	251.8	5.32	11.6	0.0	7.8	-34.59	5.1	-80.66	42.19
3. Full rate irrigation, zero fertilization	5198.8	-13.79	1426.3	9.4	--------	40.9	0.71	185.6	-22.37	11.6	-0.00	5.4	-54.15	0.01	-99.95	-------
4. 75% irrigation, full rate fertilization	6067.9	---------	1519.7	9.3	312.4	42.8	-------	236.6	--------	11.6	-------	10.5	---------	30.7	--------	17.47
5. 75% irrigation, 50% fertilization	6006.7	-1.01	1469.6	9.3	156.9	43.1	0.56	257.5	8.82	11.6	0.00	7.3	-30.55	5.9	-80.72	48.08
6. 75% irrigation, zero fertilization	5367.5	-11.54	1427.8	9.3	--------	43.4	1.37	182.0	-23.06	11.6	0.01	5.3	-49.63	0.01	-99.96	--------
7. 50% irrigation, full rate fertilization	6002.8	-0.46	1519.7	9.3	312.4	44.5	9.44	222.7	-6.85	11.5	-0.71	9.9	-16.77	38.6	45.38	13.75
8. 50% irrigation, 50% fertilization	5969.8	-1.00	1472.0	9.3	156.9	44.7	9.95	255.3	6.81	11.5	-0.71	7.0	-41.08	7.4	-72.28	48.18
9. 50% irrigation, zero fertilization	5507.7	-8.67	1428.5	9.3	--------	45.2	11.16	179.7	-24.82	11.5	-0.71	5.2	-56.11	0.01	-99.95	-------

[a] Full rate of 2005-season irrigation = 48.55 cm
[b] Full rate of 2005-season fertigation = 312.4 kg/ha
[c] Nitrogen Use Efficiency

Description of method			Total N Input (kg/ha)					Total N losses (kg/ha)								NUE[f]%
	Crop yield (kg/ha)	Percent change in crop yield	Storage (10.8m-profile)	Rain	Ferti-gation[e]	Mineral-ization	Percent change in mineral-ization	Plant uptake	Percent change in plant uptake	Deep seep-age	Percent change in deep seepage	Denitri-fication	Percent change in denitri-fication	Volatili-zation	Percent change in volatili-zation	
10. Full rate irrigation[d], full rate fertilization[e]	6054.4	--------	1559.6	9.4	434.5	40.6	--------	231.3	--------	11.6	--------	15.0	--------	58.7	--------	10.52
11. Full rate irrigation, 50% fertilization	6017.8	-0.60	1486.1	9.4	217.3	40.8	0.42	254.9	10.20	11.6	0.0	9.1	-39.12	11.3	-80.83	31.91
12. Full rate irrigation, zero fertilization	5198.8	-14.1	1426.3	9.4	--------	40.9	0.80	185.6	-19.77	11.6	-0.00	5.4	-63.76	0.01	-99.98	-------
13. 50% irrigation, full rate fertilization	5995.0	-0.98	1553.1	9.3	434.5	44.4	9.37	237.8	2.80	11.5	-0.71	12.1	-19.67	84.4	43.75	13.36
14. 50% irrigation, 50% fertilization	5978.8	-1.25	1489.6	9.3	217.3	44.5	9.74	240.5	3.96	11.5	-0.71	8.0	-46.58	16.2	-72.39	27.96
15. 50% irrigation, zero fertilization	5507.7	-9.03	1428.5	9.3	--------	45.2	11.25	179.7	-22.30	11.5	-0.71	5.2	-65.31	0.01	-99.98	-------

[d] Full rate of 2005-season irrigation = 48.55 cm
[e] Full rate of 2005-season fertigation = 434.5 kg/ha
[f] Nitrogen Use Efficiency

Publications and Presentations

Sophocleous, M. A., Townsend, M. A., Willson, T., and Vocasek, F., and Zupancic, J., 2006, Fate of nitrate beneath fields irrigated with treated wastewater in Ford County, Kansas: First-year Progress Report to KWRI, 62 p.

Sophocleous, M. A., Townsend, M. A., Willson, T., and Vocasek, F., 2006, Fate of nitrate beneath fields irrigated with treated wastewater in Ford County, Kansas: 23rd Annual Water and the Future of Kansas Conference, Topeka, KS, March 16, 2006.

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Sophocleous, M. A., Townsend, M. A., and Vocasek, F., 2007, Treated wastewater and nitrate transport beneath irrigated fields near Dodge City, Kansas: Water and the Future of Kansas Conference, March 15, 2007, Topeka, KS.

Townsend, M. A., Macko, S. A., Sophocleous, M. A., Vocasek, F., Schutte, D., and Ghijsen, R., 2007, Variations in water chemistry and plant uptake of nitrogen at a wastewater irrigation site: Water and the Future of Kansas Conference, March 15, 2007, Topeka, KS.

Note: A journal manuscript based on this report and additional ongoing work is under preparation.

Information Transfer

See Publications and Presentations above. In addition, Dodge City TV broadcasting news services recorded our dye-tracer experiments in November 2005 and interviewed co-PI Fred Vocasek on this project. See also Student Support below.

Student Support

A graduate student in the School of Engineering of the University of Kansas is being supported by this project. Main duties include data processing and numerical modeling. An MS non-thesis project based on this study is now being pursued by the graduate student (Ashok KC). An additional hourly student from Kansas State University based in the Garden City Agricultural Experiment Station has been supported for conducting periodic neutron moisture-content readings at the field sites.

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APPENDIX A

Effluent composition (nutrient variables) applied at the study sites N7 and R8 during 2005 and 2006.

Table A1. Effluent composition, irrigation stations, nutrient variables **(OMI Lab)**

Sample location	Sample date	TKN	NH_3-N	NO_3-N	Organic-Nitrogen	PO_4-P
		mg/L	mg/L	mg/L	mg/L	mg/L
Irrigation station#1	4/14/05	88.0	85.0	0.7	3.0	11.4
(irrigating site N7)	5/17/05	79.0	57.9	7.3		10.8
	6/21/05	81.0	64.0	27.0	17.0	9.6
	7/22/05	81.0	76.9	0.0	4.1	10.7
	8/30/05	80.0	65.3	1.7	14.7	9.8
	9/23/05	20.0	4.5	23.4	15.5	8.9
	10/28/05	65.0	55.2		9.8	10.4
	8/3/05	80.0	70.0	<1.0	10.0	
	4/27/06	91.0	85.7	0.0	5.3	11.2
	5/26/06	90.0	80.9	0.0	9.1	10.8
	6/15/06	130.0	86.3	0.0	43.7	11.7
	7/21/06	95.0	90.2	0.0	4.8	12.5
	8/11/06	100.0	80.2	0.0	19.8	13.9
	9/21/06	110.0	85.8	0.0	24.2	17.0
	10/25/06	110.0	90.0	0.0	20.0	16.7
Irrigation station #2	6/21/05	30.0	18.8	13.8	11.2	10.0
(irrigating site R8)	7/22/05	29.0	26.2	22.8	2.8	10.9
	8/30/05	57.0	33.3	0.8	23.8	8.6
	9/23/05	20.0	0.3	24.8	19.7	6.2
	10/28/05	15.0	0.4		14.6	4.8
	8/3/05	50.0	20.0	20.0	10.0	26.0
	4/27/06	40.0	32.5	3.6	7.5	8.7
	5/26/06	20.0	12.4	25.6	7.7	9.2
	6/15/06	51.0	36.9	0.0	14.1	10.9
	7/21/06	79.0	68.2	1.0	10.8	11.3
	8/11/06	65.0	54.2	0.0	10.8	12.0
	9/21/06	72.0	42.5	1.3	29.5	11.3

Table A2. 2005 effluent composition, irrigation stations, nutrient variables **(Servi-Tech Lab)**					
		TKN	NH_3-N	NO_3-N	PO_4-P
Sample location	Sample date	mg/L			
Irrigation station #1 (irrigating site N7)	4/14/05	88	85	0.7	11.4
	5/17/05	79	58	7.3	10.8
	6/21/05	81	64	27.0	9.6
	7/22/05	81	77	0.0	10.7
	8/30/05	80	65	1.7	9.8
	9/23/05	20	5	23.4	8.9
	10/28/05	65	55	0.0	10.4
Irrigation station #2 (irrigating site R8)	6/21/05	30	19	13.8	10.0
	7/22/05	29	26	22.8	10.9
	8/30/05	57	33	0.1	8.6
	9/23/05	20	0	24.8	6.2
	10/28/05	15	0	0.0	4.8
2005 mean values					
Irrigation station #1 (N7)		70.6	58.4	8.6	10.2
Irrigation station #2 (R8)		30.2	15.6	12.3	8.1
Irrigation station #1 (irrigating site N7)	4/27/06	91	86	0.0	11.2
	5/26/06	90	81	0.0	10.8
	6/15/06	130	86	0.0	11.7
	7/21/06	95	90	0.0	12.5
	8/11/06	100	80	0.0	13.9
	9/04/06	110	86	0.0	17.0
	10/25/06	110	90	0.0	16.7
Irrigation station #2 (irrigating site R8)	4/27/06	40	33	3.6	8.7
	5/26/06	20	12	25.6	9.2
	6/15/06	51	37	0.0	10.9
	7/21/06	79	68	1.0	11.3
	8/11/06	65	54	0.0	12.0
	9/04/06	72	43	1.3	11.3
	10/25/06				
2006 mean values					
Irrigation station #1 (N7)		103.7	85.6	0.0	13.4
Irrigation station #2 (R8)		54.5	41.2	5.3	10.6

Variations in Nitrogen Water Chemistry at a Wastewater Irrigation Site, Dodge City, Kansas (Part B)

Townsend, M. A.[1], Macko, S. A.[2], Ghijsen, R.[1], Thompson, J.[1], Schneider, N.[1] and Schuette, D.C.[3],
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[3] Servi-Tech Laboratories, Inc., Dodge City, KS

Second-year Progress Report to KWRI
(March 1, 2006 – February 28, 2007)

Keywords: wastewater fertigation; nitrate-N; seasonal variation; spatial variation; nitrogen-15 isotope, non-parametric statistics.

Table of contents

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Townsend, M. A.[1], Macko, S. A.[2], Ghijsen, R.[1], Thompson, J.[1], Schneider, N.[1] and Schuette, D.C.[3], [1] Kansas Geological Survey, Lawrence, KS; [2] Univ. of VA Dept. of Environmental Sciences, Charlottesville, VA; [3] Servi-Tech Laboratories, Inc., Dodge City, KS

Abstract

As part of the Kansas Water Resources Institute study at the Dodge City wastewater treatment area for 2006-07 the variation in nitrogen water chemistry was investigated. In the previous study in 2005-06 the water chemistry was found to vary in concentration between the spring 2005 and fall 2005 sampling times. A similar variation was found for the fall 2005 to spring 2006 sampling. Statistically significant trend variation in nitrate and chloride concentrations was found for a number of the monitoring wells at the treatment site. The nitrogen-15 natural-abundance method and additional water chemistry methods were used to determine sources of the nitrate observed in the seventeen monitoring wells and sampled domestic wells in the study area and plants grown at all three sites.

