Effects of topography on the transport of agricultural chemicals to groundwater in a sand-plain setting

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Abstract Geochemical data were collected to investigate the effects of topography and focused recharge on the transport of agricultural chemicals to groundwater through sandy soils. The research was done at a topographically high (upland) site and a depressional (lowland) site within a corn field. Agricultural chemicals that move readily with water were most directly affected by focused recharge to the lowland site. Surface runoff of water to the lowland site was the primary cause for the generally greater flux of chloride, nitrate nitrogen, and sulfate compared with the upland site. Based on data from the unsaturated zone, for example, the average annual fluxes of these chemicals in 1992–1993 were 5.1, 3.4, and 1.7 times greater, respectively, at the lowland site. Study results indicate that consideration should be given to modifying site-specific management farming technology to account for varying recharge rates in different topographic settings. By reducing chemical application rates in topographic depressions, where focused recharge of chemicals occurs because of surface runoff, farmers could improve ground-water quality as well as reduce expenditures for agricultural chemicals.

Résumé Des données géochimiques ont été recueillies dans le but d'analyser les effets de la topographie et de la recharge concentrée sur le transport des produits chimiques, utilisés en agriculture, vers les nappes au travers de sols sableux. Cette étude a été réalisée dans un secteur topographiquement élevé et dans un secteur en dépression, sur des cultures de blé. Les produits chimiques agricoles qui se déplacent facilement avec l'eau ont été le plus directement concernés par la recharge concentrée dans la zone déprimée. Le ruissellement de l'eau dans la zone déprimée a été la cause primaire du flux généralement plus important de chlorure, d'azote du nitrate et de sulfate par comparaison avec la zone élevée. En s'appuyant sur les données fournies par la zone non saturée, par exemple, les flux moyens annuels de ces substances en 1992–1993 ont été respectivement 5,1, 3,4 et 1,7 fois plus élevés dans le secteur en dépression. Les résultats de l'étude montrent qu'il faut prêter attention aux modifications des pratiques culturales de gestion de sites spécifiques en prenant en compte les taux variables de recharge selon les situations topographiques. En réduisant les taux d'application de substances chimiques dans les dépressions topographiques, où se produit la recharge concentrée des produits du fait du ruissellement, les agriculteurs peuvent améliorer la qualité des eaux souterraines tout en réduisant leurs dépenses pour ces produits.

Resumen Se ha recogido datos geoquímicos para investigar los efectos de la topografía y de la recarga localizada en el transporte de compuestos químicos de origen agrícola a través de suelos arenosos hacia las aguas subterráneas. El estudio se ha llevado a cabo en dos emplazamientos situados en un campo de maíz; el primero, en un alto topográfico; el segundo, en una depresión. Los compuestos que se desplazan rápidamente con el agua son los más afectados por la recarga localizada hacia la depresión. La escorrentía superficial hacia ésta es la causa principal de un flujo mayor de cloruro, nitrógeno nítrico y sulfato que en el punto topográficamente elevado. Con base en los datos de la zona no saturada, por ejemplo, el promedio anual de flujo de los compuestos citados fue 5,1; 3,4 y 1,7 veces mayor, respectivamente, en la depresión. Los resultados indican que se debería prestar atención a cualquier cambio en las tecnologías de gestión agrícola a la hora de evaluar modificaciones de las tasas de recarga en diferentes puntos topográficos. Reduciendo la aplicación de compuestos químicos en las depresiones, donde la recarga se acentúa por la escorrentía superficial, los agricultores podrían mejorar la calidad de las aguas subterráneas a la par que reducir los gastos en compuestos químicos.

Keywords Agriculture · Contamination · Focused recharge · Nitrate · Runoff

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Introduction

Spatial and temporal variability in the transport of agricultural chemicals to the water table is complex and poorly understood. Many agricultural chemicals are highly soluble in water, and, thus, recharge greatly affects their transport to groundwater. Because recharge is greatest (focused) beneath depressions in the land surface (Meyboom 1966; Lissey 1971; Miller et al. 1985; Delin et al. 2000) topography plays an important role in the transport of agricultural chemicals to groundwater in sand-plain settings. Preferential flow conventionally is thought of as a process affecting the transport of water and solutes to groundwater through microscale features such as earthworm borrows, macropores, and other preferential pathways (Simmers et al. 1997; Gee and Hiller 1998). It is well documented that preferential flow can result in rapid transport of agricultural chemicals to groundwater with minimal degradation at these small scales (Kladivko et al. 1991; Edwards et al. 1993; Shipitalo et al. 1994; Golabi et al. 1995). The term localized recharge has been used to describe this preferential flow and more rapid transport of agricultural chemicals to groundwater at the field scale of several meters to tens of meters (Simmers et al. 1997). Derby and Knighton (1997), for example, found that water and a tracer moved much more rapidly through an unsaturated zone of layered silt and sand under topographic depressions than under nearby flat areas. Additional research is needed to evaluate the effects of topography on the transport of agricultural chemicals to groundwater in relatively homogeneous sandy soils. Potential benefits include reduced farming costs and a reduction in chemical loading to groundwater.

The purpose of this paper is to describe differences in agricultural chemical transport rates and loading to groundwater between a depression and an upland site in sandy soils. This research was part of a larger effort to evaluate the effects of transient recharge, topography, and subsurface heterogeneities on the flux of water and agricultural chemicals to the water table (Delin and Landon 1996a; Delin et al. 2000). Data from long-term monitoring were used to evaluate how differences in ground-water recharge, and water and agricultural chemical movement through the unsaturated zone, could be attributed to differences in topography. This research was part of the Management Systems Evaluation Area (MSEA) initiative to evaluate the effects of agricultural systems on water quality in the Midwest corn belt (Anderson et al. 1991). This research contributed to the MSEA study by providing in-depth knowledge of the transport of agricultural chemicals to groundwater in relation to changes in landscape. Tomer (1994) completed a related research effort by evaluating variations in soil-water storage in relation to topography across the sand-plain setting at the Princeton, Minnesota MSEA.

