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Pergamon

0043-1354(95)00198-0

Wat. Res. Vol. 30, No. 3, pp. 559–568, 1996

0043-1354/96 $15.00 + 0.00

TEMPORAL VARIABILITY OF ORGANIC C AND NITRATE IN A SHALLOW AQUIFER

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(First received August 1994; accepted in revised form August 1995)

Abstract—The loading of organic substrates into shallow aquifers may follow seasonal cycles, which will impact the transport and fate of agrichemicals. The objective of this research was to measure temporal changes in the groundwater dissolved organic C (DOC) and nitrate concentrations. Groundwater monitoring wells were installed and sediment samples from the aquifer were collected in 1991. Sediment samples were used to evaluate denitrification potentials, while water samples were collected at periodic intervals in 1992 and 1993 from the surface of the aquifer. Water samples were analyzed for nitrate-N and DOC-C. Denitrification was observed in sediment amended with nitrate and incubated under anaerobic conditions at 10°C. Addition of algae lazed biomass increased denitrification, establishing that denitrification was substrate limited. In the aquifer, DOC concentrations followed seasonal patterns. DOC concentrations were highest following spring recharge and then decreased. Peak timing indicates that freezing and thawing were responsible for seasonal DOC patterns. These findings show that seasonally driven physical processes, such as freezing and thawing, influence organic substrate transport from surface to subsurface environments, and that this process should be taken into account when assessing agrichemical detoxification rates in shallow aquifers.

Key words—denitrification, soluble organic C, rate constants

INTRODUCTION

Subsurface microbial populations require organic C for respiration. For many aquifers, organic C may be transported to the aquifer from upgradient locations or from the soil surface. However, because dissolved organic C (DOC) concentrations within the aquifer are often low (<2.95 mg C l^{-1}) (Thurman, 1985; Barcelona, 1984) the only major source of C for many subsurface microbial communities is that which leaches from above.

Research has shown that many aquifers do not contain sufficient organic matter to produce the anaerobic conditions required for denitrification (Bryan, 1981; Parkin and Meisinger, 1989; Thurman, 1985; Barcelona, 1984; Lind and Eiland, 1989; McCarty and Bremner, 1992; Obenhuber and Lowrance, 1991). However, these studies do not exclude the possibility of denitrification occurring if sufficient organic C is transported into the aquifer from other sources.

Several different mechanisms may be involved in solubilizing organic C. Clay *et al.* (1995) reported that anhydrous ammonia solubilized organic C and that this C may be transported from surface to subsurface environments with percolating water. A second mechanism is the effect of freezing and thawing or wetting and drying on killing microbial biomass. The killed biomass may subsequently leach to groundwater where it can be mineralized (Boissier and Fontvieille, 1993; Zsolnay and Steindl, 1991).

Because both agricultural management and climatic conditions follow seasonal patterns, it is likely that C loading into aquifers also follows seasonal patterns. Therefore, to assess the potential for denitrification to reduce groundwater nitrate concentrations, temporal variation in organic C concentrations were evaluated.

MATERIALS AND METHODS

Field evaluation of organic C transport

This study was initiated in 1991 and is located near Aurora SD. The research site contained two rotational areas having dimensions of 91 by 64 m (Fig. 1). The west plot rotated corn (*Zea mays* L.) (1991) followed by soybeans (*Glycine max* L.) (1992) and corn (1993). The east plot rotated soybeans (1991) followed corn (1992) and soybeans (1993). Corn was fertilized with N fertilizer at rates of 56, 78, and 168 kg N ha^{-1} in 1991, 1992, and 1993, respectively, while N fertilizer was not applied to soybean crops.

The Brandt silty clay loam (fine-silty over sandy or sandy skeletal, mixed Pachic Udic Haploboroll) soils at the site was over a glacial outwash aquifer composed of igneous and metamorphic sized gravels. The surface soil slope was less than 1%; runoff was slow; erosion was none to slight, and

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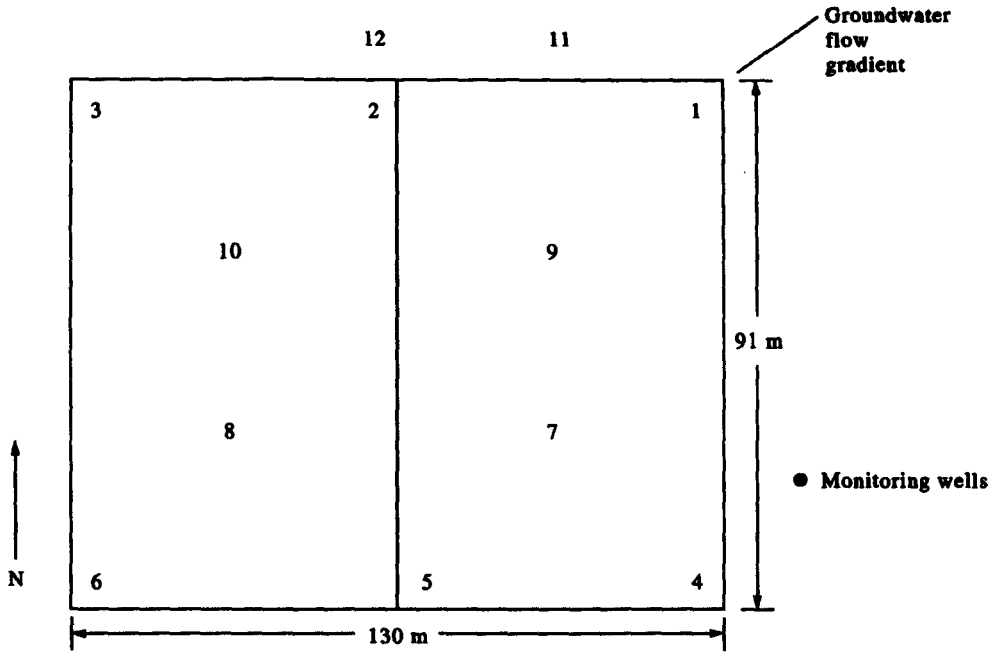

Fig. 1. Location of the monitoring wells at the research site. Monitoring wells 7, 8, 9, and 10 were sampled in 1992. Monitoring wells 1, 5, 8, 9, and 10 were sampled in 1993.

the soil was well drained with a water holding capacity of approx. 15 cm. The water table was located approx. 5 m below the soil surface. Based on measured groundwater gradients, flow was diagonal across the research plots at an estimated rate of 15 m y^{-1}.