Introduction

The purpose of the water-chemistry evaluation of the Kansas Water Resources Institute study is to identify the sources of nitrate in ground water using the nitrogen-15 natural-abundance isotope method. The nitrate-N concentrations have been increasing in the monitoring well samples since 1990. The values are generally above 2 mg/L (as nitrogen), which is above the USGS National Water Quality Assessment Program limit for water not impacted by human activities (Mueller and Helsel, 1996). Many of the samples have nitrate-N values above the U.S. EPA drinking-water limit of 10 mg/L.

The study area is the Dodge City wastewater treatment site approximately 19 km (12 mi) south of Dodge City, Kansas (Fig. 1). A schematic of the treatment process is shown in Figure 2. The input stream is from both the city wastewater and the meat packing industry wastewater. The waste flows into a collection area and then is sent to three covered anaerobic lagoons (Fig. 2). From there the water is released to an aerobic lagoon where the water is mixed with air to increase release of ammonia gas. The aerobic lagoon water is then released to storage lagoons. From these lagoons water is then land applied using sprinkler irrigation generally during the crop-growing season from April through October.

The two irrigated sites that were investigated in this study are sites R8 and N7 (Fig. 1) with Y8 as a non-wastewater irrigated cropland as a control site. The sites were selected based on length of wastewater treatment: R8 was started in 1986 and N7 was started in 1996, soil properties, and a prior history of soil coring for nitrate and chloride profiles done by Servi-Tech (Zupancic and Vocasek, 2002).

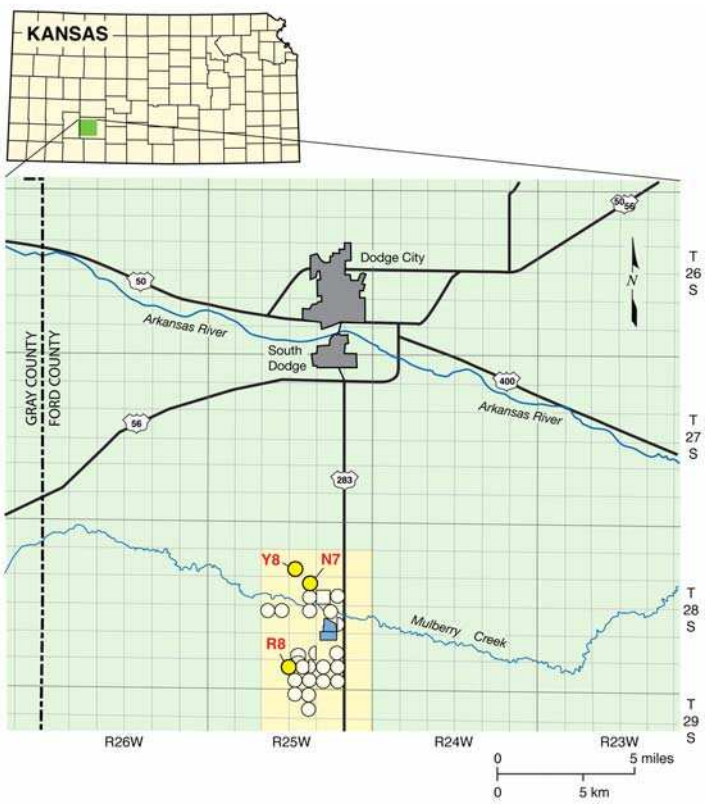

Figure 1. Location of study area south of Dodge City, Kansas. Sites N7 and R8 are wastewater irrigated, site Y8 is not wastewater irrigated.

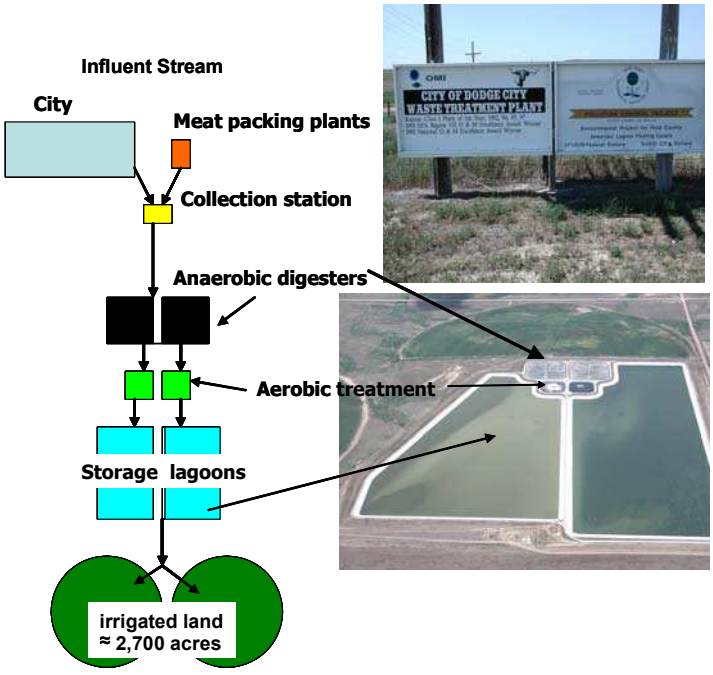

Figure 2. Schematic of waste-treatment process at Dodge City wastewater-treatment facility.

Methods

Water Sampling

There are seventeen monitoring wells in the study area (Fig. 3). Most of these wells were installed by CHM2Hill OMI, Inc. with well records available at the Kansas Geological Survey (KGS) http://www.kgs.ku.edu/Magellan/WaterWell/index.html (verified May 2007). These wells were sampled five times from the spring of 2005 to the spring of 2007. In addition, domestic wells near sites N7 and R8 were sampled twice. Other wells in the area were sampled in the summer of 2006. All analyses through 2006 are listed in Appendix A.

The monitoring wells were sampled by personnel from CH2M-Hill OMI, Inc. in the fall and spring of each year. Each well was pumped for several hours in order to clean out the well bore and sample fresh aquifer water. Samples collected for the KGS were stored in 1-L polyethylene bottles and an additional sample was collected for nitrate and other anion analyses in a 250-ml polyethylene bottle with 2-ml of HCl acid for preservation. All samples were stored on ice while in the field and in a refrigerator until shipment to the KGS with ice and ice packs. An additional 1-L to 500-ml sample was collected for isotope analysis. This sample was frozen at the CH2M-Hill OMI laboratory and sent frozen to the KGS where it was stored frozen until sent to the University of Virginia for isotope determination.

Samples were also collected by the KGS from domestic and irrigation wells in the area. Wells were pumped until the specific conductance and temperature were stable with three readings every 5 minutes; usually this took at most 20 minutes. Samples were collected in 500-ml polyethylene bottles for cations, specific conductance, pH, and temperature. A 200-ml sample was collected in a 250-ml polyethylene bottle with 2-ml HCL for preservation for nitrate and anion analyses. Samples were stored on ice until returned to the KGS where they were refrigerated until analyzed.

Sample Analysis

In the laboratory the KGS filtered the water samples through 0.45-µm membrane filter paper before analysis. Specific conductance was measured to estimate chloride concentrations and determine dilution factors for the optimum concentration range of the analytical method for bromide, iodide, and chloride measurement. Chloride, sulfate, bromide, total inorganic iodine, and iodate concentrations were determined using automated colorimetric methods on a Technicon AutoAnalyzer II. Dissolved iodide was computed from the total inorganic iodine and iodate concentrations and used to correct for its effect on the measured bromide in the analytical method. Nitrate content was determined on the AutoAnalyzer using an ultraviolet spectrophotometric method. Bicarbonate content was computed from an alkalinity determination using an automated titrimeter. Cation concentrations were measured using an inductively coupled argon plasma spectrometer. Only conductance, chloride, bromide (along with iodine species for bromide correction), and sulfate were determined in the untreated and treated wastewater samples. Charge-balance errors calculated for the well waters for which measurements of all major and substantial minor constituents were completed were all <2% and averaged 1.0%. As a part of its quality assurance steps, the KGS participates in the standard reference water program of the U.S. Geological Survey.

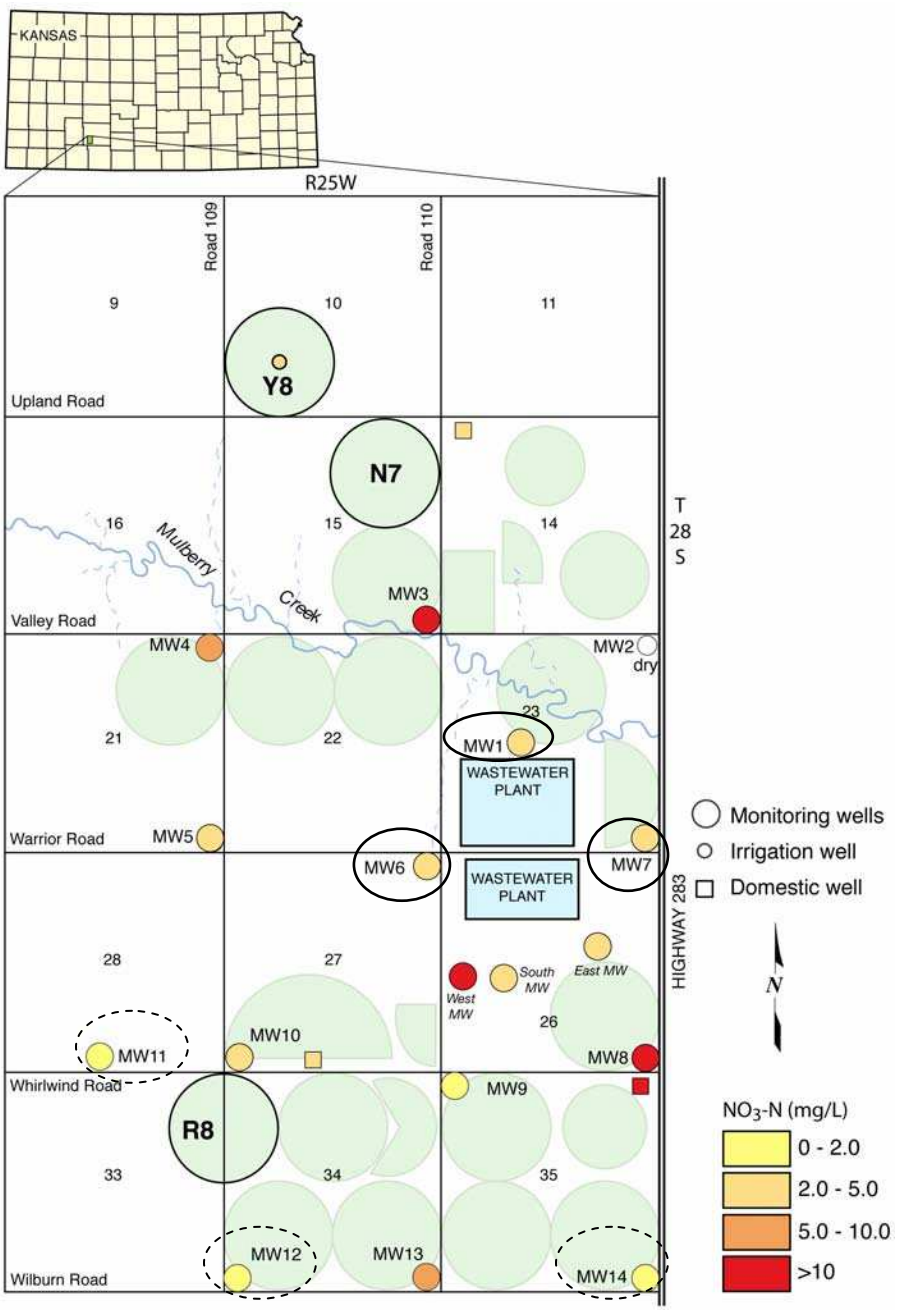

Figure 3. Location of monitoring and domestic wells located at study area. Solid black lines indicate monitoring wells with quarterly nitrate-N and chloride sampling. Dashed black lines indicate wells with decreasing trend in nitrate-N or chloride concentrations from 1985 to 2005.

