Nitrate and pesticide residue penetration into a Wisconsin central sand plain aquifer. [DNR-171] 2004

Kraft, George J. et al.
Stevens Point, Wisconsin: College of Natural Sciences, University of Wisconsin - Stevens Point, 2004

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May 24, 2004

In partial fulfillment of State of Wisconsin PO number NMB00000160 and AGC70000002

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ABSTRACT

The leakage of NO_3 and pesticide residues from agricultural landscapes to groundwater has important implications for drinking water and aquatic ecosystems. This leakage increased greatly due to the large increase in fertilizer-N and pesticide use that began about 1960 and levelled in the 1980-1990s. Good progress has been made at describing the present geographical distributions of NO_3 and pesticide residues in groundwater, but the picture is murky as to what future conditions will emerge. Conservation of mass dictates that groundwater pollutant loads will increase until they reach equilibrium with modern pollutant leakage. Equilibrium requires that either (1) denitrification and pesticide degradation eliminate pollutants, or (2) modern groundwater with its associated pollutant load penetrates an entire aquifer thickness.

We examined nitrate and pesticide penetration into an aquifer in the Stockton Study Area, located on the Wisconsin Central Sand Plain. Groundwater there is aerobic and typical of much of the upland WCSP. Six monitoring sites in the up-, mid-, and downgradient portion of the flow system were sampled at multiple intervals of the saturated thickness, and subjected to analyses for various nitrogen species (including denitrification gasses), chlorofluorocarbons for age-dating, pesticides (mainly atrazine and chloroacetanilide residues), N and O isotopes of NO_3 for attributing NO_3 source, and major ions.

Nitrate and pesticide residues penetrated most of the study area's saturated thickness. Nitrate-N averaged 20 mg L^{-1} , ranging 4.4 to 41 mg L^{-1}. Concentrations < 10 mg L^{-1} were only found near the water table immediately downgradient of nonagricultural land covers (urban, rural residential) and in the deep mid portion of the aquifer coincident with older groundwater (pre-1980). One-fourth of wells demonstrated a manure NO_3 source, with the remainder probably originating from fertilizer. Organic, NH_4, and NO_2-N concentrations were negligible. Denitrification was not an appreciable sink for NO_3. Though N_2O-N was ubiquitous, concentrations were miniscule with respect to NO_3-N. Denitrified N_2-N was observed in one-fourth of groundwater samples, but it only accounted for only 1.7 to 17% of the original NO_3-N load. Where denitrification to N_2-N was observed, a manure NO_3 source was usually implicated.

Pesticide residues were pervasive and generally followed NO_3 patterns. Detected residues were those of atrazine, alachlor, metolachlor, metribuzin, and pendamethalin. Summed residues in individual wells were typically 5 to 15 $\mu g\ L^{-1}$, but reached 41.7 $\mu g\ L^{-1}$ in one well. Alachlor and metolachlor residues, mainly the OA and ESA degradates, were the most common. One well exceeded the Wisconsin groundwater enforcement standard of 3.0 $\mu g\ L^{-1}$ of summed atrazine residues.

Most groundwater in the Stockton Study Area was dominantly of relatively recent origin - 1985 to present. Older (1969-1980) groundwater had lower pollutant concentrations, likely because it originated from relatively low-input land uses (forest, dryland agriculture) that are still present on the modern landscape. The Stockton Study Area appears to be largely in equilibrium with current land uses; i.e., modern groundwater with modern pollutant loads have mostly penetrated the entire saturated thickness. Hence, water quality and pollutant export are also close to equilibrium.

ACKNOWLEDGEMENTS

We thank the Wisconsin Department of Natural Resources, Wisconsin Department of Agriculture Trade and Consumer Protection, and the people of Wisconsin for funding this study. Staff members Jeff Postle, Bruce Rheineck, Jim VandenBrook, Timothy Asplund, and Michael D. Lemcke were helpful beyond their professional responsibilities. Randy S. Mentz contributed greatly through his diligence.

INTRODUCTION

The leakage of NO_3 and pesticide residues from agricultural landscapes to groundwater has important implications for drinking water quality and aquatic ecosystem health. This leakage increased greatly along with the large increase in fertilizer-N and pesticide use that began about 1960 (e.g., Hallberg et al., 1989). Though substantial progress has been made at describing current NO_3 and pesticide groundwater conditions (e.g., VandenBrook et al., 2002; Kolpin et al. 1993a; 1993b), what conditions the future will bring remain unclear. We expect that for a given area or a given aquifer, the average pollutant concentration and pollutant load ("load" can be thought of as the amount of pollutant stored in an aquifer) will increase until an equilibrium is reached with modern pollutant leakage. Equilibrium requires that either (1) denitrification and pesticide degradation mechanisms eliminate pollutants, or (2) modern groundwater with its associated pollutant load penetrates an entire aquifer thickness.