Groundwater monitoring wells numbers 8 and 10 were located in the corn–bean–corn rotation (west) and monitoring wells 7 and 9 were located in the beans–corn–beans rotation (east) (Fig. 1). Each monitoring well had a 5-cm i.d. and were installed at least 30 m away from a plot edge. Additional monitoring wells were installed at the corners (1, 3, 4, and 6) and upgradient of the plots (11 and 12). Following monitoring well installation, holes were backfilled with: gravel to within 2 m of the soil surface; 50% bentonite and 50% peagravel from 2 to 1.5 m from the soil surface; subsoil from 1.5 to 1 m from the soil surface; and cement from 1 to 0.5 m from the soil surface. Screened intervals initially extended from 1 m above to 2 m below the groundwater surface. Groundwater samples from the surface of the aquifer were collected at periodic intervals in 1992 (21, 69, 90, 107, 113, 147, 167, 168, 169, 174, 180, 181, 182, 183, 186, 187, 190, 196, 204, 207, 209, 216, 239, 244, 258, 294, 308, 321, and 345 day of the year) and 1993 (23, 60, 82, 93, 96, 103, 117, 124, 146, 159, 163, 171, 176, 230, 266, 287, 320, and 339 day of the year) with a surface skimmer as described by Clay *et al.* (1994). The inlet port of the surface skimmer was adjusted to within 2 cm of the surface of the water table prior to sample collection. When groundwater samples were collected, depths to groundwater were measured. Water samples were cooled to 4°C following sample collection. Dissolved organic C (DOC) and inorganic N was determined on a Dohrmann C Analyzer and Wescan Ammonia Analyzer, respectively, within 14 d of sample collection.

Field characterization

Sediment samples from above and below the water table were collected during installation of monitoring wells 9 and 10 (Fig. 1). Sediment samples were collected from an additional 4 sites outside the research plots. Of the six sites sampled three were located in cultivated fields and 3 were located in fields that had been in pasture for the previous 10 years. All sites were located within the Big Sioux Aquifer and were within 2 km of each other.

Samples from above (4.5- to 5-m below the soil surface) and below the water table (5- to 5.5-m below the soil surface) were collected by drilling down to the desired depth increment and pounding a stainless steel jacket containing a sterile (methanol rinsed) 90 cm long polycarbonate liner into unaugered sediment. To prevent contamination, samples were immediately capped with sterilized lids and cooled to 4°C. All drilling equipment was steamed cleaned

Table 1. Particle size (>4 mm), pH, and total organic N of surface soil and sediment samples collected from above and below the water table (WT) at 6 sampling locations

		Sediment from										
		Surface soil			Above WT				Below WT			
Cropping history	Site	Org N (mg/kg)	Org C	pH	Org N (mg/kg)	>4 mm (%)	<0.053 (%)	pH	Org N (mg/kg)	>4 mm (%)	<0.053 (%)	pH
Cultivated	1	2050	20200	4.9	38.7	23.5	2.0	7.8	53.7	41.1	1.8	7.7
Cultivated	2	2120	21200	4.6	41.9	32.3	1.3	7.8	57.2	41.3	2.8	7.8
Cultivated	3	2180	22200	4.7	45.3	34.9	3.4	7.9	47.4	44.7	3.7	7.8
Pasture	4	3140	33800	5.8	44.9	30.5	2.8	7.8	31.4	41.6	1.2	7.9
Pasture	5	3390	34900	4.7	40.9	54.3	5.7	7.8	34.4	44.5	1.7	7.9
Pasture	6	3250	34300	4.7	53.4	30.4	3.6	7.8	46.1	54.7	3.2	7.9

and the probe tip was washed with soapy water and rinsed with methanol between holes. Sediment from two adjacent holes were mixed together to insure that adequate sediment was available for each treatment. Surface soil (0- to 30-cm) was collected with a 5 cm stainless steel tube.

Soil and sediment samples were thoroughly mixed and sieved (4-mm screen) within a laminar flow hood to prepare them for the incubation experiment. Approximately 30 g of dry soil or sediment equivalent were placed in each serum bottle under aseptic conditions and equilibrated under anaerobic conditions (redox potential between 100 and −100 mV) for 4 h. The initial atmosphere was a mixture of N_2 and CO_2 gases. Serum bottles were injected with 1 ml of sterile aqueous solution containing 25 mg $Ca(NO_3)_2$-N l^{-1} or 25 mg NO_3-N l^{-1} plus 100 mg algae-lazed biomass-C l^{-1}. Samples collected from below the water table were incubated under saturated conditions while sediment and soil samples collected above the water table were incubated at 0.1 bars. Soil and water additions were completed under a laminar flow hood.

Short and long term experiments were used to measure denitrification rates. In the long term experiment, samples were incubated at 10°C. Samples were removed from the incubation chamber after 0, 7, 21, 42, 84, and 112 d. Sediment and soil samples were air dried (35°C) and inorganic N extracted with 1 M KCl and ammonium and nitrate-N determined (Hershey and Paul, 1982). Zero and first order equations were used to determine nitrate loss rates.

In the short term experiment, 4 ml of acetylene was added after 5 or 19 d of incubation to vials scheduled to be removed at 7 and 21 d. The acetylene addition produced an atmosphere containing 10% acetylene. Vials were shaken following the acetylene addition and a 4 ml atmospheric subsample was removed for N_2O analysis. Additional atmospheric subsamples (2 ml) were collected after incubation at 10°C for 24, 34, and 48 h. When subsamples were removed an additional 2 ml of acetylene was added. Total head space in each incubation container was 40 ml. Nitrous oxide was analyzed using a gas chromatograph equipped with an electron capture detector. Zero order rate equations were used to determine N_2O production over the 48 h period.