Servi-Tech Laboratories, Inc., performed complete analyses on the lagoon samples. Laboratory information and chemical data for the ground water and wastewater samples are listed in Appendix A. The table includes the total dissolved solids (TDS) content calculated from the major and minor constituent concentration. In the TDS computation, the bicarbonate was multiplied by 0.4917 to approximate the carbonate that would be left in the residual solids after evaporating to dryness (Hem, 1985).

Nitrogen-15 Analytical Methods

The nitrogen-15 isotopic composition in the waters was determined at the Department of Environmental Sciences, University of Virginia. Samples of the dried nitrate-containing salts dissolved in the waters were combusted at high temperature to nitrogen gas for analysis of their isotopic compositions. The $\delta^{15}N$ was determined on a Micromass Optima isotope ratio mass spectrometer (IRMS) coupled with an elemental analyzer (EA), with an overall precision better than 0.5 ‰. The data are reported relative to a standard (atmospheric N_2) defined to be 0 ‰, and expressed in δ notation as

$$\delta_{sample}(‰) = (R_{sample}/R_{standard} - 1) \times 1000$$

where δ_{sample} represents $\delta^{15}N$, and R is the molar ratio of the heavier (^{15}N) to the lighter (^{14}N) isotope for the standard or sample (Hoefs, 2001). The analyses were run on nitrate in all samples except the wastewater samples, which have ammonium as the dominant nitrogen form.

Statistical Methods

Nonparametric statistical methods were used for determining if variation occurred between sampling periods and for trend analysis. Splus version 7.02 for Windows (2005) and SAS version 9.1 (2002-03) were used for the statistical analysis. All tests used $\alpha = 0.10$ for comparison of the calculated *p* values. If the p value is less than $\alpha = 0.10$ then the alternate hypothesis for the test is accepted.

The Shapiro-Wilk test for goodness of fit to a normal distribution was used to evaluate the data. All of the tested parameters except bicarbonate, magnesium, and boron for the seasonal sampling periods showed a non-normal distribution (Appendix B). For the Shapiro-Wilk test, if the calculated p value is less than $\alpha = 0.10$ then the data is considered non-normal in distribution. Because most of the tested parameters had a non-normal distribution, non-parametric statistical methods were used.

The Kruskal-Wallis Rank Sum difference test around the median value was used to determine if the sampling periods were representative of different populations. The Kendall test for trend and the Kendall seasonal test for trend were used to determine if observed increased values were statistically significant for both the inorganic analyses and the isotope values.

Water Chemistry Results

Observed Trends in Nitrate and Chloride Data

Monitoring wells 1, 6, and 7 were installed in the early 1990s and were monitored quarterly for nitrate-N and chloride as indicators of potential wastewater leaching to the ground water (Fig.3, black circles). The quarterly monitoring was only continued for these wells until 1999 because of changes in permit regulations to sampling of two times per year.

MW #1 is located north of the lagoons, MW #7 is located east of the lagoons, and MW #6 is located west of the lagoons. Figure 3 also shows the irrigation circles where wastewater is

applied. MW #6 is not located near any wastewater irrigated circles and the water chemistry is probably representative of background water quality in the area.

Figure 4 (a, b, c) shows the variation of the quarterly nitrate-N values for wells 1, 6, and 7, and Figure 5 (a, b, c) shows the variation for quarterly chloride values. The seasonal Kendall test for trend was used to evaluate the presence of trend for samples from all six wells. For both the nitrate-N and chloride, an increasing trend was noticed for MW#7. MW #1 showed a decreasing trend for nitrate-N and an increasing trend for chloride. MW #6 shows no trend for either constituent. This result is expected for MW #6 in that its location is not near any sites of active irrigation, and therefore no immediate source of undiluted wastewater present within the pumping radius of this well (Fig. 3) is known.

Tables 1 (chloride) and 2 (nitrate-N) indicate seasonal trend for all of the monitoring wells from 1985 to 2005. The Seasonal Kendall test for trend shows an increasing trend for the two constituents in a number of the monitoring wells. The wells with samples with increasing concentrations are located within the area of wastewater irrigation. Samples from monitoring wells 11, 12, and 14 show decreasing trends for nitrate-N and/or chloride (Fig. 3 dashed black lines). These wells are located near the edges of the wastewater irrigation fields and may be impacted by regional ground-water chemistry.

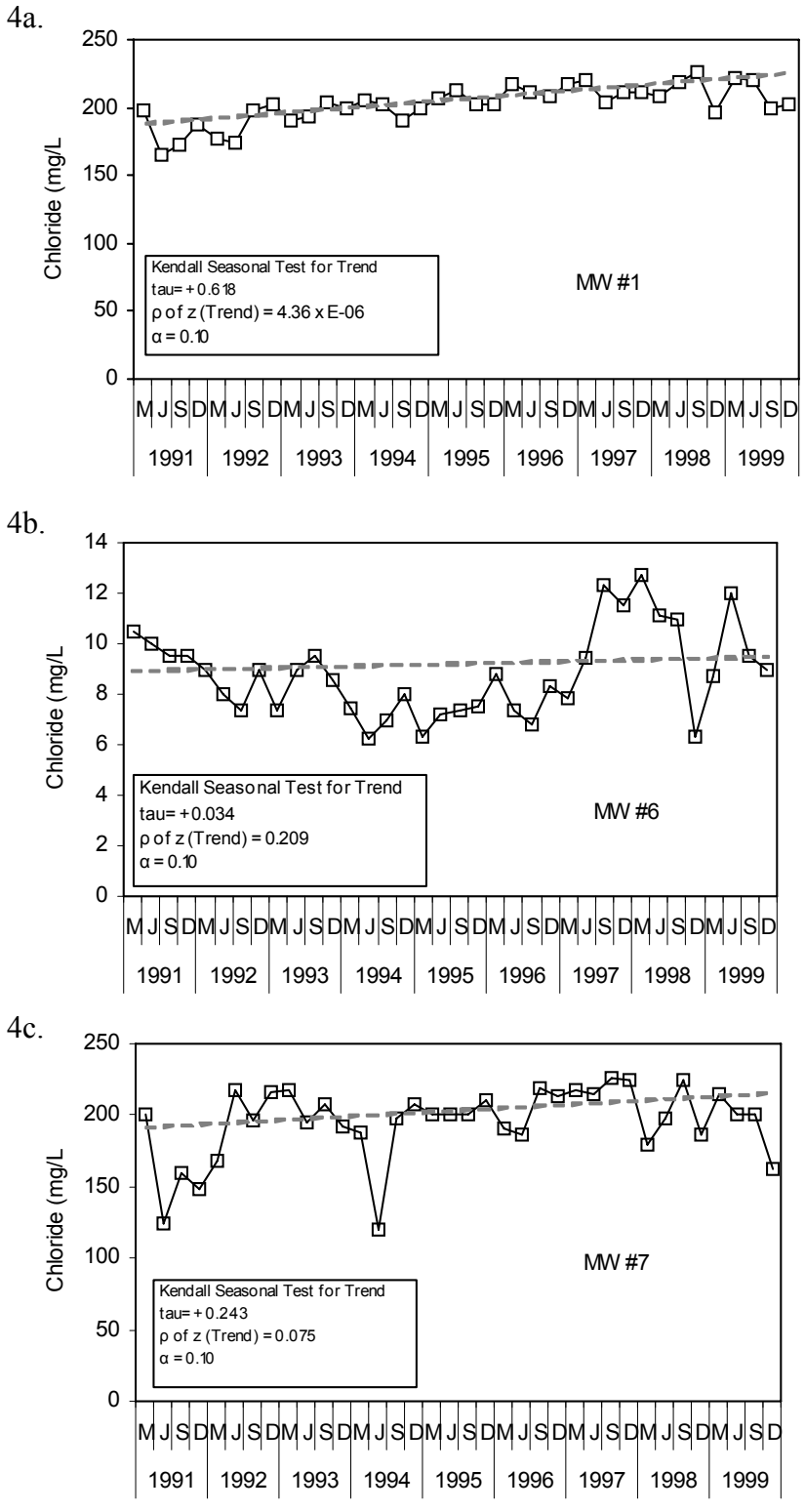

Figure 4. Kendall seasonal test for trend for monitoring wells 1 (4a), 6 (4b), and 7 (4c) for quarterly sampling from 1991 to 1999. MW #1 and MW #7 show increasing trends in concentration. MW #6 shows no trend.