This study examines the penetration of nitrate and pesticide residues into a Wisconsin central sand plain aquifer (Figure 1) in the vicinity of the Town of Stockton ("Stockton Study Area"). The objectives are to:

- understand the input, fate, and origin of groundwater nitrate in the study area;
- describe the occurrence and concentration of pesticide residues, primarily those of chloroacetanilides and atrazine;
- determine the extent to which nitrate and pesticide residues have penetrated the study-area aquifer; and
- ascertain whether the residues are accumulating, or if a steady-state condition has been reached.

Nitrate and Pesticide Groundwater Pollution

Nitrate

Nitrate is the most pervasive groundwater contaminant in the US (USEPA, 1990) and in Wisconsin (CWGC, 1994). About 2.5% of US wells and 14% of Wisconsin wells (VandenBrook et al., 2002) exceed the Maximum Contaminant Level ("MCL," a US drinking water standard) of 10 mg L^{-1} NO_3-N. Agriculture is the largest source of NO_3 pollution (Knox and Moody, 1991), accounting for > 90% of Wisconsin groundwater NO_3 (CWGC, 1994). Nitrate exceedence rates in Wisconsin wells are typically

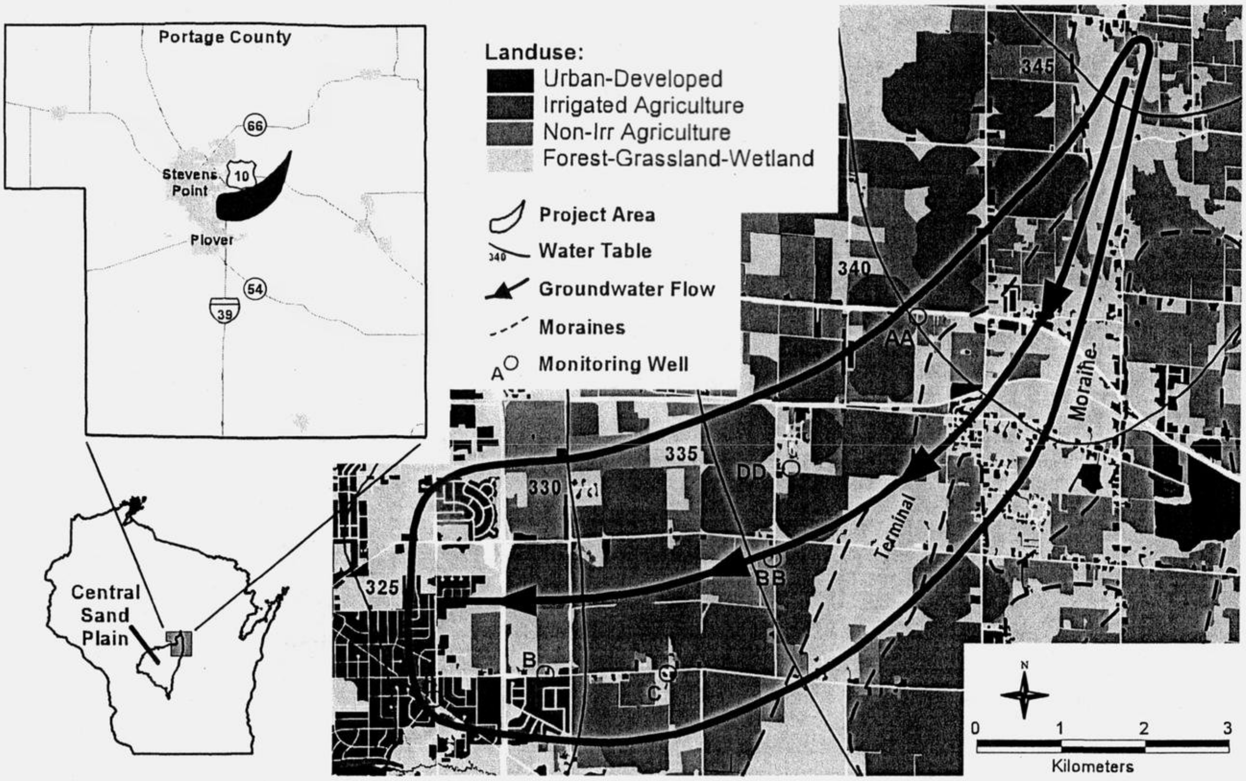

Figure 1. Location , land uses, and features of the Stockton study area.

greater in agricultural areas, averaging about 20% in predominantly agricultural reporting districts (LeMasters and Baldock, 1995) and reaching 70% in some agricultural locales (Kraft and Mechenich, 1998).

