

## MONITORING MANAGEMENT EFFECTS ON GROUND WATER QUALITY

Roy F. Spalding  
University of Nebraska-Lincoln  
Water Center  
103 Natural Resources Hall  
Lincoln, NE 68583-0844

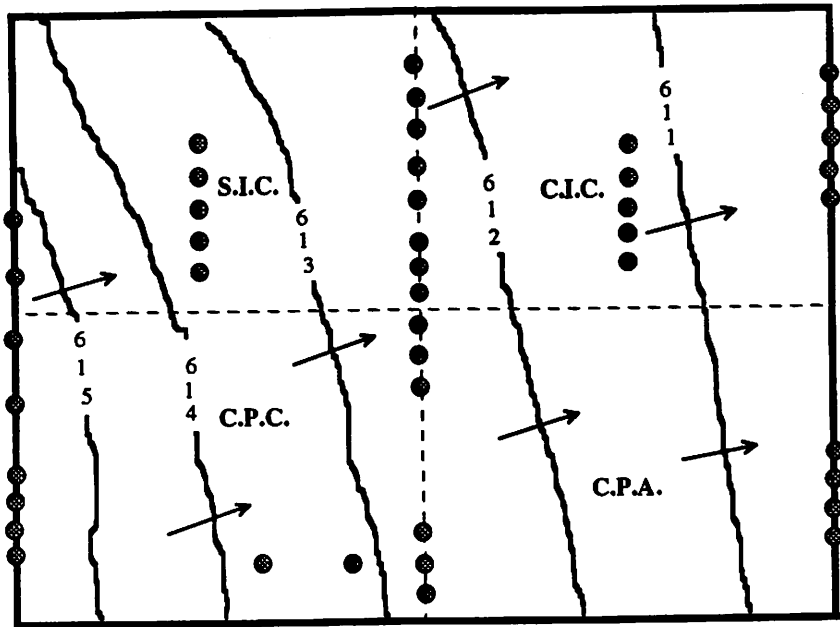
### HYDROGEOLOGY

The unsaturated zone at the MSEA management blocks (MBs) is characterized by a 1.2-m (4-ft) thick, well-drained, silt loam soil of primarily eolian origin overlying ~4.3 m (14 ft) thickness of fine to coarse-textured, clean, fluvial sands. The depth to water varies with location and fluctuates with the season (Figure 1). During the non-pumping season ground water flows to the ENE; however, during the summer pumping destroys all remnants of this pattern (Figure 1). The shallow aquifer is ~11.6-m (38-ft) thick and is composed of Quaternary Age sands and gravels. Similar fluvial sediments characterize the aquifer geology along the Platte River Valley, a distance of ~300 km (185 mi) to both the west and the east. High transmissivities of 1500 m<sup>2</sup>/day (16,140 ft<sup>2</sup>/day) are characteristic of sands and gravels in the primary aquifer. An irrigation well pump test at the MBs indicated the primary aquifer has a horizontal hydraulic conductivity of 130 m/day (426 ft/day) and a vertical conductivity of 10.4 m/day (34 ft/day). Using Darcy's Law a particle would move horizontally across the site at a rate of 0.55 m/day (1.8 ft/day). The primary aquifer is composed of a relatively homogeneous sand and gravel matrix.