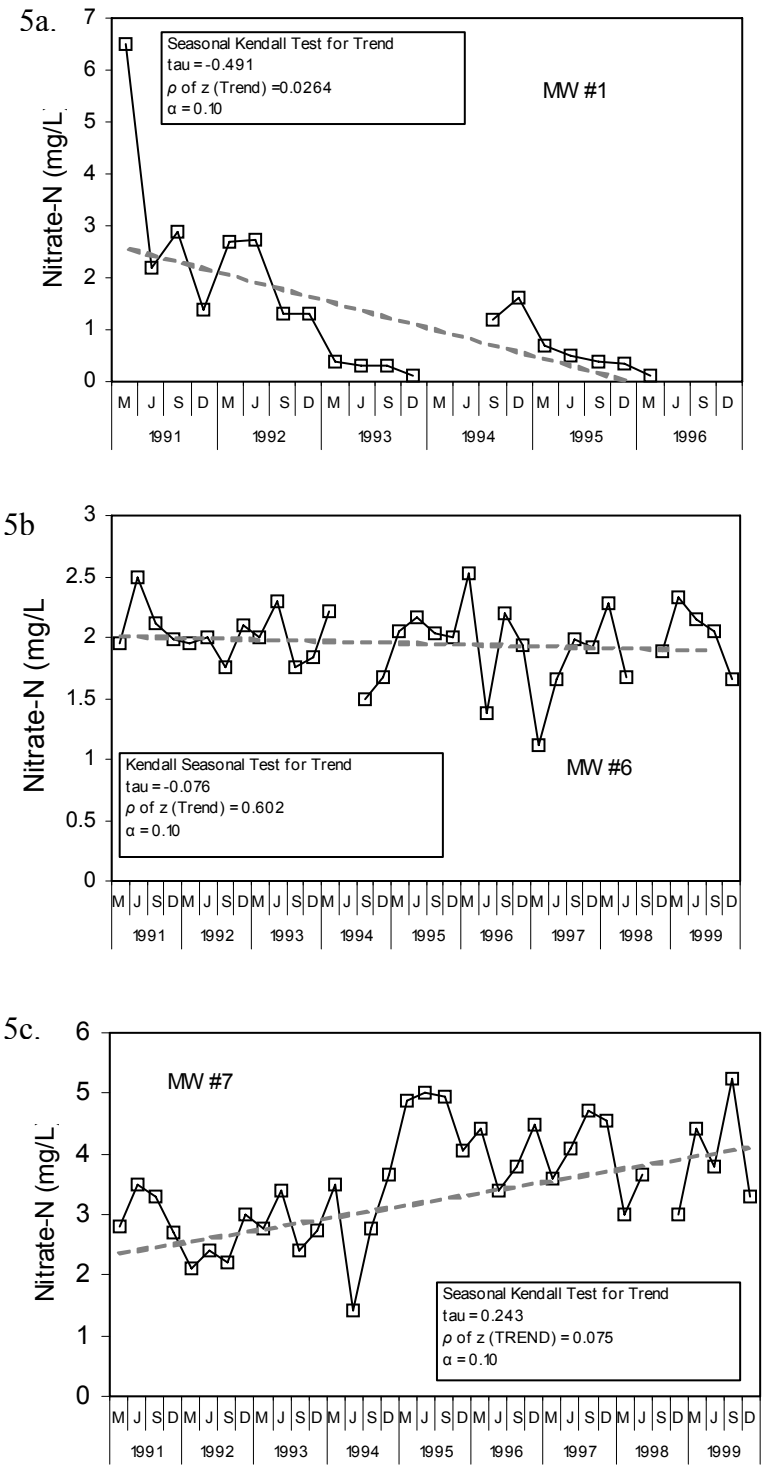

Figure 5 a, b, c. Seasonal Kendall test for trend shows a decreased trend in nitrate-N concentration for MW #1 (a) for 1991to 1996, no trend for MW #6 (b), and an increasing trend for MW #7 (c).

Table 1. Seasonal Kendall test for trend for chloride concentrations 1985 to 2005.

ID	tau	*p* value	Trend
MW 1	0.176	0.276	
MW 2	0.389	0.018	increasing
MW 3	0.605	0.0001	increasing
MW 4	-0.037	0.868	
MW 5	-0.133	0.414	
MW 6	-0.219	0.173	
MW 7	0.3	0.0605	increasing
MW 8	0.486	0.002	increasing
MW 9	0.443	0.005	increasing
MW 10	0.366	0.022	increasing
MW 11	-0.348	0.029	decreasing
MW 12	-0.133	0.413	
MW 13	0.228	0.155	
MW 14	-0.366	0.022	decreasing

Table 2. Seasonal Kendall test for trend for nitrate-N concentrations 1985 to 2005.

ID	tau	*p* value	Trend
MW 1	-0.205	0.358	
MW 2	0.295	0.074	increasing
MW 3	0.367	0.022	increasing
MW 4	0.181	0.263	
MW 5	0.328	0.039	increasing
MW 6	0.1	0.605	
MW 7	0.319	0.045	increasing
MW 8	0.324	0.043	increasing
MW 9	0.485	0.002	increasing
MW 10	0.314	0.048	increasing
MW 11	-0.281	0.079	decreasing
MW 12	-0.438	0.005	decreasing
MW 13	0.038	0.832	
MW 14	-0.057	0.739	

Trilinear Diagrams

Trilinear Piper diagrams are a method for evaluating changes in water chemistry (Hem, 1985). Work in 2005-06 (Sophocleous et al., 2007) showed that the ground water is a calcium bicarbonate water type except in those parts of the study area that were impacted by long-term wastewater application (Figures 5 and 6).

Variation in the general water chemistry is illustrated by the variation in where wells plot on the diagrams. The ground water was sampled three times (fall 2005, spring 2006, and fall 2006). The wells with stable similar water chemistry for fall 2005 and fall 2006 and fall 2006 with spring 2006 are shown in figures 5 and 6 as a separate symbol (green star). These wells are: 1, 4, 5, 6, 11, and 12 for the fall 2005 and fall 2006 time period and wells 4, 5, 6, 9, 10, 11, 12, 14, and West and South for the fall 2006 and spring 2006. The samples from the other monitoring wells show variation in the Piper diagram plot between the sampling periods.

The variation reflected in the graphs is an indication of the variation in the irrigation water chemistry as well as the potential variation in the regional ground water that mixes with the applied water. The parameters that had most spatial variation among the wells are shown in Appendix C. The Kruskal-Wallis test was used on all chemical parameters to see if variation showed up among the wells spatially and temporally.

The three domestic wells sampled during the study also show variation between the fall 2005 and spring 2006 sampling. The occurrence of chemical variation during the years of study suggests that the processes are not stable and that inputs and biological impacts are different at different periods of time. This type of variability needs to be considered when evaluating the methods to control or improve water quality by crop and land-use changes. The number of samples collected is too small to be evaluated statistically.

The two diagrams also show the variation of the wastewater samples collected in the summer of 2005 and the fall of 2006. In addition, the diagrams have the city influent and meat-packing plant influent shown on the diagrams. The city influent in more similar to the ground water of the area as would be expected than is the meat-packing waste. The chemistry of the lagoons shows that the mixing of the two waters makes the wastewater more similar to the meat packing chemistry. This is probably due to the much higher chloride and sulfate concentrations from the packing plants (Appendix A). The chemistry of the wastewater plots in slightly different areas of the graphs depending upon the season of sampling. The variation in the chemistry with time of year is a reflection of the impact of temperature and biological degradation on the chemistry of the water. The differences in the chemistry show up more explicitly in the measured nitrogen-15 isotope values that will be discussed in a later section.

Statistically, the water samples from the monitoring across the area are spatially different. However, the results for the short-term chemistry (seasonal differences) do not show a statistical difference between the sampling periods. Results for the Kruskal-Wallis test are given in Appendix C.

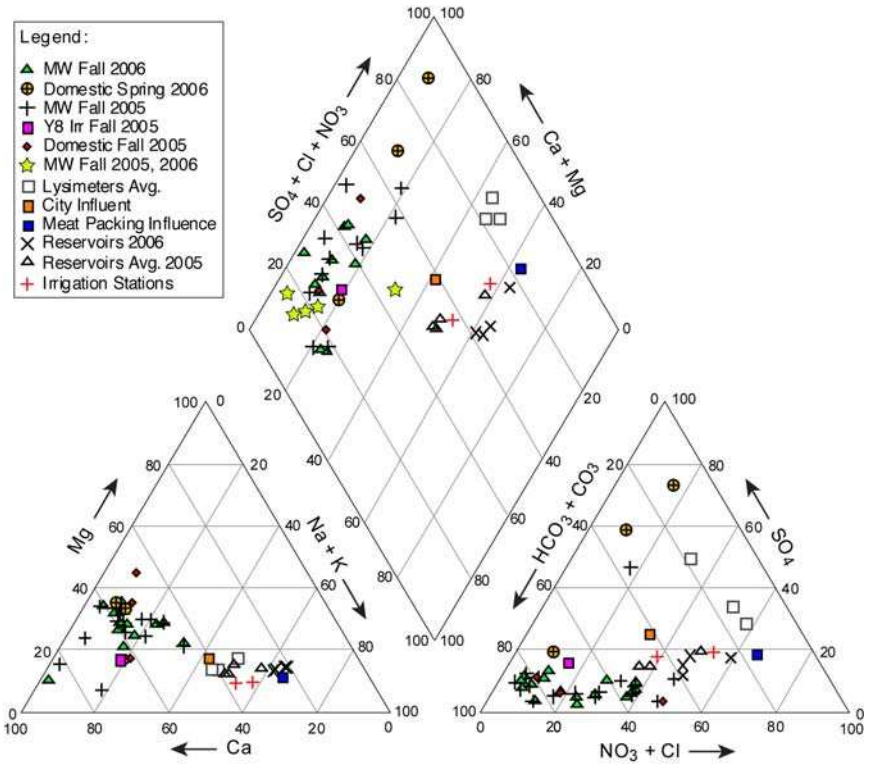

Figure 5. Trilinear diagram of fall 2005 and fall 2006 water chemistry from wells, wastewater, lysimeters, and domestic wells in the area of the Dodge City wastewater irrigation site.

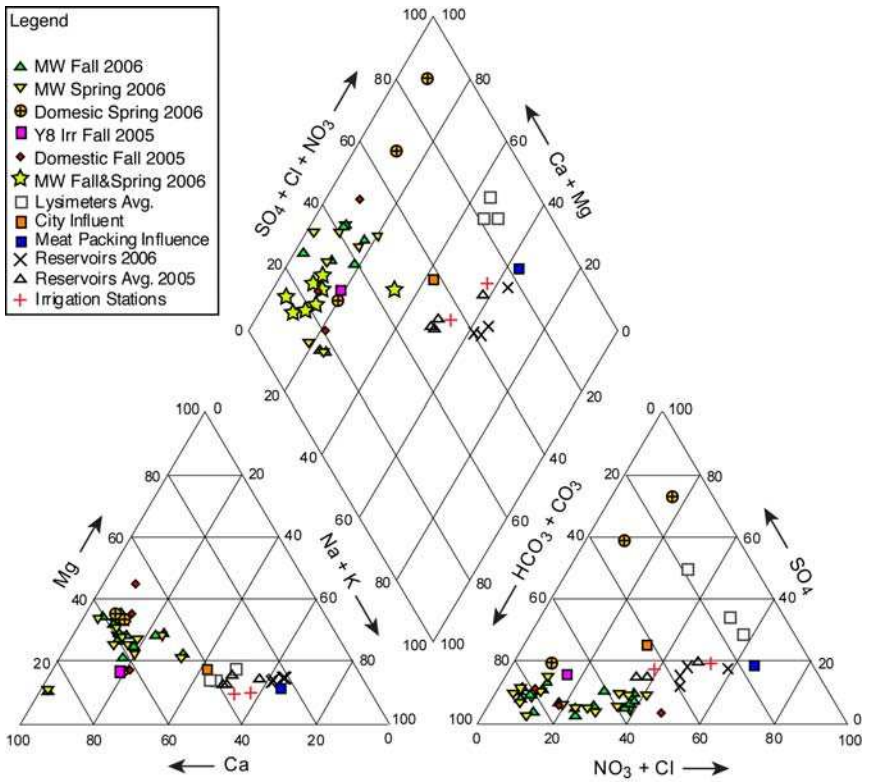

Figure 6. Trilinear diagram of fall 2006 and spring 2006 water chemistry from wells, wastewater, lysimeters, and domestic wells in the area of the Dodge City wastewater-irrigation site

Background on the Nitrogen-15 Isotope Method

Natural-abundance nitrogen-isotope analysis is frequently used to assist in determining sources of nitrogen to ground water. The isotope analysis involves establishing the ratio of nitrogen-15 (^{15}N) to nitrogen-14 (^{14}N) on the nitrogen in nitrate compared to the ratio observed in the standard, atmospheric nitrogen (air). Comparisons of these values indicate if there is more (positive) or less (negative) ^{15}N in the sample. The values thus indicate whether the sample is enriched (+) or depleted (-) in relation to the standard.