Besides degrading drinking water resources (Holden et al., 1992; Hamilton and Helsel, 1995; Kolpin et al., 1996), NO_3 pollution affects aquatic ecosystems when pollutant-bearing groundwater discharges to surface water. Nitrate concentrations typical of polluted groundwater harm the eggs and young of some salmonids and amphibians (Kincheloe et al., 1979; Hecnar, 1995; Johnston et al., 1999; Marco et al., 1999; Rouse et al., 1999), promote eutrophication in N-limited freshwaters, increase growth of rooted aquatic plants (Lillie and Barko, 1990; Rodgers et. al., 1995), and cause eutrophication in saltwater bodies such as the Chesapeake Bay and Gulf of Mexico at the mouth of the Mississippi River (e.g., Rabalais et al., 1996).

Generally, NO_3-N is present at < 1 mg L^{-1} in groundwater where human activities have not appreciably altered a landscape's N cycle (Spalding and Exner, 1993; Hamilton and Helsel, 1995). The N cycle in the midwestern US, including Wisconsin, was greatly altered by the spread of agriculture, which caused a leakage of fixed-N into surface- and ground- water from cultivation-induced mineralization of soil organic matter, fixation by legumes, additions of manure, and, beginning about 40 years ago (Figure 2), large inputs of chemical N fertilizer. The result has been widespread and apparently still-increasing groundwater NO_3 pollution (e.g., Hallberg et al., 1989; Central Wisconsin Groundwater Center, 1994; Bohlke and Denver, 1995; Mason et al., 1990). The apparent increase continues because groundwater residence times are great (averaging decades to centuries, depending on the basin) compared to the relatively recent disturbances in the N cycle.

Though NO_3 leakage from the landscape to ground and surface water increased substantially with the ca. 1960 large-scale increase in chemical N use (Hallberg 1989), NO_3 loading was probably still significant prior to this era, at least in some locales. Keeney and DeLuca (1993), for instance, demonstrated that Des Moines River NO_3 loads in the pre-chemical fertilizer era (1945) were excessive and almost identical to those of the present. They concluded that although NO_3 loading from that basin had remained fairly constant for decades, the NO_3 source transitioned from mineralized soil organic matter to chemical fertilizer. Hence a substantial NO_3-loading signature could exist in pre-chemical N groundwater.

Most groundwater NO_3 studies have examined drinking water standard exceedence rates (e.g., USEPA, 1990; LeMasters and Baldock, 1995) at various scales, or how NO_3 concentrations vary with land use and setting (e.g., Hamilton and Helsel, 1995). Relatively little work describes the evolution of present NO_3 conditions, fate, and trends for aquifers in agricultural landscapes. A notable early effort was that of Hallberg et al. (1989) which related large increases in spring-discharge NO_3 to basin-scale N inputs. Bohlke and Denver (1995) worked out the history and fate of groundwater NO_3 for two small catchments in the Atlantic Coastal Plain, Maryland, using techniques similar to those in this study. Salient conclusions were:

- Nitrate loading increased 3-6 fold over a 40 year period, with the most rapid increase coming in the 1970s.
- The rise in loading coincided with the history of chemical fertilizer use in the catchments.
- Where groundwater flowed along well-oxygenated flowpaths, NO_3 was conserved; along more reducing flowpaths, NO_3 was subject to denitrification.