Table 2. Bacteria and fungal counts at three different depths in samples collected from the Big Sioux aquifer

	Type of organism			
	Bacteria		Fungal	
Soil depth	Mean	95% CI (log microbes g^{-1})	Mean	95% CI
Surface soil	8.47	0.422	6.81	0.622
Above aquifer	7.98	0.411	3.13	0.474
From aquifer	8.20	0.18	1.28	1.49

Total soil N was determined following the method of Bremner and Mulvaney (1982). Total organic N was determined by subtracting total inorganic N from total N. Soil and sediment pH values were determined in a 0.01 M $CaCl_2$ slurry. Particle size distribution was determined following Gee and Bauder (1986). Heterotrophic aerobic microorganisms in individual core segments (<4-mm size fraction) were enumerated on two medias using dilution-plating techniques. Samples (10 g) were diluted in 0.125 M, pH 7 phosphate buffer and aliquots placed on 1% PTYG (Balkwell and Ghiorse, 1985) amended with 50 mg/l of succinate for bacteria and Rose Bengal agar media for fungi (Wollum, 1982).

RESULTS AND DISCUSSION

Field characterization

Surface soil collected from pasture fields had higher organic N and C contents than cultivated fields (Table 1). However, surface management did not influence subsurface organic N content or microbial populations (Tables 1 and 2). Surface soil pH values were less than 6.0, while subsurface pH values were greater than 7.5 (Table 1). The pH differences

Table 3. First order ($y = ae^{-kt}$) and zero order ($y = mx + b$) rate constants and correlation coefficients (r) of nitrate loss during the incubation

			$Ca(NO_3)_2$				$Ca(NO_3)_2$ + biomass			
Collection zone	Site	Previous man.	Zero order m [mg (kgd)$^{-1}$]	r	first order k (d^{-1})	r	Zero order m [mg (kgd)$^{-1}$]	r	first order k (d^{-1})	r
Surface	1	Cultivated	−0.31	−0.86**[a]	0.025	−0.94**	−1.43	−0.99**	0.171	−0.99*
	2	Cultivated	−0.30	−0.81**	0.029	−0.96**	−1.39	−0.99*	0.189	−0.97
	3	Cultivated	−0.37	−0.41	0.073	−0.98**	−1.19	−0.92	0.204	−0.98
	4	Pasture	−0.10	−0.58	0.004	−0.97**	−1.24	−0.99*	0.256	−0.99*
	5	Pasture	−0.23	−0.85**	0.012	−0.97*	−2.44	−0.99*	0.548	−0.96
	6	Pasture	−0.40	−0.92**	0.045	−0.82*	−1.01	−0.90	0.157	−0.99*
	1–6		−0.28	−0.74**	0.029	−0.81**	−1.45	−0.81**	0.254	−0.77**
	95% CI[b]		0.103		0.007		0.54		0.155	
Above aquifer	1	Cultivated	0.03	0.34	−0.002	0.08	−0.25	−0.98**	0.036	−0.98**
	2	Cultivated	0.01	0.08	−0.001	0.11	−0.22	−0.94**	0.026	−0.76
	3	Cultivated	−0.38	−0.31	0.002	−0.33	−0.16	−0.90*	0.011	−0.96**
	4	Pasture	−0.19	−0.84*	0.006	−0.83*	−0.16	−0.74	0.012	−0.89*
	5	Pasture	0.12	0.09	−0.001	0.07	−0.10	−0.92*	0.006	−0.94**
	6	Pasture	0.05	0.30	−0.001	0.26	−0.18	−0.97	0.021	−0.91*
	1–6		−0.06	−0.14	0.001	−0.16	−0.18	−0.83**	0.019	−0.70**
	95% CI		0.20		0.003		0.06		0.004	
Below aquifer	1	Cultivated	−0.34	−0.98**	0.039	−0.97**	−0.62	−0.96*	0.067	−0.98*
	2	Cultivated	−0.31	−0.83*	0.016	−0.90*	−0.63	−0.91	0.133	−0.97*
	3	Cultivated	−0.31	−0.88**	0.041	−0.96**	−0.87	−0.93	0.142	−0.95*
	4	Pasture	−0.02	−0.16	0.001	−0.09	−0.58	−0.91	0.064	−0.97*
	5	Pasture	−0.07	−0.65	0.003	−0.66	−0.66	−0.95*	0.013	−0.95*
	6	Pasture	−0.25	−0.90*	0.050	−0.99**	−0.63	−0.50	0.113	−0.98*
	1–6		−0.22	−0.66**	0.025	−0.64**	−0.68	−0.82**	0.089	−0.79**
	95% CI		0.14		0.008		0.28		0.045	

[a] * and ** are significant at the 0.05 and 0.01 level, respectively.
[b] CI is the confidence interval.