Isotopic values are reported as $\delta^{15}N$ in per mil (‰) (Hoefs, 2001):

$$\delta\ ^{15}N\ (‰) = \frac{(^{15}N/\ ^{14}N)_{sample} - (^{15}N/\ ^{14}N)_{standard}}{(^{15}N/\ ^{14}N)_{standard}} \times 1000 \qquad (1)$$

Figure 7 illustrates the range of $\delta^{15}N$ values for various sources of nitrogen and associated processes affecting the ^{15}N abundance (Heaton, 1986). Generally, biological activities use ^{14}N preferentially, resulting in an increased $\delta\ ^{15}N$ value in the remaining nitrogen. Previous work has shown that nitrate from commercial fertilizer sources has $\delta\ ^{15}N$ values of -2 to +8‰, from soil nitrogen a range of +5 to +7‰, and from animal waste generally greater than +10‰ (Heaton, 1986; Herbel and Spalding 1993). Other information such as dissolved oxygen, salinity, iron, and manganese concentrations, and proximity to potential sources aids in source determination.

Ground water impacted by fertilizer frequently has measurable nitrate-N also (generally greater than 3 mg/L in Kansas). Because of possible volatilization of anhydrous ammonia when the chemical pH is above 8, and nitrification of ammonium by bacteria, the $\delta\ ^{15}N$ values frequently are in the +2 to +8 ‰ range.

Other sources such as human-septic waste or animal waste have $\delta\ ^{15}N$ values starting around +5 ‰. Because animal waste has a high ammonia component, the release of the ammonia when the waste is produced causes an immediate enrichment of the $\delta\ ^{15}N$ because the lighter ammonia containing ^{14}N is preferentially released by volatilization. As a result, the $\delta\ ^{15}N$ of the remaining nitrogen is much higher, in the range of +10 ‰ or more. Nitrate-N values are generally also high (usually more than 10 mg/L) in animal-waste sources.

Nitrogen volatilization also can occur in soils and rocks with carbonate zones. Carbonates can increase the pH of water towards 8.5, which means the water is more basic. In this pH range nitrate can be converted to ammonia gas by a chemical reaction. The lighter $\delta\ ^{14}N$ isotope is preferentially released with the gas. The remaining nitrogen becomes enriched with a higher value $\delta\ ^{15}N$.

Another process that can result in an enriched $\delta\ ^{15}N$ value is denitrification. In this process, bacteria degrade nitrate to nitrogen gases that are released to the atmosphere. The ^{14}N of the nitrate is preferentially utilized resulting in $\delta\ ^{15}N$ enrichment in the remaining nitrate. Signs of possible denitrification are low nitrate values and enriched $\delta\ ^{15}N$ values. Table 1 lists the range of $\delta^{15}N$ values and the types of sources usually identifiable with the method.

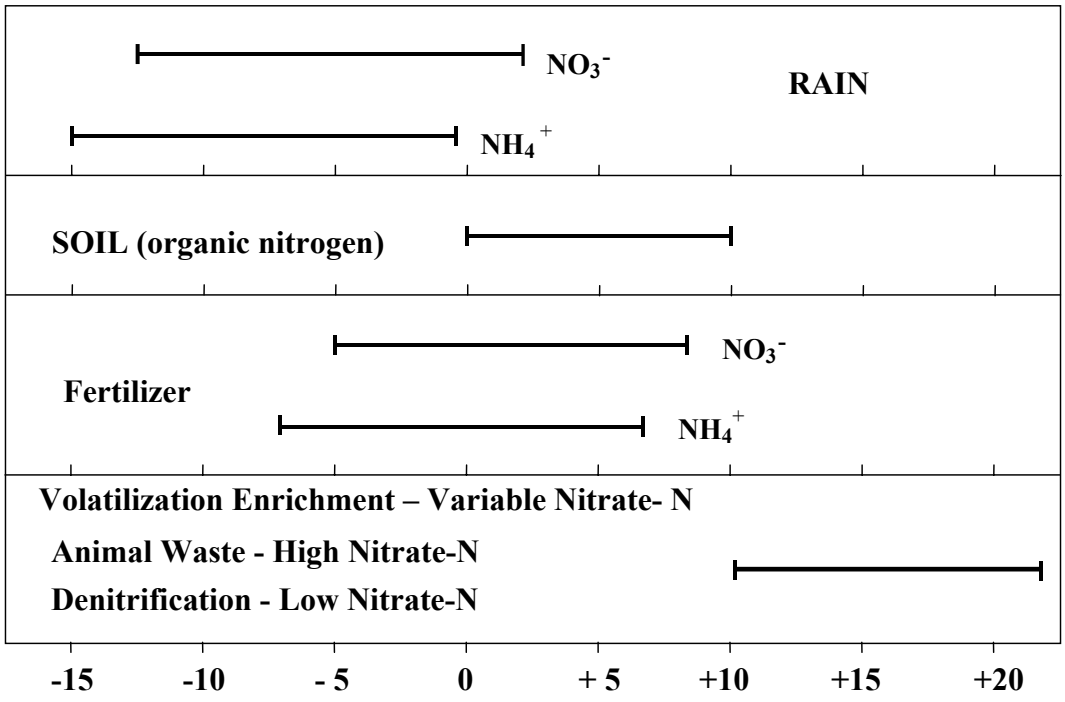

Figure 7. Range of $\delta^{15}N$ signatures for different sources of nitrogen (Heaton, 1986; Townsend et al., 1994).

Table 4. Range of nitrogen-15 and nitrogen sources

$\delta^{15}N$ Values	Nitrogen Sources
< 8 ‰	Fertilizer (Nitrate-N usually > 2 mg/L)
8 to 10 ‰	Mixed sources (Variable range of nitrate-N)
> 10 ‰	Animal waste (Nitrate-N >10 mg/L); volatilization or long-term nitrification of fertilizer from a spill (Nitrate-N > 10 mg/L); or denitrification (Nitrate-N < 1 mg/L)

Nitrogen-15 Natural Abundance Results for the Dodge City Site

The nitrogen-15 isotope natural abundance method was used to determine the sources of the nitrate that was measured in the ground water from the monitoring and domestic wells in the area. Figure 8 shows the $\delta^{15}N$ values and nitrogen concentrations for the monitoring, domestic, and irrigation wells and the reservoir nitrogen concentrations. The monitoring, domestic and irrigation wells are reported as nitrate-N. The reservoir values are reported as total nitrogen and as ammonium-N.

The graph shows that variation occurs in the reservoir samples between the fall sampling and the summer sampling. The summer values from July 2005 show lower $\delta^{15}N$ values although the nitrogen content is similar to the fall 2006 samples. The lower $\delta^{15}N$ values are most likely related to the seasonal impacts on the lagoon chemistry. During the late fall/winter time period the temperature of the ponds decreases and the activity of the bacteria in terms of denitrification of nitrogen in the lagoons also decreases. Also the volatilization enrichment process, because of release of ammonia as a gas, decreases with decreased temperature. Both of these processes utilize ^{14}N which is the lighter isotope and is preferred in terms of utilization both chemically and biologically as the bonds are easier to break. As a result of the utilization of ^{14}N in the water, the remaining nitrogen is enriched in $\delta^{15}N$.

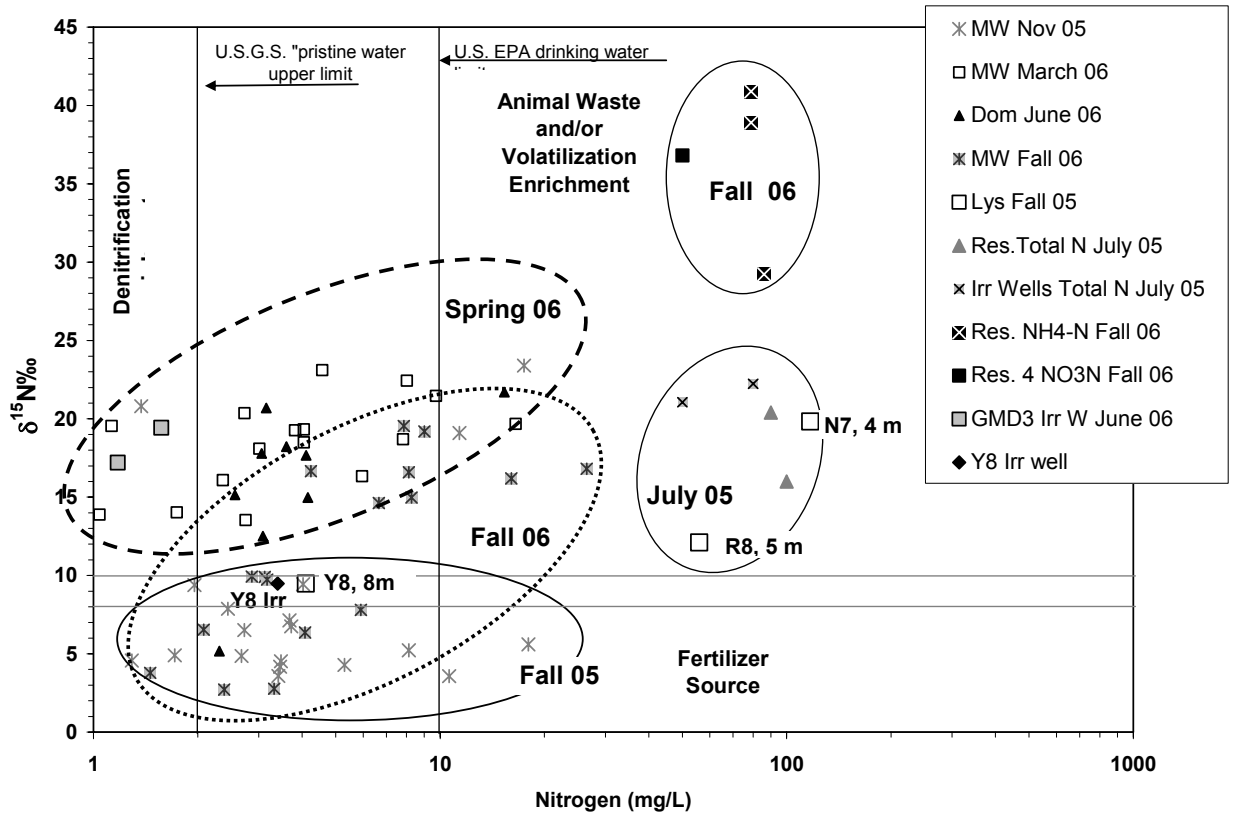

Figure 8. Figure shows variation between seasonal sampling of monitoring wells at Dodge City wastewater-irrigation site. Increased and decreased $\delta^{15}N$ values are a reflection of the chemical and biological processes that have affected the wastewater applied and are related to season of water application, not sampling period.