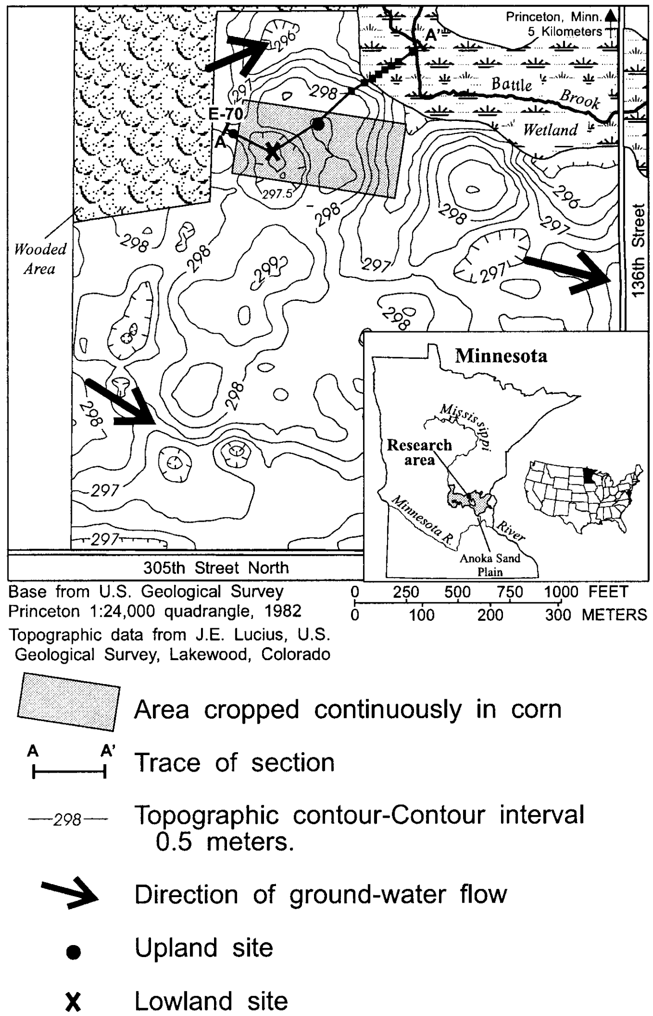

Fig. 1 Topography and layout of the research area near Princeton, Minnesota

Location and Description of the Research Area

The research was done at a topographically high (upland) site and a depressional (lowland) site within a 2.7-ha field near Princeton, Minnesota as shown in Fig. 1. The upland and lowland sites were about 78 m apart and differed in land-surface elevation by only 1.4 m (slope of about 0.02). The lowland site was selected for research in part because the slope is steeper than in most of the area (Fig. 1). During 1991–1995, depth to water at the upland and lowland sites fluctuated between 4.0–4.4 and 2.6–3.0 m, respectively. The shallowest water levels below land surface typically occurred during May–June of each year following snowmelt and spring rainfall, whereas the deepest water levels occurred during the winter months when the ground was frozen.

Field corn was grown in the field during the growing seasons. The farming system for the entire cropped area consisted of full-width tillage, split-nitrogen application, and broadcast application of the herbicide atrazine. Nitrogen fertilizer, primarily in the form of urea, and chloride, from potassium-chloride fertilizer, proved useful as

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tracers to identify groundwater affected by agricultural chemicals applied to the corn. Sulfate from zinc sulfate, ammonium sulfate, and potassium magnesium sulfate fertilizer also proved useful for comparing chemical transport between the two sites. Because above ground instrumentation prevented tractor access around the upland and lowland sites, the herbicides and fertilizers were broadcast applied to both sites using a hand sprayer. Application rates for nitrogen, chloride, sulfate, and atrazine (averages of 231.2, 46.4, 13.4, and 1.7 kg/ha, respectively) were generally consistent during most years of the study. These estimates do not include applications as part of a recharge experiment during October 1993. Anderson et al. (1991), Delin et al. (1994), and Landon et al. (1997) provide detailed descriptions of the farming practices at the site.

Yearly natural precipitation totals were 94, 52, 77, 66, and 70 cm for 1991–1995, respectively. The average precipitation rate during this period was 72 cm/year, which is about 9% less per year than the 30-year normal precipitation average of 78 cm/year at nearby Santiago, Minnesota (Minnesota Department of Natural Resources 2000). Water was applied with a linear-move irrigation system beginning in 1992 to supply crop needs for growth. Yearly irrigation totals during 1992–1995 were 11, 14, 14, and 17 cm, respectively. Because the irrigation water was applied only as necessary to sustain crop growth (J.A. Lamb, University of Minnesota, personal communication, 1996), it is reasonable to assume that none of this irrigation water reached the saturated zone as recharge. Mean pan evaporation for the period 1991–1995 was about 80 cm/year (US Department of Commerce 1991–1995). Mean monthly temperatures varied from about 22 °C in July to about –13 °C in January (Minnesota Department of Natural Resources 2000).

Topsoil at the upland and lowland sites are 0.4 and 0.8 m thick, respectively (Delin et al. 1996) with less than 1% organic matter (US Dept. of Agriculture 1968). The greater thickness of topsoil at the lowland site is presumably because of movement of finer soil particles into the depression by surface runoff of water, herein referred to as run-on. The glacial outwash deposits at both sites to a depth of 2 m below the land surface are generally similar, being composed of about 95% sand and 5% silt and clay (Delin and Landon 1996a). However, the organic carbon content is greater at the lowland site (0.42%) compared with the upland site (0.23%) (Delin et al. 2000).

Average recharge based on three methods (groundwater hydrograph analysis, an unsaturated-zone water balance, and age dating of groundwater based on chlorofluorocarbons) was 18 cm/year at the upland site and 29 cm/year at the lowland site during the study (Delin et al. 2000). The increased, or focused, recharge and more rapid movement of wetting fronts at the lowland site is attributed to three factors: (1) surface run-on of water, (2) lamellae that may impede the vertical transport of water at the upland site, and (3) coarser grained sediments at the lowland site at depths greater than about 1.5 m (Delin et al. 2000). Because of spatially variable recharge, the direction and velocity of ground-water movement in the surficial aquifer varied seasonally during 1991–1995. Throughout much of each year, however, ground-water movement was approximately from the lowland site toward the upland site (Fig. 1). Groundwater velocities typically varied seasonally from about 7–15 cm/day and the magnitude of the horizontal hydraulic gradients varied from about 0.001–0.002 (Delin et al. 1994). The magnitude of the vertical hydraulic gradient (downward) beneath both sites was about 0.0001.

Methods of Investigation

Two multiport wells (MPORTs) (Delin and Landon 1996b) were installed at each site to facilitate collection of water samples at 0.5- to 2.0-m intervals in the upper 12 m of the saturated zone. Suction lysimeters were installed in the unsaturated zone at depths of 0.8, 1.8, 2.6, and 2.8 m at the upland site and at depths of 0.8, 1.8, 2.4, and 2.5 m at the lowland site. The suction lysimeters were constructed of Teflon with a porous ceramic cup. Wick samplers were also installed in the unsaturated zone at depths of 0.8 and 1.5 m at the upland site and at the 1.6-m depth at the lowland site. The wick samplers were constructed of fiberglass attached to a glass plate, based on the design of Brown et al. (1986). Results from field tests indicated that water collected from the wick samplers was more representative of mobile soil water that recharged groundwater during or soon after a recharge event than soil water from the suction lysimeters (Landon et al. 1999). Soil moisture content was measured at each site with two sets of time-domain reflectometry (TDR) probes installed at depths of 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, 2.5, and 3.0 m. Water levels were measured continuously in a water-table well installed at each site. Precipitation was measured at each site using a tipping-bucket rain gage.