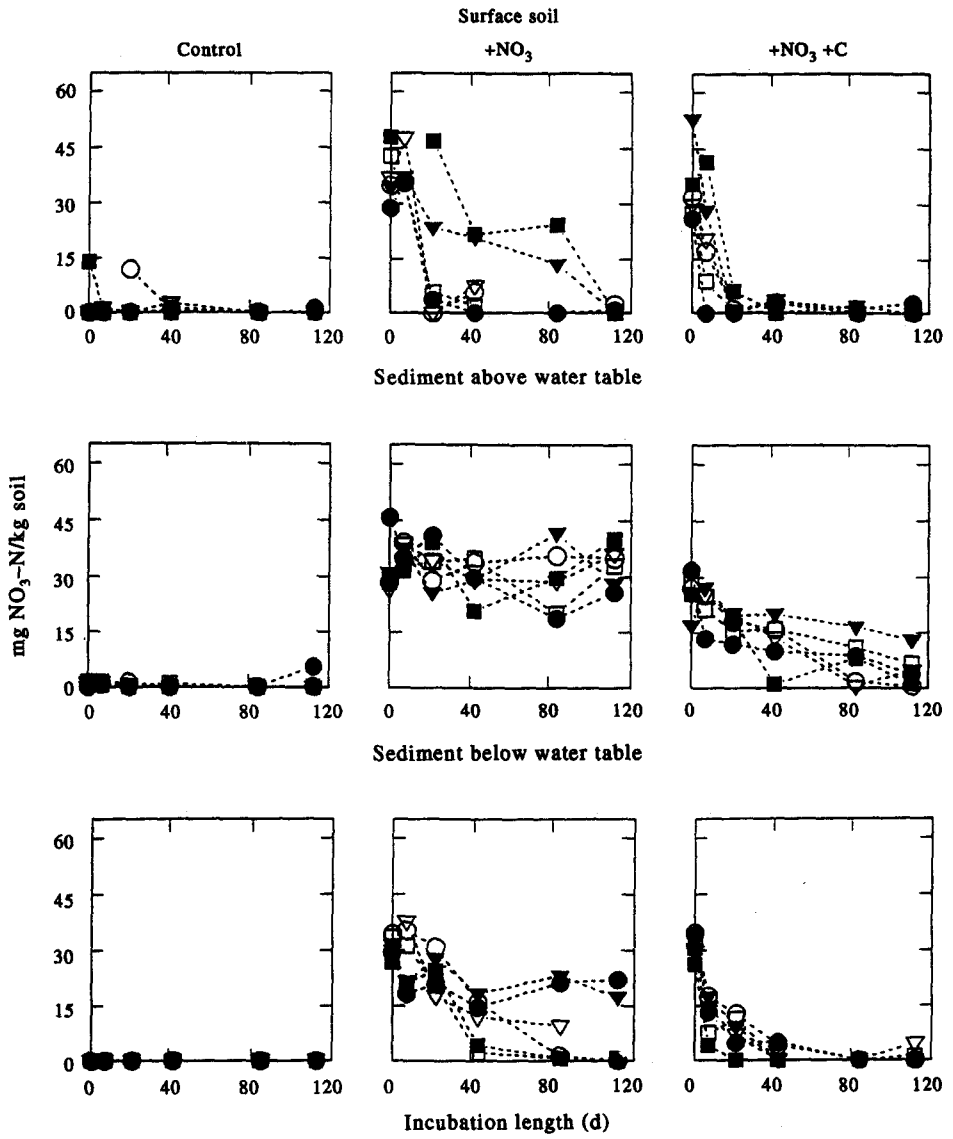

Fig. 2. The influence of $Ca(NO_3)_2$ and algae biomass (+C) on nitrate-N concentrations during the 112 d incubation in samples collected from cultivated (open) and pasture (solid) fields in surface soil, and sediment.

were due to free $CaCO_3$ in the subsurface environment. Fungal populations decreased 5 orders of magnitude from the surface to sediment collected below the water table (Table 2). Bacterial counts decreased 50% from the surface to sediment collected below the aquifer.

Sampling depth, site, treatment, and zero or first order model selection influenced nitrate rate loss estimates (Table 3 and Fig. 2). Generally, the two models (zero and first order) estimated that significant (at the 0.05 level) nitrate loss occurred for identical treatments. However, there were important differences. For example, nitrate loss did not occur when zero order kinetics and did occur when first order kinetics for $Ca(NO_3)_2$ treated surface soil at sites 3 and 4. Model differences were a function of uniform or nonuniform N loss rates. Differences between the models indicate that for some sites zero order kinetics should be used, while for other first order kinetics should be used.

A wide range of nitrate loss rates for the zero and first order equations were measured for all soils and sediments (Table 3). In surface soil, nitrate loss occurred up to 18 times faster in some samples relative other samples. The wide range of nitrate loss rates in $Ca(NO_3)_2$ treated sediments, collected from below and above the water table show that substantial spatial variability existed in this environment (Fig. 2 and Table 3). Given that these samples were collected from within 2 km of each other, these findings demonstrate the complexity of defining agrichemical detoxification rates for modeling purposes.