The variation in the $\delta^{15}N$ values are a reflection of the seasonal time period of application of the wastewater and are not related to the sampling time. As discussed in Sophocleous et al. (2007), recharge at the site is strongly impacted by macropore flow. The travel times of recharge to the ground water are also variable because of the presence of matrix flow (no macropores) and preferential flow via macropores. The presence of macropores as shown in the part A portion of this report indicates that rapid movement of wastewater can occur and can impact the vadose-zone water and ground water more rapidly than previously expected. If the plant uptake of wastewater is not sufficient to remove most of the nitrogen in the wastewater, then the remainder has a good chance of being converted to nitrate and moving to the ground water.

The higher $\delta^{15}N$ values in the ground water from the spring of 2006 indicate that water was most likely applied late in the summer or in the fall after much volatilization enrichment and nitrification of the waste had occurred in the lagoons. Figure 8 shows that the wastewater from the fall 2006 is more highly enriched in $\delta^{15}N$ than the samples collected in the summer of 2005. The starting enriched values moving through the vadose zone result in higher observed $\delta^{15}N$ values in the sampled ground water.

Although the $\delta^{15}N$ values vary by sampling periods, the relative nitrate-N values from the ground-water monitoring wells and the three domestic wells in the irrigation area are relatively stable. No statistical difference is found in nitrate-N concentration between the three sampling periods. The statistical trend discussed previously is seen only with a long term record. This type of statistical difference between the lengths of sampling record is a good indication of the need for long-term ground-water monitoring.

Figure 8 also shows the variation in the $\delta^{15}N$ values for the wastewater and lysimeter samples. Although the relative quantity of nitrogen remains relatively constant, the wastewater $\delta^{15}N$ values for the summer of 2005 and the fall of 2006 show the impact of winter storage (lower values for summer of 2005 because of cold temperatures) and summer heat effects (fall 2006 with higher temperatures over the summer). The values for the lysimeter-water samples collected in the fall 2005 for sites N7 and R8 are close to the wastewater applied, indicating a rapid movement to 4- and 5-m depths.

Except for the fall 2005 samples, the other two sampling periods reflect an animal waste source. The fall 2005 samples appear to reflect the previous farming practices of fertilizer application with ground-water irrigation. The samples from the Y8 irrigation well and Y8 lysimeter are within the fertilizer range also. These values suggest that some volatilization or nitrification enrichment has occurred as the water moved through the vadose zone to the aquifer.

The two irrigation wells from GMD3 also reflect that denitrification may have occurred because of their low nitrate-N values but much enriched $\delta^{15}N$ values.

The domestic wells sampled around the area showed a variety of nitrate-N and $\delta^{15}N$ values indicating the likelihood of variable sources impacting the water quality. Some of the farmsteads had small feedlots nearby, and septic-tank sources are a possibility.

Conclusions

Variability in water chemistry at the Dodge City wastewater treatment site is indicative of different processes occurring in the area due to soil differences, compositional differences in wastewater over the years, varying application rates, macropore versus matrix flow in the soil, temperature effects on the wastewater-treatment process due to seasonal variation, and the effects of bacteria and plant utilization of the wastewater. The chloride and nitrate-N sampling from monitoring wells indicates that certain areas of the wastewater-application site are being impacted by wastewater. The concentrations are increasing yearly at many, but not all, of the wells. A mixing effect with regional ground water is occurring at the edges of the site (wells #11, #12, #13, and #14, and in areas where wastewater application is not occurring, such as at Well #6 to the west of the lagoons but not surrounded by wastewater application fields.

The nitrogen-15 values are elevated at most of the wells, but there is a seasonal component to the values related to the original wastewater composition. Future work at the site should include sampling of the wastewater for nitrogen-15 isotopes on at least a quarterly basis to determine the range of variation that occurs within the lagoon waters.

Continued sampling of nitrate and chloride at the monitoring wells will assist in determining how quickly the nitrate and chloride concentrations are increasing. Use of these data will assist the farmer and consultants to determine the optimal land use and cropping patterns to utilize the wastewater and minimize leaching of future wastewater to the ground water.

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Appendix A. Monitoring and domestic wells at the Dodge City wastewater treatment site fall 2005.

ID	Date Sampled	Spec. Cond. (µmhos/cm)	pH	SiO_2	Ca	Mg	Na	K	Sr	B	CO_3^{-2}	HCO_3^-	SO_4^{-2}	Cl^-	F^-	NO_3^-
MW #1	Fall 2005	1501	7.8	33.1	140.0	40.0	117.0	6.0	2.1	0.147		530	64.9	210.2	0.443	10.8
MW #2	Fall 2005															
MW #3	Fall 2005	522	7.5	16.8	81.0	9.2	3.2	3.1	0.4	0.080		169	9.3	44.5	0.01	79.7
MW #4	Fall 2005	774	8.0	30.6	65.0	21.6	5.3	3.5	1.2	0.045		295	9.4	5.0	0.426	36.0
MW #5	Fall 2005	415	8.3	30.8	52.6	15.7	14.3	4.1	1.0	0.047		207	23.3	10.5	0.609	8.7
MW #6	Fall 2005	484	8.1	31.2	59.9	17.8	13.6	4.3	1.1	0.049		260	20.2	10.4	0.525	12.1
MW #7	Fall 2005	771	8.1	17.5	80.2	21.8	36.7	3.9	1.1	0.223		201	39.5	122.6	0.114	15.4
MW #8	Fall 2005	595	8.0	38.1	66.8	23.9	13.8	4.0	1.4	0.073		248	13.0	35.3	0.702	47.1
MW #9	Fall 2005	587	8.3	44.8	139.0	28.1	12.9	5.2	1.6	0.064		238	18.2	48.6	0.926	23.5
MW #10	Fall 2005	238	8.0	11.9	26.2	9.4	5.7	2.3	0.6	0.029		111	7.2	11.3	0.506	16.3
MW #11	Fall 2005	398	8.3	65.8	43.4	16.0	25.3	4.6	1.1	0.109		210	24.8	6.2	1.49	5.7
MW #12	Fall 2005	414	8.1	42.4	52.0	18.3	9.5	3.7	1.1	0.046	10.13	232	14.3	7.4	0.864	7.6
MW #13	Fall 2005	474	8.2	58.0	48.4	17.5	22.1	4.1	1.0	0.115		262	23.2	5.0	0.107	6.1
MW #14	Fall 2005	233	9.6	24.4	32.1	1.9	9.0	3.1	0.5	0.060		42	43.2	7.1	0.647	8.3
East MW	Fall 2005	1022	8.0	35.4	128.0	33.6	37.5	5.6	2.1	0.088		380	53.7	118.0	0.307	16.5
South MW	Fall 2005	589	8.1	34.5	72.2	23.1	15.1	4.7	1.5	0.069		297	15.1	28.5	0.595	17.8
West MW	Fall 2005	989	8.1	35.1	110.0	38.3	42.2	6.6	2.1	0.142		355	28.0	112.1	0.782	50.4
Nicholson	Fall 2005	641	7.9	22.3	58.4	34.6	12.7	5.1	1.5	0.060		187	10.0	62.1	0.471	77.4
Gepford (N7)	Fall 2005	304	8.0	14.4	38.8	6.6	15.0	2.8	0.4	0.033		154	17.4	4.0	0.414	11.8
Kolbeck (R8)	Fall 2005	322	7.9	18.1	34.1	13.8	9.3	3.2	0.8	0.049		154	9.8	13.9	0.674	15.3
Y8 Irr	Fall 2005	421	8.0	25.6	58.0	9.2	18.7	3.5	0.5	0.062		173	31.6	14.5	0.338	15.1

Appendix A. Monitoring and domestic wells at the Dodge City wastewater treatment site fall 2005 (cont.).

ID	Date Sampled	NO_3-N	PO_4^{-2}	Br^-	Fe (ug/L)	Mn (ug/L)	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰
MW #1	Fall 2005	2.4		0.034	421.9	5.7	-24.4	7.9
MW #2	Fall 2005							
MW #3	Fall 2005	18.0		0.131	0.2	1.8	-20.7	5.6
MW #4	Fall 2005	8.1		0.070	0.0	7.2	-21.6	5.2
MW #5	Fall 2005	2.0		0.089	2.2	0.8	-20.6	9.4
MW #6	Fall 2005	2.7		0.093	1.9	1.2	-21.9	6.5
MW #7	Fall 2005	3.5		0.339	0.3	0.1	-22.0	4.5
MW #8	Fall 2005	10.6		0.168	0.4	1.3	-20.7	3.6
MW #9	Fall 2005	5.3		0.233	48.1	0.0	-22.0	4.3
MW #10	Fall 2005	3.7		0.058	0.0	0.0	-21.1	7.1
MW #11	Fall 2005	1.3		0.069	568.5	26.7	-22.7	4.6
MW #12	Fall 2005	1.7		0.063	447.8	16.2	-21.4	4.9
MW #13	Fall 2005	1.4		0.064	4.7	1.2	-21.6	20.8
MW #14	Fall 2005	1.9		0.044	6.1	1.2		
East MW	Fall 2005	3.7		0.379	0.0	0.0	-22.0	6.8
South MW	Fall 2005	4.0		0.014	0.5	0.6	-20.4	9.4
West MW	Fall 2005	11.4		0.269	0.2	0.4	-21.4	19.1
Nicholson	Fall 2005	17.5		0.201	0.2	1.2	-20.7	23.4
Gepford (N7)	Fall 2005	2.7		0.056	0.0	18.9	-24.1	4.9
Kolbeck (R8)	Fall 2005	3.5		0.085	70.0	11.4	-20.8	4.2
Y8 Irr	Fall 2005	3.4		0.126	2.2	1.0	-23.2	3.6

Appendix A. Monitoring wells and domestic wells at the Dodge City wastewater treatment site spring 2006.