Water samples for chemical analysis were collected monthly from the water-table wells, unsaturated-zone samplers, and MPORTs during 1991–1995. Samples of the irrigation water and precipitation also were collected.

Specific conductance, pH, temperature, dissolved-oxygen concentration, and oxidation–reduction potential of groundwater were measured in the field using a multiparameter probe. Most analyses for dissolved major cations and anions were completed by the Geochemistry Laboratory in the Department of Geology and Geophysics at the University of Minnesota, Minneapolis; cations were analyzed using inductively-coupled plasma-mass spectroscopy and anions were analyzed using ion chromatography. Anion samples were also analyzed using ion chromatography at a research laboratory in Denver, Colorado (R.B. Wanty, US Geological Survey 1996, personal communication). Analyses for atrazine and its metabolites de-ethylatrazine and de-isopropylatrazine were completed at a US Geological Survey laboratory in Navarre, Minnesota using gas chromatography/mass spectrometry (Larson et al. 1996). Sample collection and lab-

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oratory analysis quality assurance/quality control protocols were followed and are described in detail by Delin et al. (1994) and Larson et al. (1996).

During October 1993, a recharge experiment was conducted that is herein referred to as the catastrophic experiment, in reference to the relatively large amount of water and chemicals applied. Chloride (29 kg/ha), nitrogen (418 kg/ha), sulfate (34 kg/ha), atrazine (116 kg/ha), and 27.4 cm of water were applied to the upland and lowland sites as part of the experiment. These applications, by design, resulted in the increased flux of chemicals to groundwater above the effects from that of the MSEA farming system. Schroyer (1999) provides a detailed description of the catastrophic recharge experiment.

As a result of the catastrophic recharge experiment, data and results presented in this paper are presented in two data sets. Data collected during 1991–1993, prior to the catastrophic experiment, are considered representative of the farming system and natural hydrologic conditions. All data collected during 1994–1995, after the experiment, are considered useful in evaluating the effects of topography on the transport of the agricultural chemicals.

Univariate statistics plus the Kruskal–Wallis rank sum test were used to evaluate the differences in agricultural chemical concentrations between the upland and lowland sites. The Kruskal–Wallis rank sum test is a nonparametric alternative to a one-way analysis of variance. The null hypothesis is that the true median is the same in each of the groups. The alternative hypothesis is that it is different in at least one of the groups. Unlike a one-way analysis of variance, this test does not require normality. Herein, use of the term “significant” means that the Kruskal–Wallis rank sum test indicated statistically significant differences between groups, as indicated by a significance level (p-value) of less than 0.05. All statistics were determined using SAS statistical software (SAS Institute Inc. 1989).

The fluxes of chloride, nitrate, sulfate, and atrazine, plus its metabolites de-ethylatrazine and de-isopropylatrazine, that reached the saturated zone from applications during 1991–1994 to the continuous corn farming system were estimated for individual recharge events and summed to compute annual fluxes. Two methods were used: (1) an analysis of unsaturated-zone concentrations, herein referred to as the unsaturated-zone method, and (2) a mass-balance estimate of excess concentrations in the upper 2 m of the saturated zone beneath each site, herein referred to as the saturated-zone method.

For the unsaturated-zone method, the annual flux of each chemical (M) was estimated as the sum of fluxes from each individual recharge event at time t_j as follows:

$$M = \sum_{j=1}^{y} [R(t_j) \times C_u] \tag{1}$$

where $R(tj)$ is recharge based on changes in soil moisture storage in the unsaturated zone, C_u is the average concentration of a constituent in all suction and wick samplers at each site during the recharge event, and y is the total number of recharge events in a given year. The concentration C_u was the average of all unsaturated-zone samples collected during sampling periods that occurred within about 1 month of a given recharge event. In general, however, the concentration was equivalent to the average of all unsaturated-zone samples collected during the sampling period closest to the recharge event.

The unsaturated-zone recharge $R(tj)$ for each event was estimated based on a modified version of the zero-flux plane method (Richards 1956). The method is based on the premise that water in the soil above the zero-flux plane moved upward in response to evapotranspiration (ET) and that water below that depth drained downward to the water table as recharge. Integration of changes in soil-moisture content over time for the region between the zero-flux plane and the water table yielded an estimate of recharge [$R(tj)$] as follows:

$$R(t_j) = \sum_{i=0}^{x} [\theta\nu_i(t_j) - \theta\nu_i(t_{j-1})\Delta z_i] \tag{2}$$

where i is an index to the TDR probes equal to zero for the probe nearest the water table increasing upward to a value of X for the soil-moisture probe nearest the zero-flux plane, $\theta\nu_i(t_j)$ is the soil moisture content at sample point i, and time tj, and Δz_i is the vertical interval of the unsaturated zone represented by measurements at each TDR probe i. The time interval over which recharge was estimated equaled the difference in time between when the maximum soil-moisture storage occurred during the recharge event and the time of minimum soil-moisture storage immediately following the recharge event. Recharge was calculated for each precipitation event that exceeded about 1.5 cm, and produced a wetting front below the modified zero flux plane. Delin et al. (2000) provide a detailed description of this method for estimating recharge.

Fluxes based on the saturated zone method were estimated by comparing concentrations from the MPORTs in the upper 2 m at the upland and lowland sites to those at the same depth and time in MPORT E-70 (Fig. 1), which represents non-agricultural background concentrations (Landon et al. 1998). Concentrations at the upland and lowland sites that exceeded concentrations from the same depths beneath MPORT E-70 were assumed to have recharged from the overlying cropped area and are herein called “excess concentrations.” The shaded areas shown in Fig. 2 represent the mass of agricultural chemicals that were transported to groundwater based on this method. The mass of applied chemicals at the upland and lowland sites that was in the upper 2 m of the saturated zone at the time of sampling (M) was computed as follows:

$$M = \sum_{i=0.5}^{2.0} [V(i) \times -C_M(i)] \tag{3}$$

where i is the index to the 0.5-m depth interval in the upper 2 m of saturated zone beneath the site, $V(i)$ is the vol-