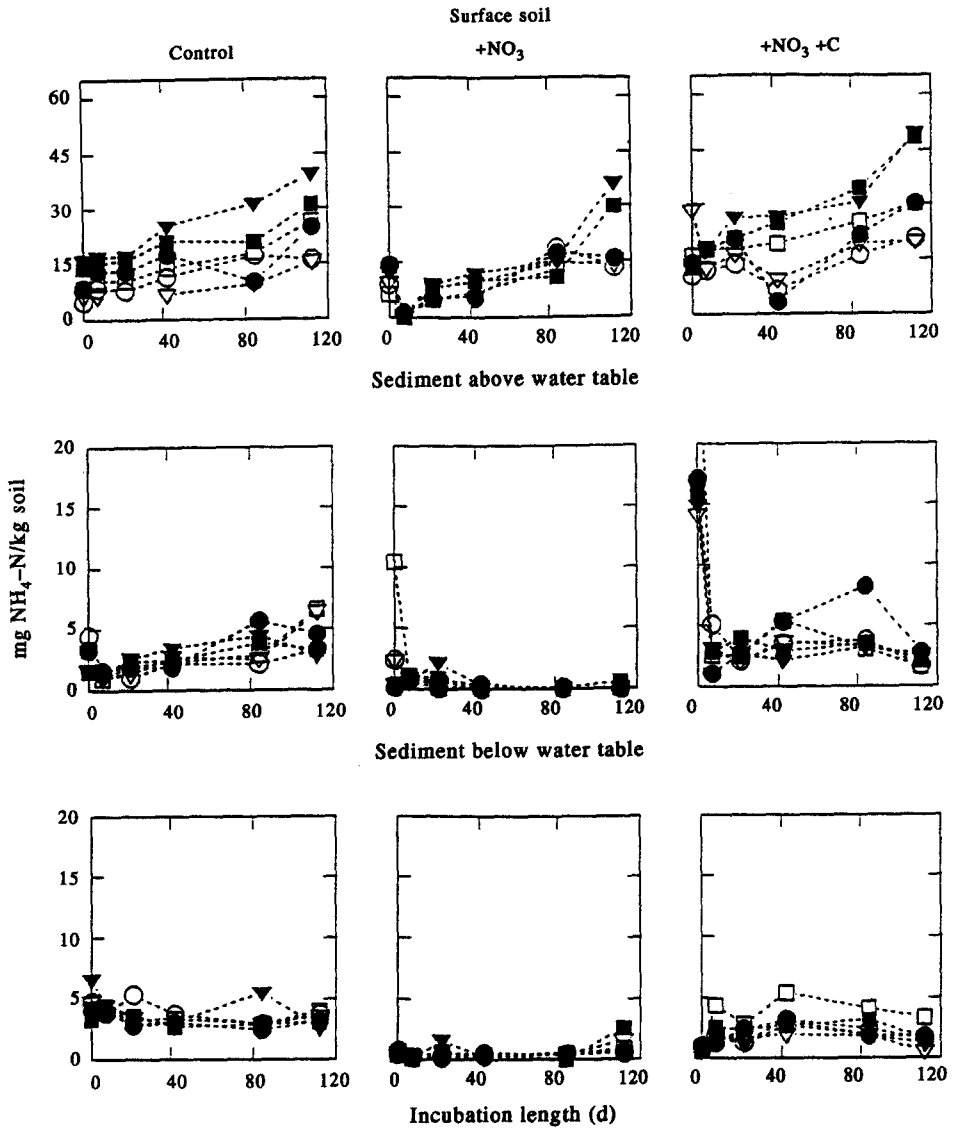

Fig. 3. The influence of $Ca(NO_3)_2$ and algae biomass (+C) on ammonium-N concentrations during the 112 d incubation in samples collected from cultivated (open) and pasture (solid) fields in surface soil sediment.

In sediment samples from above the water table that were treated with $Ca(NO_3)_2$, nitrate loss occurred at 1 of the 6 sites. However, in sediment samples from below the water table nitrate loss was measured in 4 of the 6 sites. Adding lysed algae biomass increased nitrate loss rates for both depths. These findings indicate that nitrate loss was limited by substrate availability and was spatially dependent.

Untreated and $Ca(NO_3)_2$ treated sediments collected from above the water table initially had similar ammonium concentrations (Fig. 3). The NH_4-N concentrations were lower in the $Ca(NO_3)_2$ treated than control sediments. The low ammonium concentrations and the lack of changes in organic (Table 4) and nitrate N (Fig. 2) when only $Ca(NO_3)_2$ was added

Table 4. Total organic N as influenced by sample collection zone, incubation length, and treatment

Treatment NO_3	Biomass	Incubation length	Collection zone		
			Surface	Above	Below
	d		(mg N kg^{-1})		
No	No	0	2670	51.3	45.8
No	No	21	2670	63.1	39.0
No	No	112	2680	50.3	41.1
t value			NS[a]	NS	NS
Yes	No	0	2600	40.6	48.6
Yes	No	21	2690	26.7	44.0
Yes	No	112	2780	29.5	49.9
t value			NS	NS	NS
Yes	Yes	0	2600	63.9	57.4
Yes	Yes	21	2640	61.9	63.2
Yes	Yes	112	2700	59.8	57.6
t value			NS	NS	NS

[a]NS is not significant.