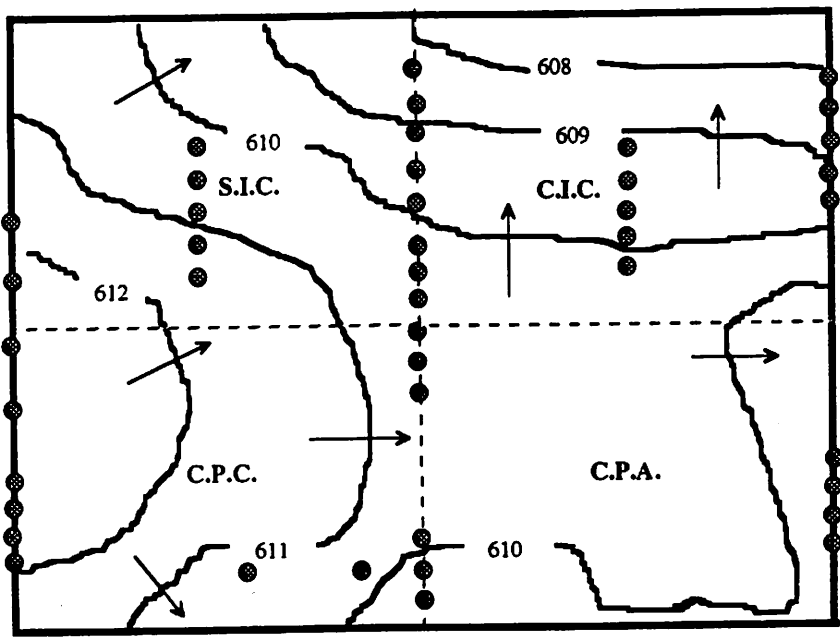
The primary aquifer unconformably lies on older Quaternary silts. The silts are interbedded with clays, sands, and some gravels. Deep boreholes at three corners of the MBs indicate the silts range in thickness from 9 m (30 ft) to ~20 m (64 ft). The silts lie unconformably on the Miocene Age sandstone Ogallala formation which is ~15.2 m (50 ft) thick beneath the MBs. During the pump test of the southwest irrigation well at the MBs, no upward leakage from the Ogallala Group into the primary aquifer was detected. The silts and clays thus present an effective aquitard separating the water in these aquifers. Because the Ogallala in this area lacks agrichemical contamination, it serves as a secondary aquifer for domestic wells. The Ogallala rests on impermeable Cretaceous Pierre Shale.

### WATER QUALITY SAMPLING

Initially a network of 11 multilevel samplers (MLSs) with gas-drive samplers was installed at the four MBs and in the half section directly upgradient. Samples from these



**Regional**



**Pumping Season**

	Contour 1m interval		Multi-level samplers		Direction of groundwater flow
S.I.C.	Surge Irrigated Corn	C.I.C.	Conventional Irrigated Corn		
C.P.C.	Center Pivot Corn	C.P.A.	Center Pivot Alfalfa		

APPROX. SCALE IN METERS

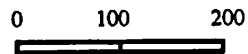


Figure 1. Water table contours for regional flow during non pumping season (April, 1992) and for high stress period during pumping season (August, 1991).

MLSs provided baseline concentrations for the project. After one season, a defective ball valve made the gas-drive samplers inoperable and they were pulled, renovated, and reinstalled at their present locations. An additional 30 MLSs were also installed at that time (Figure 1). All 41 MLSs were assembled on site and placed in their respective boreholes in a continuous string. The MLSs contain eight 1.6-cm (5/8-in) x 0.5-cm (3/16-in) coaxial high density polyethylene (HDPE) tubes attached to eight stainless steel gas-drive samplers. All 41 MLSs had a backup low density polyethylene (LDPE) tube affixed to the string at each depth in case the water table was high enough to remove the sample with a peristaltic or suction pump.

By monitoring the analytes of interest during purging, it was shown that analyte stability occurred after three tube volumes were evacuated. In a paired T-test ( $p > 0.1$ ) no significant differences in analytical concentrations were observed in samples collected with the nitrogen-drive samplers, peristaltic pumps, or suction pumps.

#### Baseline samples.

The intermediate vadose zone (the area below the root zone and above the water table) was cored in an X-pattern across the MBs with a CME auger rig equipped with a continuous core barrel. The lined cores were frozen in the field and kept frozen until analysis. Aliquots from each foot of composited sediment were extracted for nitrate and atrazine by KCl and super critical fluid extraction (SFE), respectively. Pesticide extraction and analysis was by procedures detailed in Cassada et al. (in press).