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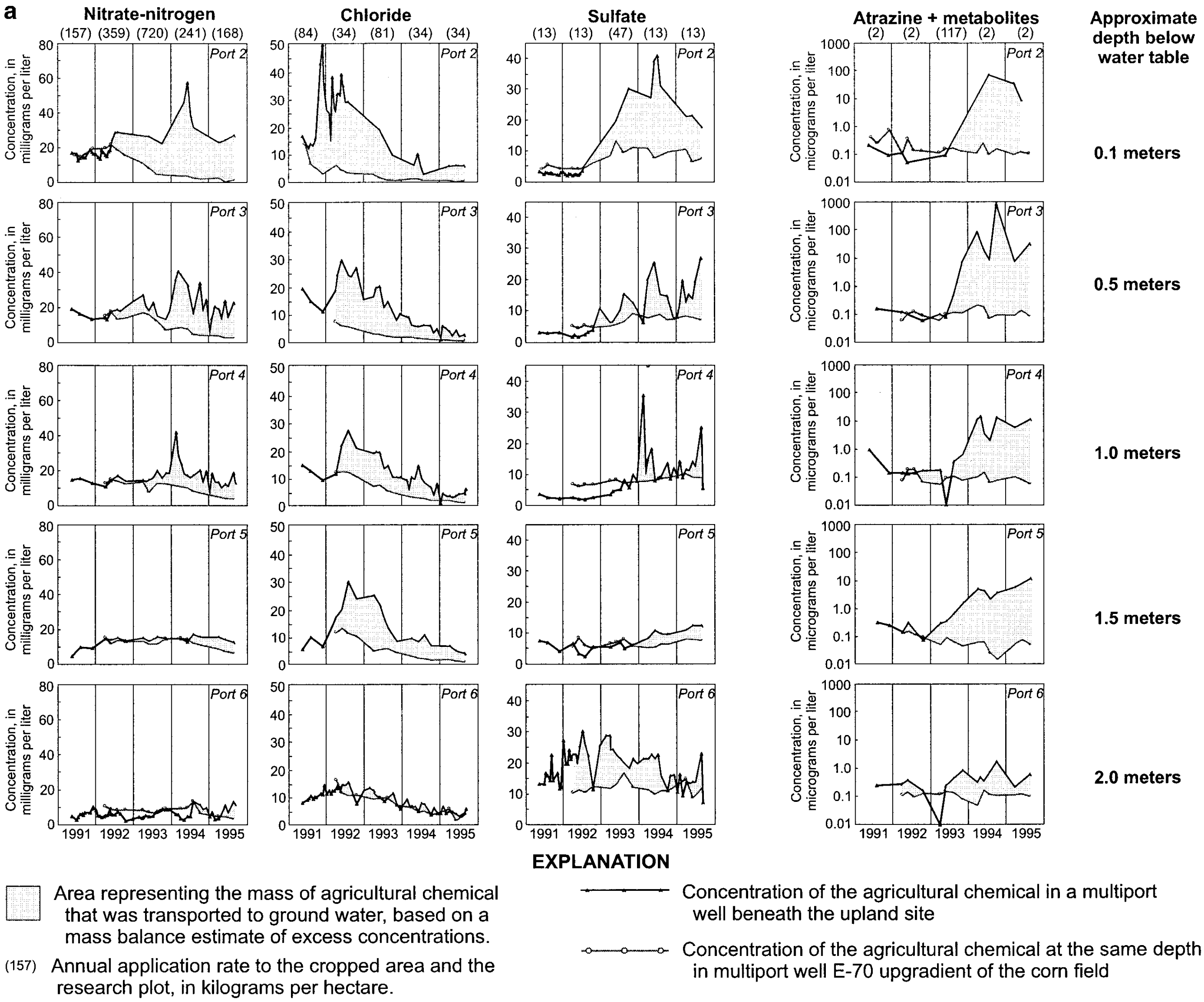

Fig. 2 a Concentrations of nitrate nitrogen, chloride, sulfate, and atrazine plus metabolites beneath the upland site compared with background concentrations, 1991–1995. **b** Concentrations of nitrate nitrogen, chloride, sulfate, and atrazine plus metabolites beneath the lowland site compared with background concentrations, 1991–1995

ume of water in a 0.5-m depth interval of the upper 2 m of saturated zone beneath the site, and $C_M(i)$ is the difference in concentration of a constituent and its concentration at the same depth in upgradient well E-70. A value of M was computed for each sampling period. Because the transit time of water in the unsaturated zone was as much as 12 months (Landon et al. 1998, 2000), the effects of applications in a given year typically were not detected in the saturated zone until the following calendar year. The mass (M) that most accurately represented applications during a given year was assumed to be the maximum M detected during the following year (Landon et al. 1998). All masses and volumes were computed using a porosity of 0.40 (Delin et al. 1994). Landon et al. (1997, 1998) present a detailed description of this method.

Results

Agricultural Chemical Concentrations at the Upland and Lowland Sites

Agricultural chemicals that move readily with water were most directly affected by focused recharge to the lowland site. Mean concentrations of chloride and nitrate nitrogen (nitrate) in the unsaturated zone were significantly greater at the lowland site than at the upland site during 1991–1993 (both with p-values of <0.0001) as well as during 1994–1995 (p-values of 0.0012 and 0.0010, respectively), as shown in Table 1. Conversely, the mean concentration of sulfate was significantly greater ($p=0.0046$) at the upland site during 1994–1995. The observed differences between the upland and lowland sites during 1991–1993 in sulfate concentration, as well as the atrazine plus metabolite concentrations, for