ID	Date Sampled	Spec. Cond. (µmhos/cm)	pH	SiO_2	Ca	Mg	Na	K	Sr	B	CO_3^{-2}	HCO_3^-	SO_4^{-2}	Cl^-	F^-	NO_3^-
MW #1	Spring 2006	1473	7.1	32.1	138.6	39.6	114.6	6.8	2.1	0.087		512	66.1	188.4	0.425	12.1
MW #2	Spring 2006															
MW #3	Spring 2006	973	7.1	42.8	177.5	13.7	4.2	4.7	0.7	0.010		411	18.2	64.2	0.113	73.2
MW #4	Spring 2006	504	7.6	30.7	66.5	22.0	5.2	3.6	1.2	0.033		287	7.2	2.9	0.79	34.7
MW #5	Spring 2006	428	7.8	30.8	52.1	15.2	13.9	4.2	0.9	0.040		214	22.7	10.9	0.712	13.3
MW #6	Spring 2006	483	7.8	32.8	61.1	17.6	14.2	4.5	1.1	0.037		257	21.9	11.2	0.572	12.2
MW #7	Spring 2006	1418	7.2	34.8	171.3	39.7	66.8	7.2	2.2	0.056		424	60.4	192.4	0.304	17.9
MW #8	Spring 2006	571	7.5	40.9	66.5	23.2	13.6	4.5	1.3	0.056		240	14.0	34.8	0.782	35.5
MW #9	Spring 2006	643	7.7	39.1	76.2	28.0	13.3	5.1	1.6	0.055		230	17.8	62.4	1.01	26.4
MW #10	Spring 2006	491	7.7	42.2	56.8	20.7	11.8	4.4	1.3	0.054		233	15.4	25.5	0.858	17.9
MW #11	Spring 2006	434	7.8	67.5	44.0	16.1	25.4	4.6	1.1	0.107		234	25.2	6.6	1.82	5.0
MW #12	Spring 2006	414	7.7	40.7	49.0	17.4	9.1	3.7	1.1	0.040		233	15.0	7.7	0.996	7.7
MW #13	Spring 2006	460	7.8	63.2	58.0	17.7	22.0	4.4	1.0	0.115		265	24.0	5.1	1.3	4.6
MW #14	Spring 2006	339	8.6	33.1	44.1	11.0	10.3	3.8	0.9	0.050	6.59	158	25.5	8.0	0.704	10.5
East MW	Spring 2006	1101	7.1	35.5	135.0	35.4	43.6	6.5	2.1	0.047		399	54.2	126.8	0.348	16.9
South MW	Spring 2006	669	7.4	34.6	81.7	26.2	16.6	5.0	1.6	0.044		300	15.7	47.4	0.581	20.3
West MW	Spring 2006	1023	7.5	38.4	122.8	41.9	22.4	6.6	2.5	0.068		370	23.7	121.2	0.727	43.1
Nicholson	Spring 2006	725	7.6	39.5	83.9	31.9	13.2	4.9	1.9	0.065		268	11.3	58.5	0.515	67.9
Gepford (N7)	Spring 2006	399	8.0	24.9	54.7	8.9	19.1	3.0	0.5	0.047		213	23.6	5.1	0.444	11.3
Kolbeck (R8)	Spring 2006	473	7.7	39.6	55.1	20.3	12.8	4.4	1.2	0.068		234	14.3	21.4	0.73	16.0

Appendix A. Monitoring wells and domestic wells at the Dodge City wastewater treatment site spring 2006 (cont.).

ID	Date Sampled	NO_3-N	PO_4^{-2}	Br^-	Fe (ug/L)	Mn (ug/L)	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰
MW #1	Spring 2006	2.7	0.028	0.446	0.0	0.0	-19.9	20.4
MW #2	Spring 2006							
MW #3	Spring 2006	16.5	0.165	0.167	0.0	0.0	-19.3	19.7
MW #4	Spring 2006	7.8	0.046	0.068	87.2	5.3	-23.5	18.7
MW #5	Spring 2006	3.0	0.017	0.085	186.9	0.0	-23.5	18.1
MW #6	Spring 2006	2.7	0.024	0.086	421.9	5.7	-15.3	13.5
MW #7	Spring 2006	4.0	0.030	1.646	0.0	18.9	-18.2	19.3
MW #8	Spring 2006	8.0	0.018	0.170	299.2	10.9	-19.6	22.4
MW #9	Spring 2006	6.0	0.018	0.256	447.8	16.2	-20.9	16.3
MW #10	Spring 2006	4.0	0.026	0.121	0.0	0.0	-19.2	18.5
MW #11	Spring 2006	1.1	0.029	0.059	0.0	0.0	-18.8	19.6
MW #12	Spring 2006	1.7	0.038	0.057	30.7	0.0	-20.1	14.0
MW #13	Spring 2006	1.0	0.024	0.055	568.5	26.7	-21.4	13.9
MW #14	Spring 2006	2.4	0.029	0.068	34.5	0.0	-23.4	16.1
East MW	Spring 2006	3.8	0.021	0.870	28.6	15.2	-19.8	19.3
South MW	Spring 2006	4.6	0.048	0.114	48.1	0.0	-20.2	23.1
West MW	Spring 2006	9.7	0.032	0.276	93.0	27.7	-19.1	21.5
Nicholson	Spring 2006	15.3	0.019	0.201	30.2		-20.2	21.7
Gepford (N7)	Spring 2006	2.6	0.059	0.061	9.7		-20.3	15.2
Kolbeck (R8)	Spring 2006	3.6	0.020	0.112	29.8		-20.6	18.2

Appendix A. Domestic wells and irrigation wells surrounding the Dodge City wastewater treatment site summer 2006.

ID	Date Sampled	Spec. Cond. (µmhos/cm)	pH	SiO_2	Ca	Mg	Na	K	Sr	B	CO_3^{-2}	HCO_3^-	SO_4^{-2}	Cl^-	F^-	NO_3^-
Dodge City COOP	Summer 2006	664	8.2	9.2	3.2	1.7	151.1	3.3	0.1	0.502	0.50	263	97.0	9.9	3.570	0.1
Gary Bell	Summer 2006	630	7.9	10.8	10.3	2.6	133.8	3.0	0.1	0.488	0.49	248	96.8	9.3	2.820	1.0
C. Nicholson	Summer 2006	394	7.7	24.6	52.8	8.7	19.0	3.5	0.5	0.044	0.04	208	24.8	4.9	0.374	10.2
Dowling	Summer 2006	405	7.8	24.5	55.9	9.0	18.7	3.5	0.5	0.043	0.04	214	21.3	5.9	0.356	13.7
Frink/Scoggings	Summer 2006	499	7.8	24.6	67.1	11.1	21.8	3.6	0.6	0.043	0.04	207	31.6	29.3	0.368	18.2
Roesener	Summer 2006	454	8.1	27.0	60.6	10.3	20.1	3.8	0.6	0.042	0.04	209	27.7	19.9	0.380	14.0
Kolbeck	Summer 2006	473	7.7	39.6	55.1	20.3	12.8	4.4	1.2	0.068	0.07	234	14.3	21.4	0.730	16.0
G. Harshberger	Summer 2006	475	7.7	32.7	58.5	20.0	10.0	3.4	1.2	0.052	0.05	228	14.2	24.1	0.689	18.4
Stewart	Summer 2006	436	7.8	41.0	52.1	17.4	13.7	4.3	1.1	0.057	0.06	218	22.5	14.3	0.987	13.5
M. Nicholson	Summer 2006	725	7.6	39.5	83.9	31.9	13.2	4.9	1.9	0.065	0.07	268	11.3	58.5	0.515	67.9
R. Harshberger Jr.	Summer 2006	816	7.5	32.2	102.5	37.3	17.2	4.5	2.1	0.068	0.07	409	5.8	67.7	0.422	1.6
Gepford	Summer 2006	399	8.0	24.9	54.7	8.9	19.1	3.0	0.5	0.047	0.05	213	23.6	5.1	0.444	11.3
GMD3 Well F029	Summer 2006															30.8
GMD3 Well F035	Summer 2006															23.1
Dodge City COOP	Summer 2006	664	8.2	9.2	3.2	1.7	151.1	3.3	0.1	0.502	0.50	263	97.0	9.9	3.570	0.1
Gary Bell	Summer 2006	630	7.9	10.8	10.3	2.6	133.8	3.0	0.1	0.488	0.49	248	96.8	9.3	2.820	1.0
C. Nicholson	Summer 2006	394	7.7	24.6	52.8	8.7	19.0	3.5	0.5	0.044	0.04	208	24.8	4.9	0.374	10.2
Dowling	Summer 2006	405	7.8	24.5	55.9	9.0	18.7	3.5	0.5	0.043	0.04	214	21.3	5.9	0.356	13.7
Frink/Scoggings	Summer 2006	499	7.8	24.6	67.1	11.1	21.8	3.6	0.6	0.043	0.04	207	31.6	29.3	0.368	18.2
Roesener	Summer 2006	454	8.1	27.0	60.6	10.3	20.1	3.8	0.6	0.042	0.04	209	27.7	19.9	0.380	14.0

Appendix A. Domestic wells and irrigation wells surrounding the Dodge City wastewater treatment site summer 2006 (cont.).

ID	Date Sampled	NO_3-N	PO_4^{-2}	Br^-	Fe (ug/L)	Mn (ug/L)	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰
Dodge City COOP	Summer 2006	3.6	0.020	0.112	29.8		-20.6	18.2
Gary Bell	Summer 2006	0.0	0.177	0.090	175.8	v	-21.00	8.73
C. Nicholson	Summer 2006	0.2	0.050	0.090	44.6	30.2	-21.30	2.79
Dowling	Summer 2006	2.3	0.042	0.060	< 43	< 43	-20.90	5.17
Frink/Scoggings	Summer 2006	3.1	0.037	0.055	< 43	< 43	-20.10	12.51
Roesener	Summer 2006	4.1	0.036	0.151	< 43	< 43	-19.80	17.66
Kolbeck	Summer 2006	3.2	0.039	0.111	77.6	< 43	-20.70	20.69
G. Harshberger	Summer 2006	3.6	0.020	0.112	< 43	< 43	-20.60	18.23
Stewart	Summer 2006	4.2	0.019	0.132	49.5	< 43	-20.30	14.98
M. Nicholson	Summer 2006	3.1	0.017	0.110	< 43	< 43	-21.40	17.79
R. Harshberger Jr.	Summer 2006	15.3	0.019	0.201	< 43	< 43	-20.20	21.70
Gepford	Summer 2006	0.4	0.029	0.367	151.5	86.0	-19.10	8.77
GMD3 Well F029	Summer 2006	2.6	0.059	0.061	< 43	< 43	-20.30	15.15
GMD3 Well F035	Summer 2006	7.0					-20.40	19.43
Dodge City COOP	Summer 2006	5.2					-20.20	17.20
Gary Bell	Summer 2006	3.6	0.020	0.112	29.8		-20.6	18.2
C. Nicholson	Summer 2006	0.0	0.177	0.090	175.8	v	-21.00	8.73
Dowling	Summer 2006	0.2	0.050	0.090	44.6	30.2	-21.30	2.79
Frink/Scoggings	Summer 2006	2.3	0.042	0.060	< 43	< 43	-20.90	5.17
Roesener	Summer 2006	3.1	0.037	0.055	< 43	< 43	-20.10	12.51

Appendix A. Monitoring and domestic ground-water samples fall 2006.