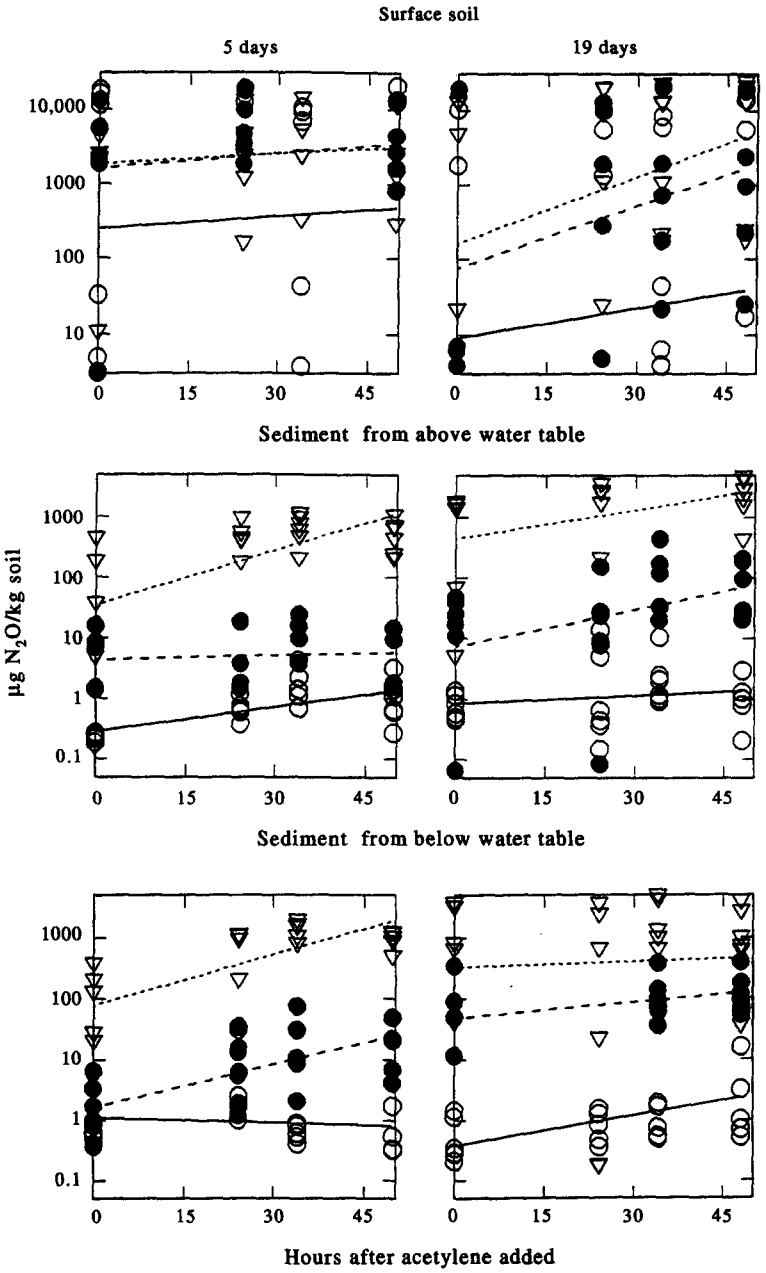

Fig. 4. Nitrous oxide concentrations as influenced by prior incubation length of 5 or 19 d and sample depth in untreated (○), $Ca(NO_3)_2$ treated (●), and $Ca(NO_3)_2$ plus algae biomass treated (▽) sediments. Regression equations for the untreated (—), $Ca(NO_3)_2$ (----), and $Ca(NO_3)_2$ plus lysed algae biomass (····) treated sediments are given in Table 5.

suggests that denitrification was not sufficiently rapid to significantly reduce nitrate concentrations.

Ammonium concentrations were higher in untreated sediments from below the water table than those treated with $Ca(NO_3)_2$ (Fig. 3). Low ammonium concentrations and relatively stable organic N contents (Table 4) indicates that nitrate conversion to ammonium or organic N was of limited importance.

Prior to the addition of acetylene, nitrous oxide was produced in many of the incubation containers during the preincubation period of 5 or 19 d (Fig. 4). In surface soil, N_2O concentrations exceeded 1000 μg-N kg^{-1} soil in many of the samples, while in subsurface samples concentrations were as low as 0.4 μg-N kg^{-1} of soil. Again, a substantial amount of spatial variability was observed in N_2O production. The degree of variation was similar to that observed for the nitrate loss experiment.

Nitrous oxide concentrations in subsurface sediments after 5 and 19 d of incubation were increased by treatment with $Ca(NO_3)_2$ only or treatment with

$Ca(NO_3)_2$ plus algae biomass (Fig. 4 and Table 5). The increase in the nitrous oxide concentrations in sediment from above the aquifer treated with $Ca(NO_3)_2$ show that denitrification occurred in this treatment even though rates were relatively slow. These results are different from the nitrate loss experiment and demonstrate that the nitrate loss and acetylene inhibition methods complimented each other. The acetylene inhibition technique was more sensitive and confirmed that denitrification occurred in sediments from above the water table treated with nitrate. However, the nitrate loss experiment was well suited for calculating a rate loss using first order kinetics that can be used to calculate half lives. These results show that denitrification is a valid method to reduce nitrate concentrations in the Big Sioux Aquifer and that denitrification was limited by substrate availability.

Field transport of nitrate and carbon

1992. Biweekly rainfall totals were low (<4 cm) between 1 and 150 DOY (Fig. 5) resulting in a relatively stable depth to groundwater. After 150 DOY, precipitation increased and the depth to groundwater decreased. The change in the depth to groundwater was approximately 25 cm from 150 to 250 DOY.

Temporal variations in the nitrate-N concentrations were a function of monitoring well location rather than cropping sequence (Fig. 5). Comparisons between the depth to the water table and nitrate concentrations changes over time indicates that when the depth to water table was relatively constant (21–150 DOY) nitrate-N concentrations also were relatively constant.

Dissolved organic C (DOC) concentrations on 21 DOY ranged from 2.4 to 4.3 mg C l^{-1} (Fig. 5). In three of the monitoring wells, DOC concentrations were similar 69 d later (90 DOY). However, a DOC peak was observed in monitoring well 10. This peak did not correspond to a nitrate-N peak. By 167 DOY, DOC concentrations decreased to values ranging from 0.3 to 1.2 mg C l^{-1} for all wells. After 167 DOY, DOC concentrations fluctuated with decreases followed by increases. Samples collected at 21 and 69 DOY were taken prior to groundwater recharge, while samples collected after 90 DOY were post groundwater recharge.

1993. Between 1 and 80 DOY, biweekly precipitation totals were less than 4 cm (Fig. 6). However, 55 cm of precipitation were collected between 80 and 233 DOY. Depth to groundwater responded to high rainfalls and decreased by over 200 cm.

Temporal changes in nitrate-N and DOC-C were a function of monitoring well location rather than cropping sequence (Fig. 6). Nitrate concentrations decreased at all sites between 103 and 117 DOY. In wells 5 and 10 decreases were as much as 10 mg N l^{-1}. Dilution of groundwater with percolate or denitrification may be responsible for temporal changes.

Groundwater DOC and nitrate N had different temporal patterns (Fig. 6). Peaks in groundwater DOC concentrations were observed in several monitoring wells on 83 DOY. DOC peaks followed spring recharge. After these peaks, DOC concentrations decreased over the next 20 d. Decreases in DOC concentrations may have been due to microbial respiration in the aquifer or dilution of groundwater with percolating water containing low amounts of DOC. DOC decreases predated nitrate decrease discussed above. Since groundwater depth was relatively constant between 103 and 124 DOY, it is likely that microbial activity played a role in reducing DOC concentrations.