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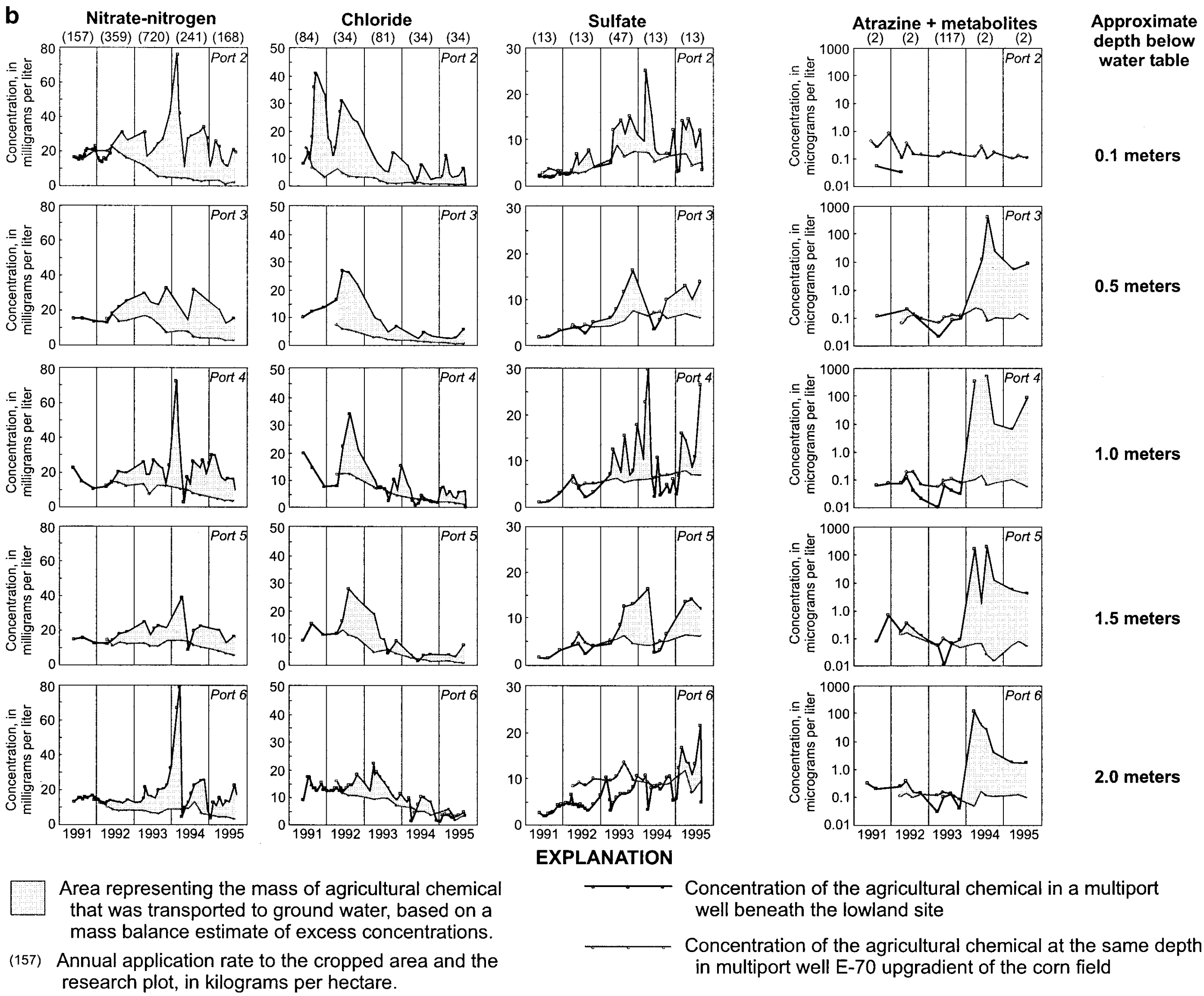

Fig. 2b Legend see page 447

both unsaturated-zone data sets (Table 1), were insignificant.

Despite the elevated application rates for chloride, nitrogen, and sulfur as a result of the October 1993 catastrophic recharge experiment, median unsaturated zone concentrations of these constituents declined from 1991–1993 to 1994–1995 at both sites, except for chloride at the upland site (Table 1). However, only the sulfate and atrazine plus metabolite differences were significant ($p<0.0001$). The 1994–1995 concentrations for atrazine plus metabolites in the unsaturated zone at both sites increased two to three orders of magnitude compared with 1991–1993, similar to the two order of magnitude increase in the atrazine application rate from the October 1993 experiment.

Table 2 shows that the results based on the saturated zone data were generally consistent with results based on the unsaturated zone data. The mean nitrate concentration was significantly greater at the lowland site than at the upland site for 1991–1993 ($p<0.0001$) as well as for 1994–1995 ($p=0.0196$). The mean atrazine plus metabolite concentration ($p=0.0002$) was only significantly greater at the upland site for 1991–1993. Contrary to results based on the unsaturated zone data, chloride concentrations were significantly greater at the upland site for both the 1991–1993 ($p=0.0182$) and the 1994–1995 ($p<0.0001$) data sets. This result is inconsistent with other results from the study, the reasons of which are unclear at this time. All other differences in concentrations between the sites shown in Table 2 were insignificant.

Chemical data from this study indicate the likelihood of transient mounding of water at the water table, resulting in a relatively large vertical component of groundwater flow and deeper penetration of recharge water and agricultural chemicals at the lowland site (Figs. 2a, b and 3). This focused recharge affected the distribution of agricultural chemicals in the saturated zone, resulting in greater concentrations at the lowland site at most depths. Concentrations of nitrate near the water table during April 1993, for example, were 5–15 mg/L greater at the

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Table 1 Summary statistics for selected agricultural chemicals in the unsaturated zone at the upland and lowland sites, 1991–1995

Variable and year collected	Chloride (mg/L)	Nitrate nitrogen (mg/L)	Sulfate (mg/L)	Atrazine plus metabolites[a] (μg/L)	Chloride (mg/L)	Nitrate nitrogen (mg/L)	Sulfate (mg/L)	Atrazine plus metabolites[a] (μg/L)
	Upland site				Lowland site			
1991–1993 (prior to the catastrophic recharge experiment)								
Median	1.75	17.0	28.0	0.000	7.65	24.0	27.0	0.000
Mean	4.19	18.3	33.2	0.061	10.9	24.9	29.5	0.039
SD	6.31	13.0	24.1	0.208	11.0	14.6	17.8	0.176
Count	140	172	169	135	130	153	142	137
1994–1995 (after the catastrophic recharge experiment)								
Median	4.00	8.85	19.0	5.83	5.00	19.4	11.0	4.65
Mean	4.67	14.8	26.8	209	8.85	35.3	23.0	54.1
SD	3.47	15.0	32.0	690	11.3	66.0	37.0	117
Count	95	100	99	65	69	74	66	62

[a] De-ethylatrazine and de-isopropylatrazine

Table 2 Summary statistics for selected agricultural chemicals in the upper 2 m of the saturated zone at the upland and lowland sites, 1991–1995. *Count* Number of samples

Variable and year collected	Chloride (mg/L)	Nitrate nitrogen (mg/L)	Sulfate (mg/L)	Atrazine plus metabolites[a] (μg/L)	Chloride (mg/L)	Nitrate nitrogen (mg/L)	Sulfate (mg/L)	Atrazine plus metabolites[a] (μg/L)
	Upland site				Lowland site			
1991–1993 (prior to the catastrophic recharge experiment)								
Median	14.5	14.2	3.30	0.159	13.0	16.4	3.42	0.060
Mean	17.4	13.0	6.74	0.243	15.0	17.9	4.54	0.100
SD	8.29	6.09	7.19	0.361	8.40	4.71	3.58	0.118
Count	110	110	107	50	103	102	100	47
1994–1995 (after the catastrophic recharge experiment)								
Median	5.60	15.4	8.17	9.20	3.48	17.9	8.15	6.10
Mean	5.69	16.8	9.55	68.8	4.23	21.1	8.73	56.3
SD	2.57	9.90	4.69	173	2.62	14.3	4.80	110
Count	95	96	95	49	88	88	88	35

[a] De-ethylatrazine and de-isopropylatrazine

lowland site than at the upland site as shown in Fig. 3. Also, the 5-mg/L nitrate isoline in April 1993 extended about 4 m deeper into the saturated zone at the lowland site than at the upland site. This greater depth of penetration is also evident in the zone of active denitrification, which was identified by use of nitrogen gas analyses (Böhlke et al. 2002) along a transect of wells extending through the upland and lowland sites (Fig. 3). This zone of active denitrification occurred at greater depth below the lowland site, further reflecting the effects of focused recharge.