In 1990 the first samples were collected from the 11 MLSs and perimeter Ogallala wells for agrichemicals, conductance, pH, major ions, and dissolved organic carbon (DOC) in both the primary Quaternary aquifer and the underlying secondary Ogallala aquifer (Table 1). The average concentrations indicate that the ground water of the primary aquifer is a Ca-HCO<sub>3</sub>+ SO<sub>4</sub> type with a pH near neutrality. Ground water in the Ogallala is a Ca-HCO<sub>3</sub> type and has very low concentrations of agrichemicals.

Table 1. Parameter concentrations in the primary and secondary aquifer beneath management blocks.

Analyte	Primary Aquifer Concentration	Secondary Aquifer Concentration
pH	6.8 ± 0.3	6.7 ± 0.0
Conductance	930 ± 170 uS	380 ± 85 uS
NO <sub>3</sub> -N	26.1 ± 4.7 mg/L	0.1 ± 0.1 mg/L
NH <sub>4</sub> -N	0.15 ± 0.15 mg/L	0.2 mg/L
TKN	0.63 ± 0.39 mg/L	0.2 ± 0.2 mg/L
DOC	3.3 ± 0.3 mg C/L	0.6 ± 0.1 mg C/L
HCO <sub>3</sub> <sup>-</sup>	315 ± 80 mg/L	283 ± 2 mg/L
Cl <sup>-</sup>	24.4 ± 2.9 mg/L	8.5 ± 3.1 mg/L
SO <sub>4</sub> <sup>-2</sup>	211 ± 54 mg/L	34.6 ± 2.8 mg/L
Na <sup>+</sup>	67.5 ± 19.0 mg/L	24.1 ± 2.8 mg/L
K <sup>+</sup>	20.0 ± 10.8 mg/L	7.9 ± 1.3 mg/L
Ca <sup>+2</sup>	144 ± 25 mg/L	66 ± 3 mg/L
Mg <sup>+2</sup>	28.9 ± 5.1 mg/L	10.8 ± 0.4 mg/L
Atrazine	2.02 ± 1.19 µg/L	<0.05 ± <0.05 µg/L

The pH and major ion data were inputted in the phase mineral equilibria program (PHREEQE). About 30% of the samples from the primary aquifer were slightly supersaturated with respect to the minerals aragonite, calcite, and dolomite. The remaining samples were slightly undersaturated with respect to these mineral phases thus the data suggest solubility control on calcium and magnesium concentrations. No other geochemical controls were in evidence. Ground water from the Ogallala was undersaturated with respect to mineral phases.

The predominant form of nitrogen in the primary aquifer was nitrate. Total Kjeldahl-N and ammonia-N comprised less than 3% of the total soluble N in the primary aquifer. Concentrations of both NO<sub>3</sub>-N and atrazine were at or below method detectability in the Ogallala. TKN at 0.2 mg/L was the dominant form of nitrogen.

## AGRICHEMICALS BENEATH MANAGEMENT BLOCKS

Since the baseline was established, the 41 MLSs have been sampled eight times. Sampling occurred in early spring, summer, and fall and represents times of maximum and minimum water levels. Representative samples from a total of ~4500 discrete samplings for nitrate and for atrazine and its degradates were used to calculate average concentrations at each depth. During the first two years of monitoring, nitrate-N concentrations from the upper vadose zone pore water to the bottom of the primary aquifer were invariant with depth. The combination of a long-term continuous, agrichemical leachates from fertilized and irrigated corn, an oxidizing aquifer void of denitrification, and an absence of continuous silt and clay lenses had led to this steady state condition with respect to nitrate. The impacts of management changes on shallow

ground water nitrate-N concentrations were first observed in the spring of 1993 (Figure 2). Concentrations in the shallow downgradient wells in the MBs suggest a lessening in the nitrate levels such that MBs with best management practices in terms of irrigation and nutrient applications have the lowest nitrate concentrations. Tritium-<sup>3</sup>He dates reveal that the impacted waters are less than 2 years old.