ID	Date Sampled	Spec. Cond. (µmhos/cm)	pH	SiO_2	Ca	Mg	Na	K	Sr	B	CO_3^{-2}	HCO_3^-	SO_4^{-2}	Cl^-	F^-	NO_3^-
MW #1	Fall 2006	1469	7.2	32.1	136.4	40.6	115.7	6.3	2.0	0.100		486	68.1	192.3	0.372	13.8
MW #2	Fall 2006	737	7.4	39.4	132.1	9.6	3.9	4.1	0.5			344	8.5	28.2	0.127	71.2
MW #3	Fall 2006															117.4
MW #4	Fall 2006	490	7.5	30.5	61.0	21.1	5.7	5.2	1.2	0.032		273	9.1	4.9	0.643	34.8
MW #5	Fall 2006	427	7.7	29.9	50.8	15.3	14.7	4.5	0.9	0.045		216	23.5	11.4	0.613	14.0
MW #6	Fall 2006	473	7.8	30.8	58.1	17.1	14.0	4.5	1.0	0.044		252	21.3	10.0	0.515	12.7
MW #7	Fall 2006	1134	7.3	32.3	146.7	30.7	46.4	6.1	1.6	0.058		391	41.8	145.0	0.284	29.5
MW #8	Fall 2006	556	7.7	59.7	64.0	23.6	15.3	5.6	1.3	0.075		295	14.9	35.8	0.658	36.6
MW #9	Fall 2006	656	7.8	36.6	72.8	28.2	14.4	5.5	1.6	0.068		239	19.1	72.6	0.819	36.0
MW #10	Fall 2006	458	7.6	40.3	54.9	20.1	12.0	4.4	1.2	0.056		231	16.0	22.7	0.733	18.1
MW #11	Fall 2006	436	7.9	63.4	42.5	15.7	25.4	5.1	1.0	0.112		234	25.7	6.3	1.54	6.5
MW #12	Fall 2006	415	7.7	39.9	48.8	17.3	9.7	3.7	1.0	0.044		231	16.2	6.7	0.837	9.2
MW #13	Fall 2006	467	8.0	59.7	52.2	18.1	27.5	7.4	c	0.149		264	25.4	4.7	1.04	10.6
MW #14	Fall 2006	351	8.6	32.3	43.0	11.3	10.6	6.7	0.9	0.059	6.00	177	24.3	8.2	0.579	14.7
East MW	Fall 2006	937	7.6	32.9	110.3	29.2	40.4	6.9	1.7	0.062		370	48.6	93.1	0.331	18.8
South MW	Fall 2006	673	7.6	32.7	74.0	26.3	17.2	9.2	1.6	0.051		295	18.3	58.1	0.477	26.2
West MW	Fall 2006	979	7.7	36.8	120.1	39.6	21.7	6.7	2.3	0.075		364	25.1	113.4	0.528	39.9

Appendix A. Monitoring and domestic ground-water samples fall 2006 (cont.)

ID	Date Sampled	NO_3-N	PO_4^{-2}	Br^-	Fe (ug/L)	Mn (ug/L)	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰
MW #1	Fall 2006	3.1	0.064	0.517			-26.3	9.9
MW #2	Fall 2006	16.1	0.586	0.128			-24.6	16.2
MW #3	Fall 2006	26.5	0.140				-27.5	16.8
MW #4	Fall 2006	7.9	0.074	0.051			-27.4	19.5
MW #5	Fall 2006	3.2	0.151	0.126			-26.0	9.7
MW #6	Fall 2006	2.9	0.183	0.124			-27.9	9.9
MW #7	Fall 2006	6.7	0.029	1.056			-25.9	14.6
MW #8	Fall 2006	8.3	1.276	0.164			-26.9	15.0
MW #9	Fall 2006	8.1	0.219	0.294	276.3		-25.0	16.6
MW #10	Fall 2006	4.1	0.114	0.152			-29.3	6.4
MW #11	Fall 2006	1.5	0.017	0.064		13.6	-29.9	3.8
MW #12	Fall 2006	2.1	0.139	0.058			-27.9	6.5
MW #13	Fall 2006	2.4	0.037	0.049			-26.7	2.7
MW #14	Fall 2006	3.3	0.080	0.056			-29.6	2.8
East MW	Fall 2006	4.2	0.024	0.625			-28.0	16.7
South MW	Fall 2006	5.9	0.035	0.173			-24.1	7.8
West MW	Fall 2006	9.0	0.053	0.299	86.5		-24.1	19.2

Appendix A. Wastewater samples from Dodge City wastewater treatment site 2005-07.

ID	Date Sampled	Spec. Cond. (µmhos/cm)	pH	SiO_2	Ca	Mg	Na	K	Sr	B	CO_3^{-2}	HCO_3^-	SO_4^{-2}	Cl^-	F^-	NO_3^-
Wastewater samples																
#1 Res. (North)	Summer 2005	2352			180.0	34.3	250.0	37.0		0.318		756	181.3	309.4		
#2 Res. (Middle)	Summer 2005	2475			164.8	32.0	237.1	36.7		0.352		739	175.0	303.7		
#3 Res. (South)	Summer 2005	2473			157.0	41.8	256.0	37.4		0.300		686	175.0	322.0		
#4 Res. (Final)	Summer 2005	2291			121.8	37.0	288.8	33.0		0.299		355	181.3	325.1		
Irr. Sta. #1	Summer 2005	2315			148.0	23.0	240.5	38.0		0.451		624	200.0	305.4		
Irr. Sta. #2	Summer 2005	2027			126.2	22.8	253.8	41.9		0.581		314	175.0	314.8		
N7 Medium	Summer 2005	3142			293.3	62.5	365.0	15.8		0.390		278	465.0	376.7		518.3
R8 MEDIUM	Summer 2005	2970			296.0	63.2	386.0	8.0		0.184		382	828.0	250.0		247.5
R8 SHALLOW	Summer 2005	6030			423.3	140.0	736.7	27.3		0.397		573	1070.0	793.3		655.6
Municipal Influent	Fall 2006	1491	8.0		110.0	29.0	130.0	15.0		0.290		390	186.8	180.0		
National Beef Influent	Fall 2006	4304	7.0		180.0	52.0	560.0	69.0		0.220		380	333.6	871.0		
#1 Res. (North)	Fall 2006	2714	8.3		82.0	35.0	290.0	33.0		0.430	46.00	540	226.0	434.3		
#2 Res. (Middle)	Fall 2006	2678	8.2		82.0	34.0	280.0	32.0		0.490	39.00	580	188.5	422.9		
#3 Res. (South)	Fall 2006	3046	8.3		110.0	36.0	310.0	37.0		0.380	68.00	670	160.5	483.7		
#4 Res. (Final)	Fall 2006	2688	7.9		110.0	42.0	350.0	40.0		0.370		290	172.6	519.2		

Appendix A. Wastewater samples from Dodge City wastewater treatment site 2005-07 (cont.).

ID	Date Sampled	NO_3-N	PO_4^{-2}	Br^-	Fe (ug/L)	Mn (ug/L)	$\delta^{13}C$ ‰	$\delta^{15}N$ ‰	Organic N (mg/L)	Total Kjeldahl N (mg/L)	NH4-N (mg/L)
Wastewater samples											
#1 Res. (North)	Summer 2005	3.4									93.2
#2 Res. (Middle)	Summer 2005	2.5					-19.89	16			94.6
#3 Res. (South)	Summer 2005	5.1					-15.40	20.4			67.1
#4 Res. (Final)	Summer 2005	22.9									20.1
Irr. Sta. #1	Summer 2005	33.1					-16.41	22.24			63.6
Irr. Sta. #2	Summer 2005	72.8					-15.23	21.06			16.5
N7 Medium	Summer 2005	117.0			465.0	278.3	-19.26	19.82			376.7
R8 MEDIUM	Summer 2005	55.9			828.0	382.0	-19.86	12.11			250.0
R8 SHALLOW	Summer 2005	148.0			1070.0	573.3	-20.27	9.48			793.3
Municipal Influent	Fall 2006	1.3	0.013	0.183					12	36	24
National Beef Influent	Fall 2006		0.089	2.014	5200.0	690.0			200	230	30
#1 Res. (North)	Fall 2006	16.9	0.013	0.525	350.0	340.0			16	95	79
#2 Res. (Middle)	Fall 2006	16.7	0.012	0.436	450.0	350.0			17	96	79
#3 Res. (South)	Fall 2006	12.4	0.032	0.409	300.0	360.0			14	100	86
#4 Res. (Final)	Fall 2006	55.6	0.023	0.399	350.0	240.0	-12.60	21.78	20	22	

Appendix B. Shapiro-Wilk *W* statistic and *p* value. Parameter is non-normal in distribution if $p < \alpha = 0.10$.

Samples	NO3-N	CL	SPCD	HCO3	SO4	Ca	Mg	Na	B	N15
All Wells	*0.781* *p<0.0001*	*0.765* *p<0.0001*	*0.846* *p<0.0001*	*0.961* *p=0.072*	*0.836* *p<0.0001*	*0.859* *p<0.0001*	*0.954* *p=0.0377*	*0.621* *p<0.0001*	*0.830* *p<0.0001*	*0.908* *p=0.0005*
Fall 2005	*0.74* *p=0.0001*	*0.734* *p=0.0001*	*0.866* *p=0.010*	*0.938* *p =0.225*	*0.865* *p=0.0096*	*0.877* *p=0.016*	*0.961* *p=0.5688*	*0.612* *p<0.0001*	*0.827* *p=0.0023*	*0.708* *p<0.0001*
Spring 2006	*0.845* *p=0.0056*	*0.753* *p=0.0003*	*0.815* *p=0.0019*	*0.934* *p=0.213*	*0.800* *p=0.0012*	*0.807* *p=0.0015*	*0.929* *p=0.1667*	*0.629* *p<0.0001*	*0.923* *p=0.1276*	*0.952* *p=0.4347*
Fall 2006	*0.733* *p=0.0003*	*0.805* *p=0.0032*	*0.836* *p=0.0088*	*0.922* *p=0.187*	*0.820* *p=0.0052*	*0.831* *p=0.0074*	*0.941* *p=0.3655*	*0.647* *p<0.0001*	*0.861* *p=0.0248*	*0.915* *p=0.1195*

Appendix C. Kruskal-Wallis *p* values for tests of seasonal (fall 2005 and spring and fall 2006) and spatial variation among samples from monitoring wells.

	NO3N	CL	SPCD	^{15}N	SO4	^{13}C	B	Ca	Mg	Na	K	HCO3	F	Br
Spatial (21 groups)	0.0037	0.0015	0.0003	0.4163	0.0007	0.9909	0.0071	0.0009	0.0003	0.0002	0.0229	0.0013	0.0074	0.0451
Seasonal (3 groups)	0.2313	0.8337	0.5551	<.0001	0.7749	<.0001	0.1968	0.4989	0.5748	0.7945	0.0043	0.1632	0.0474	0.1671

* Seasonal groups are fall 2005, spring 2005, and fall 2006.