Concentrations of inorganic chemicals in the unsaturated and saturated zones varied in response to recharge events and varying application rates. Peak concentrations were associated with substantial recharge events or chemical applications and generally occurred during the spring and fall of each year. During the spring of 1995, for example, concentrations of nitrate in the saturated zone (Figs. 2a, b) decreased at both sites because of reduced application rates during the previous year, as well as dilution from spring recharge (Delin et al. 1997). Chemicals detected each spring were from applications 7–12 months earlier. Conversely, the fall detections were from applications only 2–6 months earlier (Landon et al. 2000). Nitrate and sulfate peak concentrations frequently lagged behind the chloride peaks (Figs. 2a, b), probably because chloride moved more conservatively.

Atrazine plus metabolite concentrations beneath both sites during 1991–1993 generally were less than or similar to concentrations in up-gradient MPORT E-70 (Figs. 2a, b). Concentrations during this time period reflect the effects of the continuous corn farming system because greater amounts of atrazine had not yet been applied as part of the October 1993 catastrophic recharge experiment. Concentrations increased by several orders of magnitude during spring 1994 in response to the catastrophic recharge experiment. Although some degradation undoubtedly occurred, these detections indicate that

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some atrazine moved with recharge water and had insufficient time to degrade in the unsaturated zone because of the short residence time.

Estimated Flux of Agricultural Chemicals to the Water Table

Table 3 and Fig. 4 show that, based on the unsaturated-zone method, the average annual fluxes of chloride, nitrate, and sulfate in 1992–1993 were 5.1, 3.4, and 1.7 times greater, respectively, at the lowland site than at the upland site. Similarly, the average annual fluxes of these chemicals in 1994–1995 were 3.9, 3.6, and 2.6 times greater, respectively, at the lowland site. Flux estimates for atrazine plus metabolites did not follow this trend, being 1.6 and 1.1 times greater at the upland site during 1992–1993 and 1994–1995, respectively. Greater sorption to organic carbon likely was the principal factor causing the lower atrazine plus metabolite flux estimates at the lowland site. The October 1993 catastrophic recharge experiment caused the anomalously large flux estimates for nitrate at both sites and sulfate at the lowland site for 1994 as well as the anomalously large atrazine plus metabolite estimates at both sites for 1994–1995.

Based on the saturated-zone method, flux estimates for applications were mixed compared with estimates based on the unsaturated-zone method. The annual fluxes of nitrate and sulfate at the lowland site in 1993 were 1.4 and 1.8 times greater, respectively, than at the upland site (Table 3). Conversely, the average annual fluxes of chloride and atrazine plus metabolites in 1992–1993 were greater at the upland site. Flux estimates for applications in 1993–1994 followed a pattern similar to estimates based on data from the unsaturated zone, with the fluxes of all chemicals being greater at the lowland site than at the upland site.

As a percent of applied chemical, the average annual flux of nitrate and atrazine plus metabolites at the upland site in 1992–1993 was 16 and 0.1%, respectively, based on the unsaturated-zone method. Based on the saturated-zone method, the average annual flux of nitrate and atrazine plus metabolites at the upland site in 1992–1993 was 20 and 0.8%, respectively. These numbers compare favorably with the 1992–1993 average flux estimates for nitrate and atrazine plus metabolites for the entire cropped area of 25 and 0.2%, respectively (Landon et al. 1998). Thus, flux estimates at the upland site are representative of the entire cropped area and the continuous corn farming system. Corresponding percentages for the lowland site in 1992–1993 were about 60 and 0.02% for nitrate and atrazine plus metabolites, respectively, using

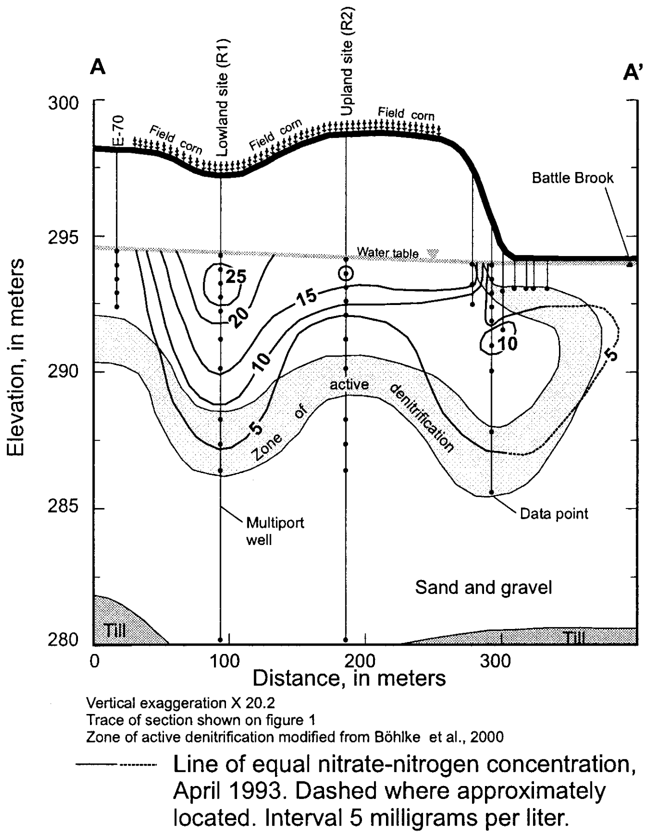

Fig. 3 Nitrate-nitrogen concentrations along a transect through the upland and lowland sites, April 1993. Modified from Böhlke et al. (2002)

Table 3 Estimated annual flux of selected agricultural chemicals that reached the saturated zone during 1992–1995 at the upland and lowland sites based on concentrations in the unsaturated and saturated zones in kilograms per hectare. Unsaturated-zone estimate listed on left, saturated-zone estimate in parentheses. *1992–1993 avg.* Average of the fluxes prior to the catastrophic recharge experiment; 19*93–1994 avg.* average of the fluxes after the catastrophic recharge experiment