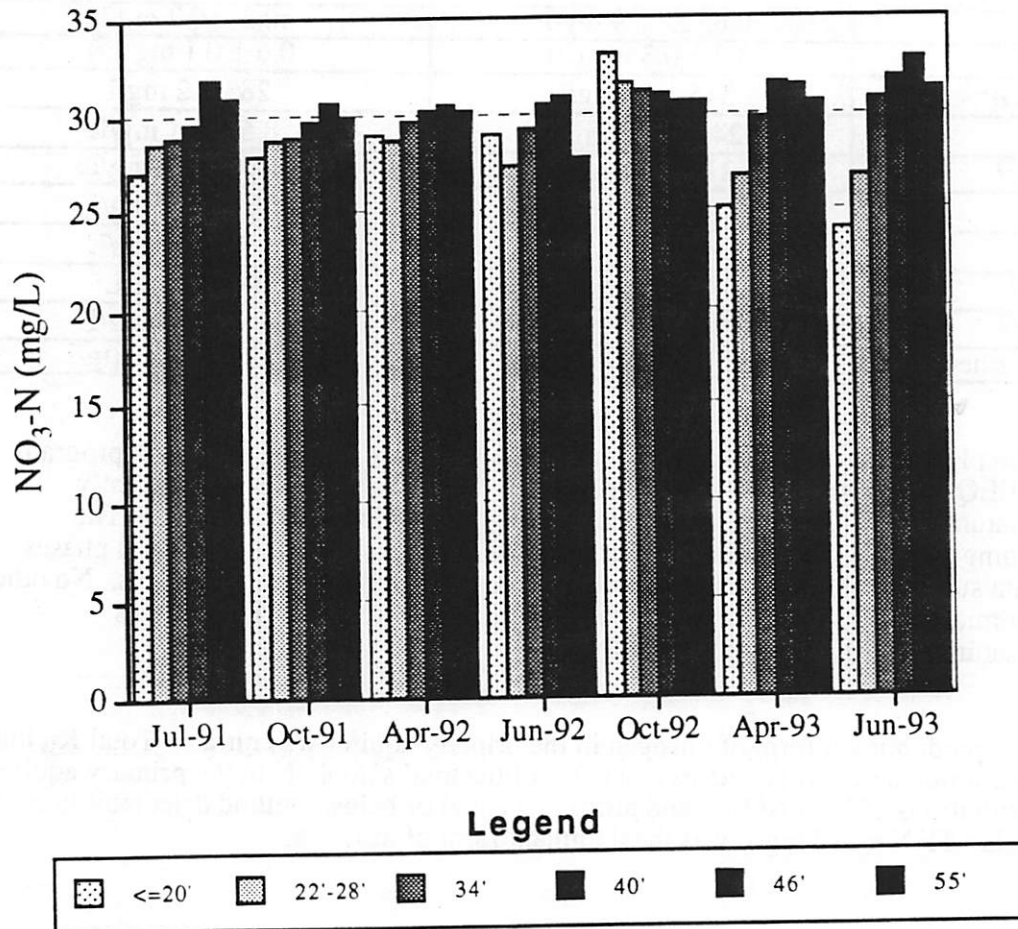


Figure 2. Average NO<sub>3</sub>-N concentrations in vertical intervals beneath MBs (July, 1991 - June, 1993).

Atrazine concentrations in the saturated zone decrease with depth from about 3.5  $\mu\text{g/L}$  to < 1.5  $\mu\text{g/L}$ . Both deethyl and deisopropylatrazine, microbial degradates of atrazine, decrease at almost the same rate as the parent compound, which suggests that hydrolysis may be the primary process controlling atrazine concentrations (Figure 3). The vertical distribution of atrazine combined with tritium-<sup>3</sup>He dates suggest its half life is between 10 and 20 years. The metabolite didealkylated atrazine and hydroxyatrazine occur in low part per trillion levels. The hydroxyatrazine is thought to be constantly replenished through hydrolysis; however, the molecules concentration is controlled by rapid sorption. The process maintains soluble ground water hydroxyatrazine at ultra trace levels.