SUMMARY AND CONCLUSIONS

Following DOC peaks, DOC concentrations decreased and thereafter generally remained less than 4 mg C l^{-1}. In 1993, decreases in nitrate concentrations lagged behind decreases in the DOC concentrations. This pattern would be expected if water percolating into the aquifer was saturated with O_2 and if anaerobic conditions were required for denitrification. If declines in nitrate concentrations were due to denitrification alone, then the laboratory rates of denitrification would appear to approximate the

Table 5. Regression equations for data shown in Fig. 4. The equations show the impact of incubation date and nitrate (+N) and nitrate plus algae biomass (+N+C) on log N_2O concentration. The 95% confidence intervals are shown in parenthesis

	Incubated for 5 d				Incubated for 19 d			
Sample treatment	Mean (SD) (μg N_2O/kg)	Y-intercept	Slope [μg N_2O/(kg h)]	r	Mean (SD) [μg N_2O/kg]	Y-intercept	Slope [μg N_2O/(kg h)]	r
Surface none		2.38	0.006	0.05	2210 (1770)	0.96	0.013	0.124
+N	5550 (2310)	3.21	0.007	0.16	6180 (3800)	1.87	0.028	0.335
+N+C	5280 (2270)	3.27	0.005	0.11	8386 (3880)	3.19	0.030	0.364
Above none	0.955 (0.439)	−0.55	0.0136	0.664***	2.14 (1.50)	−0.077	0.0043	0.157
+N	7.89 (3.19)	0.64	0.0023	0.095	72.5 (44.9)	0.865	0.0202	0.400
+N+C	483 (160)	1.57	0.0303	0.618	1970 (624)	2.64	0.016	0.434*
Below none	4.49 (13.9)	−0.415	0.017	0.532**	2.33 (2.84)	0.405	−0.0027	−0.108
+N	124 (121)	1.67	0.009	0.407*	16.9 (9.83)	0.217	0.024	0.630**
+N+C	1553 (1600)	2.51	0.003	0.045	809 (261)	1.88	0.028	0.696**

[a] * and ** are significant at the 0.05 and 0.01 level respectively.

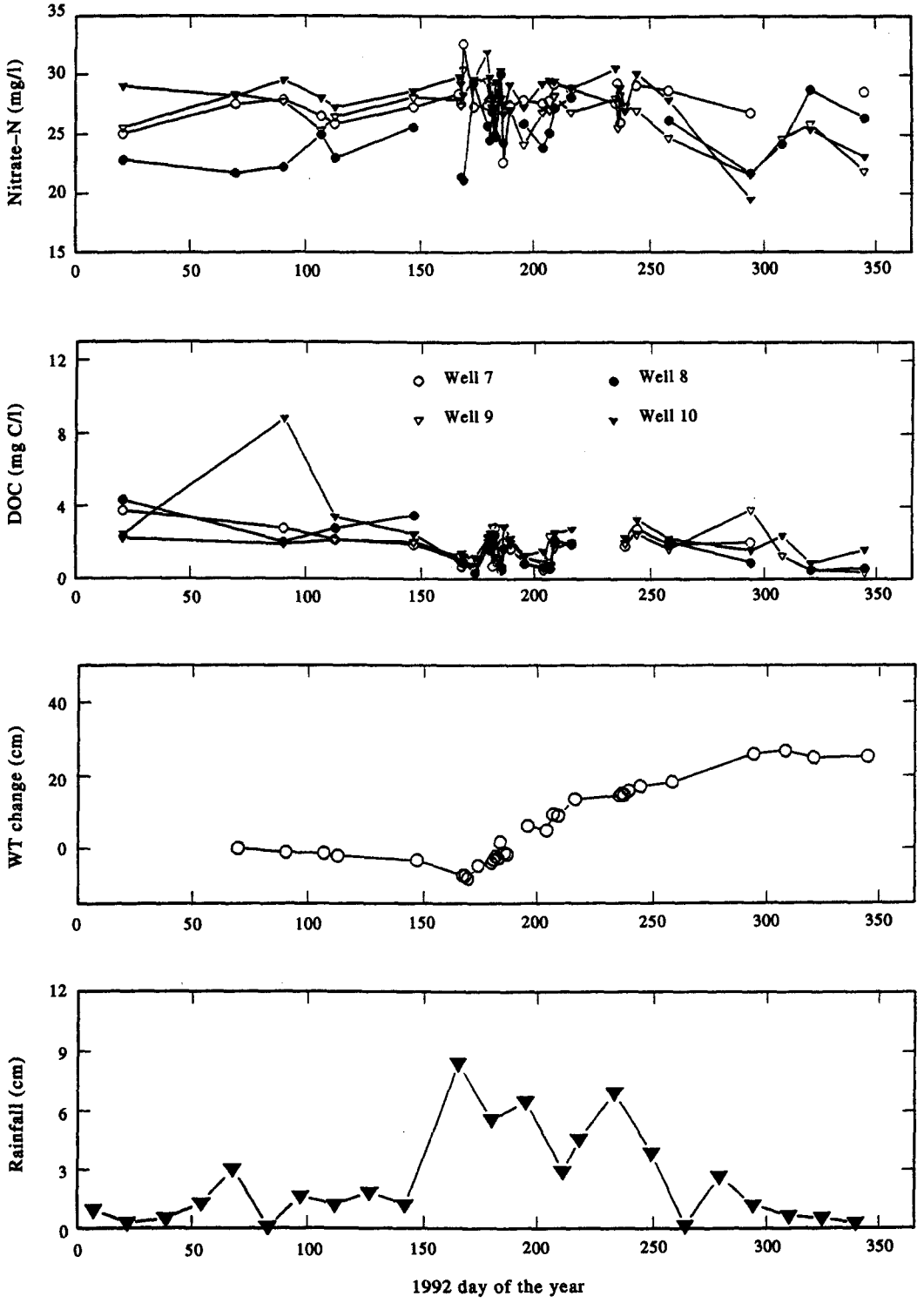

Fig. 5. Biweekly rainfall totals, groundwater depths (WT), dissolved organic-C (DOC), and nitrate-N concentrations in monitoring wells during 1992. Solid symbols represent corn-soybean-corn rotation fertilized in 1992. Open symbols represent the soybean–corn–soybean rotation fertilized in 1993.

observed rates of change in nitrate concentration in the aquifer. We estimate that about 90 d are required to denitrify 20 mg N l^{-1} at a rate of 0.22 mg-N $l^{-1}d^{-1}$ in the saturated sediment. Alternatively, using the first order rate constant of 0.025 d^{-1}, the nitrate halflife is estimated to be approx. 28 d in the saturated material.