Year[a]	Chloride	Nitrate nitrogen	Sulfate	Atrazine plus metabolites[b]	Chloride	Nitrate nitrogen	Sulfate	Atrazine plus metabolites
	Upland site				Lowland site			
1992	27 (140)	35 (39)	77 (–)	0.30 (0.00)	120 (130)	180 (57)	200 (1)	0.80 (0.00)
1993	1 (64)	33 (55)	84 (8)	1.3 (0.03)	23 (31)	56 (79)	82 (14)	0.10 (0.00)
1992–1993 avg.	14 (102)	34 (47)	81 (8)	0.80 (0.02)	72 (81)	116 (68)	141 (8)	0.50 (0.00)
1994	18 (19)	85 (81)	79 (17)	390 (1.83)	77 (20)	320 (300)	230 (23)	230 (2.3)
1995	10 (31)	19 (95)	40 (25)	54 (0.16)	31 (44)	61 (63)	91 (25)	190 (0.17)
1994–1995 avg.	14 (25)	52 (88)	60 (21)	222 (1.00)	54 (32)	189 (181)	158 (24)	207 (1.23)

[a] Year that the samples were collected
[b] Metabolites, de-ethylatrazine and de-isopropylatrazine

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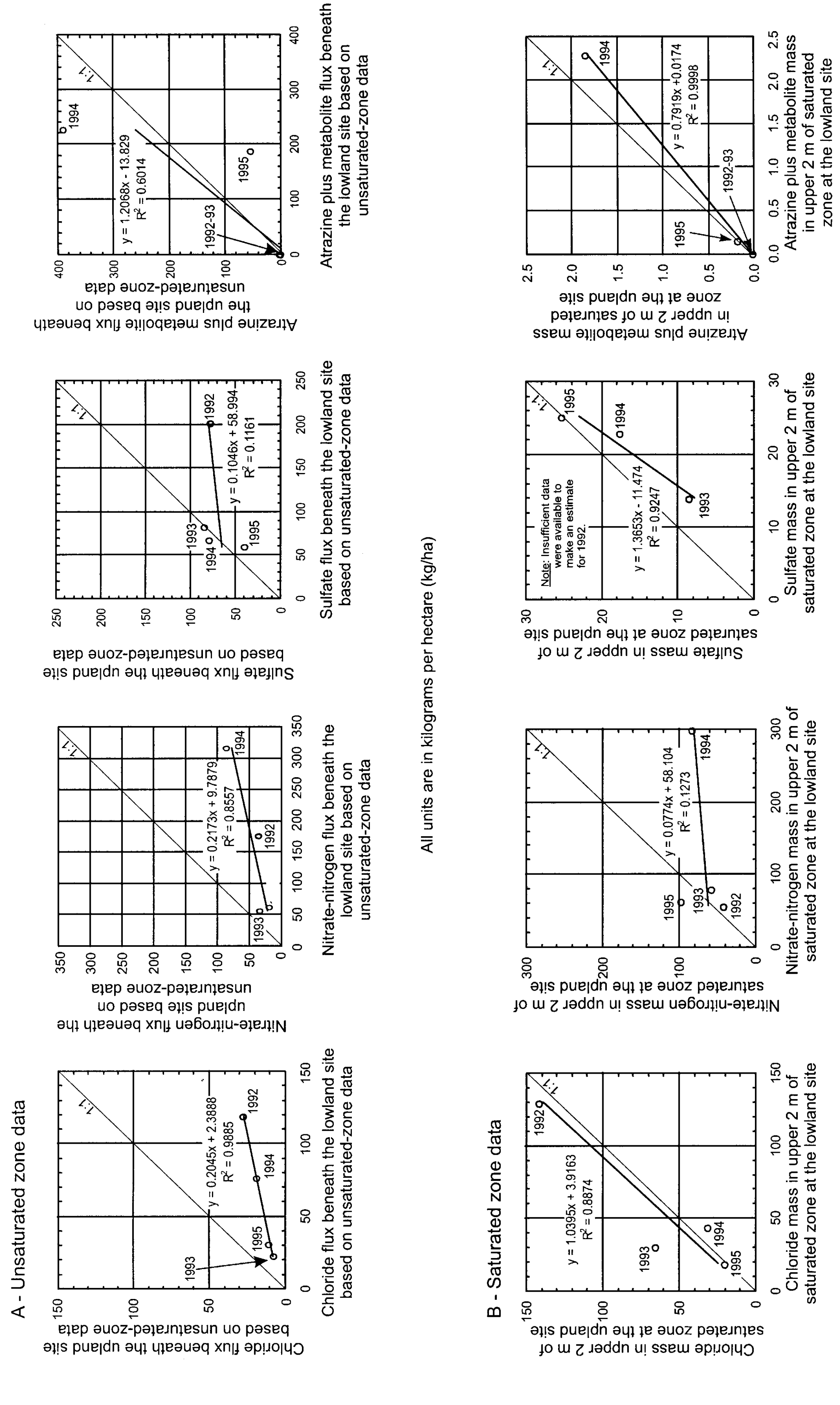
Fig. 4 Relation between the estimated flux of selected agricultural chemicals that reached the saturated zone during 1992–1995 beneath the upland and lowland sites based on data from the **a** unsaturated zone, and **b** saturated zone. The linear regression equation is presented for the trend line through each data set. The 1:1 correspondence line is also shown for reference. Each *data point* is labeled with the year that the samples were collected



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both methods. These results underscore that nitrate flux estimates at the lowland site are elevated and atrazine plus metabolite fluxes reduced compared with background levels.

With the exception of chloride fluxes from the upland site, the average flux estimates for 1992–1993 and 1994–1995 were only about 5–40% different for chloride and nitrate based on the unsaturated- and saturated-zone methods. This indicates a generally good corroboration of the two methods, which is remarkable considering their many uncertainties and limitations. Inspection of Fig. 4, however, illustrates an inconsistency in the two methods for the chloride flux estimates. The main difference between the two methods is that the chloride flux estimates for the upland site are much greater based on the saturated-zone method. It is unclear why this method apparently overestimates chloride fluxes at the upland site.

The unsaturated-zone method generally estimated greater fluxes for constituents that are moderately (sulfate) to strongly (atrazine) sorbed in the unsaturated zone, compared with the saturated-zone method (Fig. 4, Table 3). This was expected for atrazine because it strongly sorbs to organic matter in the soil (Clendening et al. 1990; Komor and Emerson 1994; Seybold et al. 1994; Flury et al. 1995). Sulfate concentrations and flux estimates based on the unsaturated-zone data (Tables 1 and 3), however, are not representative of sulfate reaching the upper 2 m of the saturated zone (Fig. 4, Tables 2 and 3). The sulfate flux rates range from 230–1,050% of the annual sulfur application rates, which is unrealistic. The unsaturated-zone flux estimates for sulfate are as much as two orders of magnitude greater than the flux estimates based on saturated-zone data at the lowland site (Table 3). These results indicate that there was a moderately large reservoir of sulfate stored in the unsaturated zone of which only a small fraction leached to the groundwater. The reasons and mechanisms behind such a phenomenon are unclear.