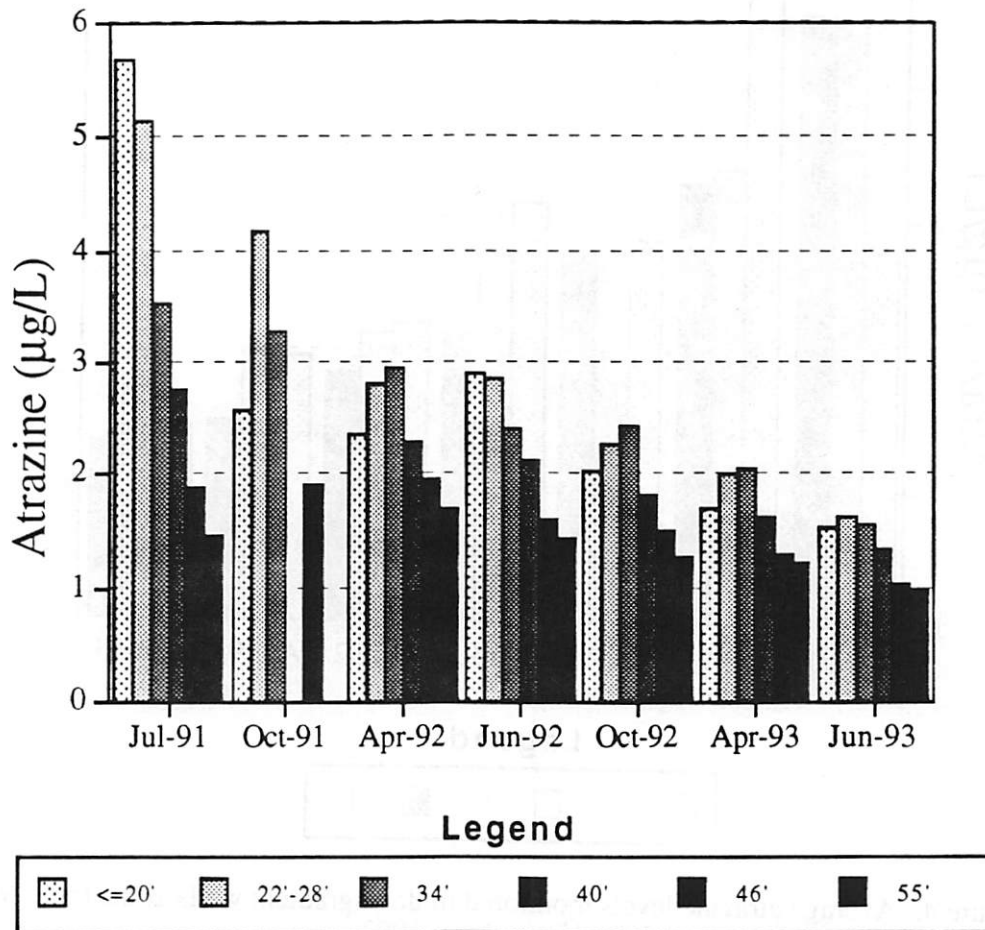


Figure 3. Average atrazine levels in designated vertical intervals at MBs (July, 1991 - June, 1993).

Shallow ground water atrazine levels have rapidly responded to improved water management. Since atrazine application rates have slightly increased since BMPs were introduced to the MBs in 1991, the only practice effecting the atrazine leaching has been water management. By applying significantly less water, average atrazine levels have decreased by ~50% (Figure 4). The lowest atrazine levels were associated with MB downgradient wells characterized by the lowest and most uniform water application.