Dissolved organic carbon peaks were observed immediately following soil thawing. Timing of the DOC peak suggests that freezing and thawing were

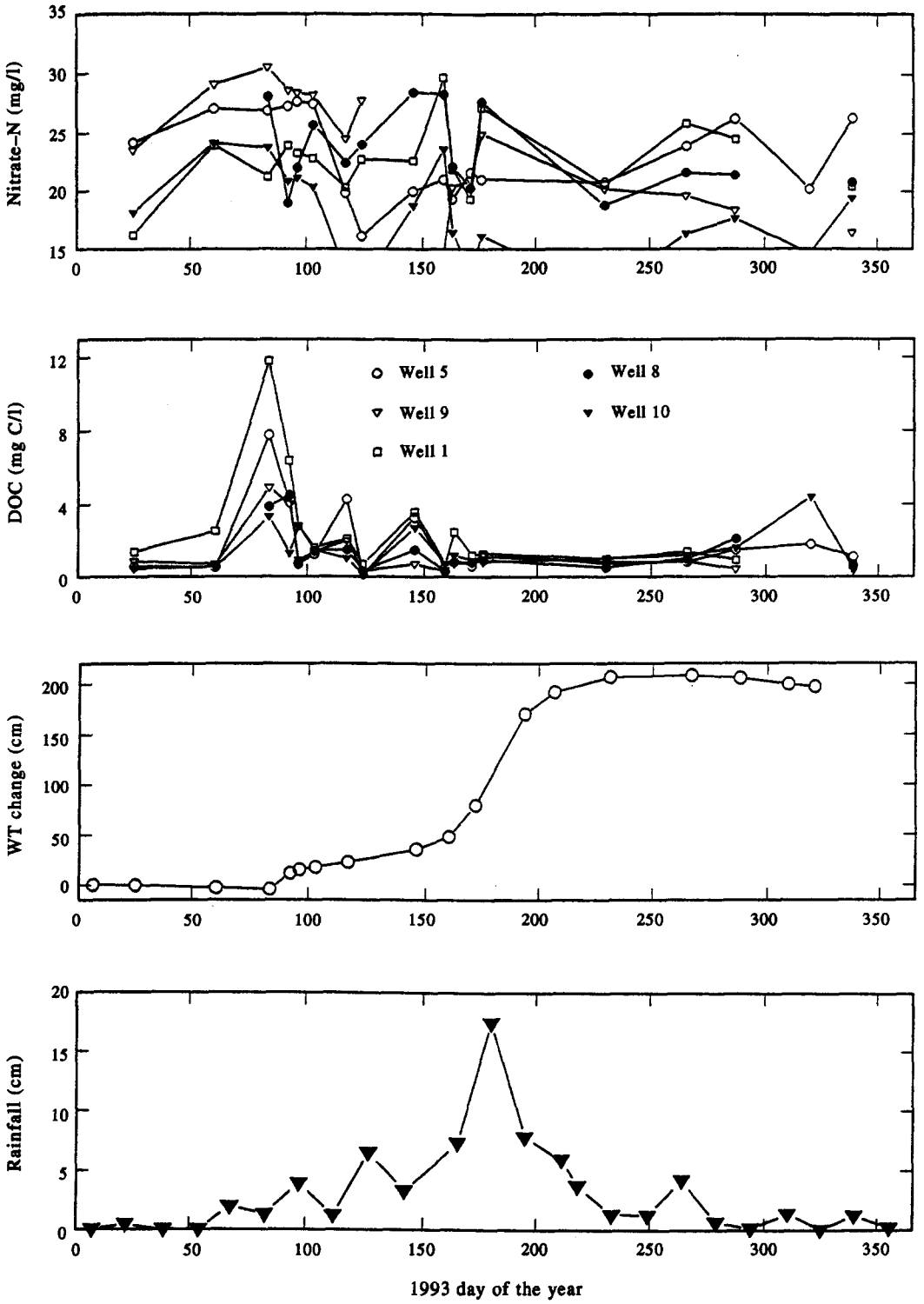

Fig. 6. Biweekly rainfall totals, change in the depth to groundwater (WT), dissolved organic-C (DOC) concentration, and nitrate-N concentrations in 5 monitoring wells during 1993. Solid symbols represent corn–soybean–corn rotation that was fertilized in 1992. Open symbols represent the soybean–corn–soybean rotation fertilized in 1993.

the mechanisms responsible for temporal DOC patterns. Temporal patterns in organic substrates have been linked to microbial activity. For example, DeLuca and Keeney (1994) reported that soluble amino N declined and microbial biomass and N mineralization increased following soil thaw.

Thawing also produces environments where denitrification can occur (Christensen and Tiedje, 1990).

This research shows that freezing and thawing produces conditions where organic C can be transported from the soil surface to the aquifer. However, due to the biological reactivity of this material DOC peaks may be short lived (Zsolnay and Steindl, 1991). In some cases, DOC concentrations may or may not be sufficient to produce the anaerobic conditions required for denitrification. McCarty and Bremner (1992) reported that DOC concentrations of 2.9 mg C l^{-1} were insufficient to produce denitrification, while Obenhuber and Lowrance (1991) reported that denitrification occurred when DOC concentrations were increased to 10 mg C l^{-1}. In this study DOC concentrations exceeded 10 mg C l^{-1} following only soil thawing. These findings show that seasonally driven physical processes, such as freezing and thawing impact the transport of organic substrate from surface to subsurface environment, which in turn, may impact subsurface agrichemical detoxicification mechanisms.

Acknowledgements—Partial support provided by USGS-104, South Dakota Groundwater Research and Education Fund, and USDA-CSRS Midwest Systems Evaluation Area.

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