Discussion

Study results indicate that chemical concentrations and flux estimates generally were greater at the lowland site largely as a result of (1) localized recharge from run-on, (2) the presence of lamellae at the upland site, and (3) the coarse texture of the unsaturated zone at the lowland site.

Run-on was the principal factor that caused focused recharge of water and agricultural chemicals at the lowland site. Run-on, and subsequent infiltration, was observed at the lowland site during spring snowmelt and during periods of intense or prolonged rainfall. Snowmelt typically began during March each year. Because the soils were still frozen, snowmelt would run-on to the lowland areas and infiltrate as the soil thawed, causing focused recharge. Although the mass of agricultural chemicals in surface sediments at this time of year typically was minimal, a significant mass of the chemicals was still present in the unsaturated zone from applications during the previous season (Delin et al. 1997). Consequently, the increased flux of recharge water flushed the agricultural chemicals in the unsaturated zone down to the water table. Stable isotope data from both the upland and lowland sites support this conclusion (Landon et al. 2000). The occurrence of run-on in an area of coarse-textured soils with a relatively gentle slope of 0.02 is noteworthy. The phenomenon of focused recharge of agricultural chemicals in depressional areas is likely to exist in most sand-plain areas. It is also likely that run-on and focused recharge would be even more accentuated in areas where the soils have a greater percentage of silt, clay, and organic matter and a slope that exceeds 0.02. Additional research on the influences of topography on the transport of agricultural chemicals to groundwater in other geologic settings and soil types is needed.

Lamellae in the unsaturated zone at the upland site likely form barriers that retard the vertical flow of water because of iron-oxide cement and a higher percentage of silt- and clay-sized particles compared with the surrounding soil (Delin et al. 2000). Thus, the lamellae retarded the downward movement of water and agricultural chemicals that would otherwise have penetrated deeper into the unsaturated zone at the upland site. The lamellae may also result in lateral water movement in the unsaturated zone on the field scale (Tomer 1994), which could contribute subsurface water and agricultural chemicals to the lowland site, accentuating the effects of focused recharge because of surface run-on. Similar results of subsurface lateral (through flow) movement of water, which in some cases was linked to depression-focused recharge, have been observed in numerous investigations in different geologic settings (Gunn 1983; Stephens and Heermann 1988; Kung 1990a, 1990b; Schmidt 1995).

The presence of coarse-grained sand below the 1.5-m depth at the lowland site likely resulted in increased recharge of water and agricultural chemicals locally compared with the upland site. Athavale and Rangarajan (1988) indicated a similar direct correlation between recharge and soil texture.

As a result of the above factors, as well as a shallower depth to the water table, transport times of recharge water and agricultural chemicals through the unsaturated zone generally were shorter at the lowland site than at the upland site. During spring snowmelt or intense rainfall events, transport times of less than 1 week were detected at the lowland site. Based on stable isotope concentrations of $\delta^{18}O$ in groundwater (Landon et al. 2000), the average transport time for spring, summer, and fall recharge events during 1993–1994, for example, was about 4 months at the lowland site and 4.5 months at the upland site. Analysis of soil moisture and soil temperature data indicate that spring thaw, and the resulting water movement through the unsaturated zone, typically occurred about 2 weeks earlier at the lowland site than at the upland site.

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Consideration should be given to modifying site-specific management (SSM) farming technology to account for varying water and chemical recharge rates in different topographic settings. The SSM technology allows farmers to apply agricultural chemicals at the appropriate rates and in the most appropriate locations in a field where they are needed (Pierce et al. 1994; Khakural et al. 1995; Kitchen et al. 1995; Johnson et al. 1997). Using the SSM technology, chemical application rates and tillage practices are varied to account for variability in factors such as soil type, nutrient and pesticide content in the soil, and organic matter content. By reducing chemical application rates in topographic depressions, where focused recharge of chemicals occurs because of run-on, farmers could improve ground-water quality and reduce costs. Additional research is needed to evaluate whether this modification to SSM farming technology would continue to provide adequate crop nutrients and pest control while reducing ground-water contamination. The cost effectiveness of this modified SSM farming technology should also be evaluated with regard to improved crop yields.

Summary and Conclusions

Geochemical data were collected to investigate the effects of topography and focused recharge on the transport of agricultural chemicals to groundwater through sandy soils. The research was done at a topographically high (upland) site and a depressional (lowland) site within a corn field near Princeton, Minnesota. The two sites were 78 m apart with a difference in elevation of 1.4 m.

Agricultural chemicals that move readily with water were most rapidly transported by focused recharge to the lowland site. Elevated concentrations of chloride and nitrate generally extended 2–3 m deeper into the saturated zone at the lowland site, for example. The concentrations of chloride, nitrate, and sulfate in the saturated and unsaturated zones were generally greater at the lowland site. Conversely, atrazine plus metabolite concentrations generally were greater at the upland site.

Run-on to the lowland site was the primary cause for the generally greater flux of chloride, nitrate, and sulfate compared with the upland site. Based on data from the unsaturated zone, for example, the average annual fluxes of these chemicals from applications during 1991–1992 were 5.1, 3.4, and 1.7 times greater, respectively, than at the lowland site. The generally lower flux of atrazine plus metabolites at the lowland site was likely caused by greater sorption to organic carbon, as well as dilution from the focused recharge. Flux estimates for atrazine plus metabolites based on data from the unsaturated zone, for example, were 1.6 times greater at the upland site in 1992–1993.

Another factor that contributed to the greater flux of water and chemicals at the lowland site was lamellae in the unsaturated zone at the upland site, which likely formed barriers that retarded the vertical flow of water and agricultural chemicals. In addition, the presence of coarse-grained sand below the 1.5-m depth at the lowland site likely resulted in increased recharge of water and agricultural chemicals locally compared with the upland site.

Study results indicate that consideration should be given to modifying site-specific management farming technology to account for varying recharge rates in different topographic settings. By reducing chemical application rates in topographic depressions, where focused recharge of chemicals occur because of surface runoff, farmers could improve ground-water quality as well as reduce expenditures for agricultural chemicals. Additional research on the influences of topography on the transport of agricultural chemicals to groundwater in other geologic settings and soil types is needed.

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