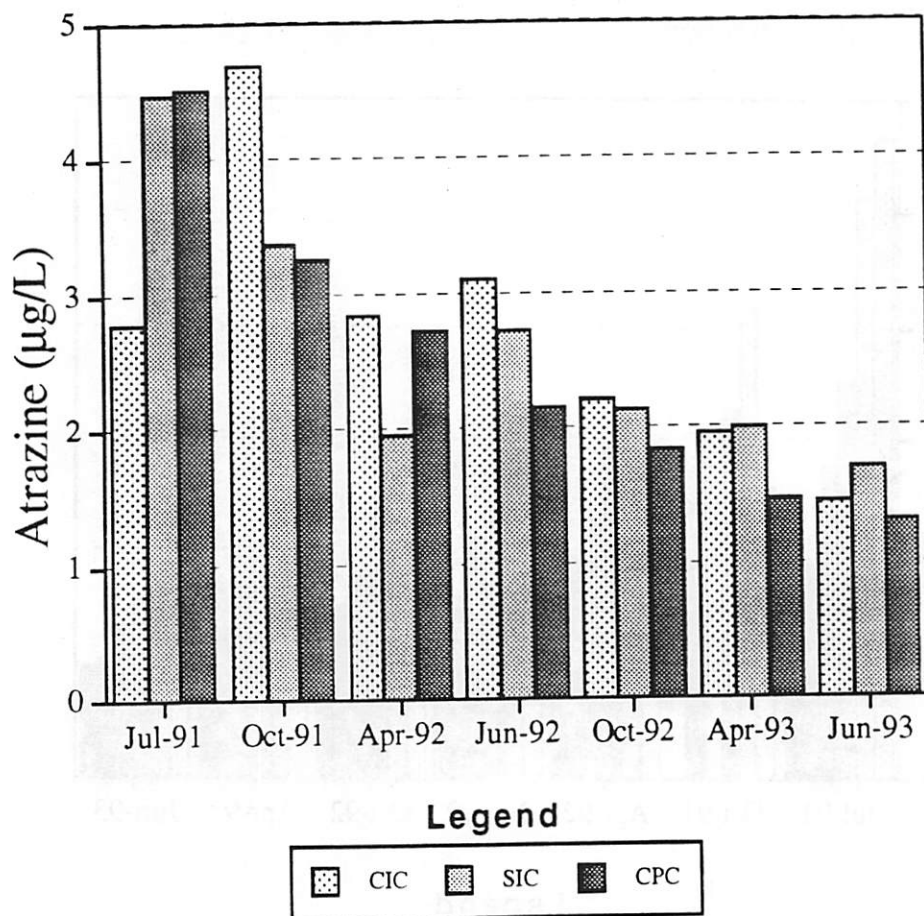


Figure 4. Average atrazine levels monitored in downgradient wells at the three MBs that received atrazine treatments (July, 1991 - June, 1993).

During the first two years, additional pesticides and degradates detected beneath the MBs and their average concentrations and standard deviations in µg/L include: alachlor ( $0.03 \pm 0.26$ ), deethylatrazine ( $3.5 \pm 1.50$ ), deisopropylatrazine ( $0.20 \pm 0.20$ ), metolachlor ( $0.07 \pm 0.41$ ), prometon ( $0.02 \pm 0.14$ ), propachlor ( $<0.01 \pm 0.06$ ), propazine ( $0.02 \pm 0.02$ ), simazine ( $0.02 \pm 0.02$ ), and trifluralin ( $<0.01 \pm 0.01$ ). Commonly reported molar deethylatrazine to atrazine ratios (DARs) averaged 1.5 and molar deisopropylatrazine to deethylatrazine ratios D<sup>2</sup>R averaged 0.06. These ratios indicate a nonpoint source problem in which significant atrazine degradation occurs in the soils prior to introduction to the ground water.

#### REFERENCES

Cassada, D.A., R.F. Spalding, Z. Cai and M.L. Gross. In press. Determination of atrazine, deethylatrazine, and deisopropylatrazine in water and sediment by isotope dilution GC/MS. *Analytica Chimica Acta*.