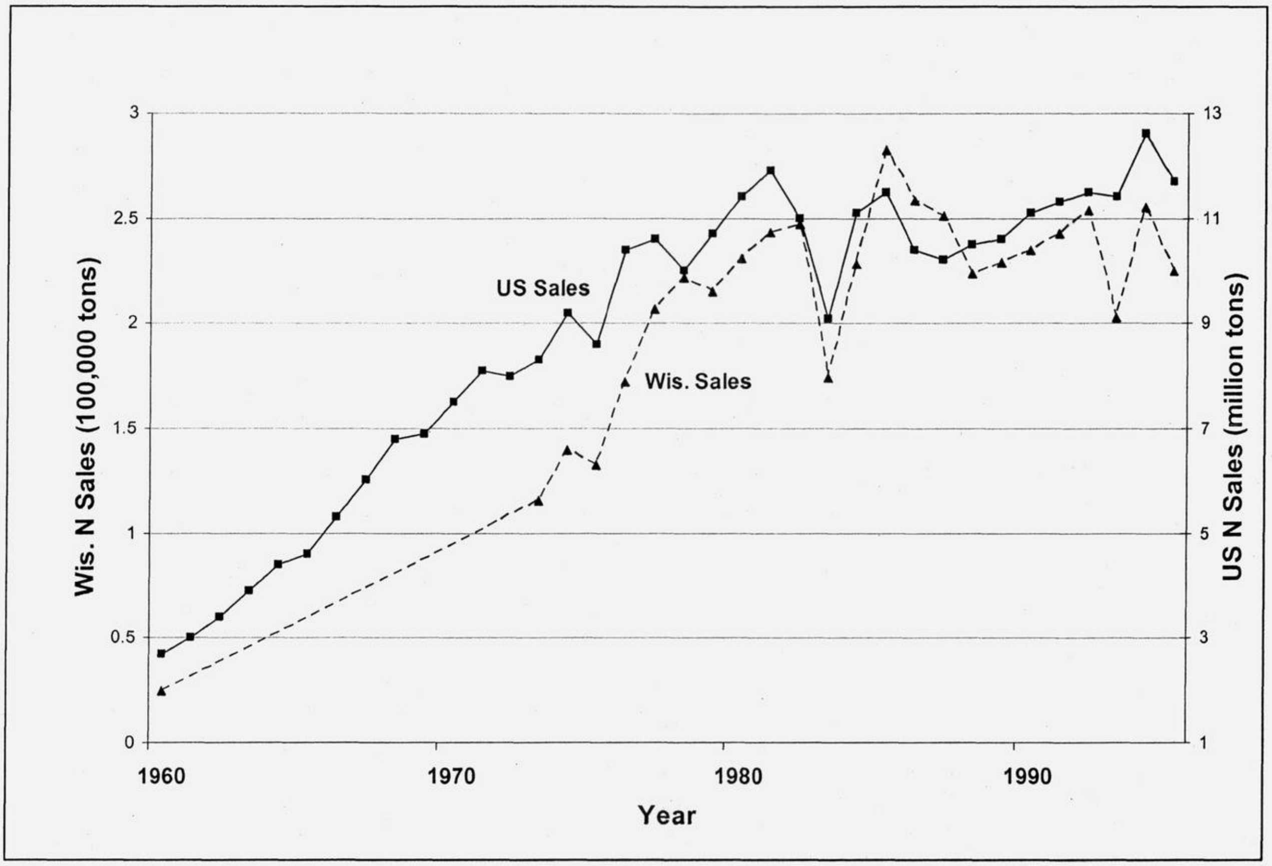

Figure 2. Increase in US and Wisconsin fertilizer-N since 1960.

- Nitrate discharges to surface water were smaller than loading to groundwater, primarily because old groundwater discharging from the system originated as low-NO_3 recharge, but also because of localized denitrification processes.

Puckett and Cowdery (2002) performed a similar study for a glacial outwash aquifer near in Otter Tail County, Minnesota USA. They concluded that:

- Nitrate loads to groundwater have been increasing since the 1940s and especially since 1960, corresponding with the rapid increase in use of chemical fertilizer.
- Denitrification in groundwater was almost complete, caused by reducing conditions induced by a large organic C content (average 0.15%) of aquifer sediment.
- Though denitrification rates were slow (0.005-0.47 mmol NO_3- yr^{-1}), sufficient residence time in the aquifer (50-70 years residence time) enables effective NO_3 removal.

The Otter Tail County study was conducted in an area with similar climate and geology as the present study, but differed in substantial ways. The agricultural systems there use much smaller applications of chemical fertilizer, about 94 kg ha^{-1} compared to about 100-250 kg ha^{-1} in the Stockton study area. Also, sediments in the WCSP have lower organic C (< 0.05%; Kraft, 1990), which leads to groundwater that is predominantly oxic in upland areas.

Pesticides

The pesticide emphases of this study are the residues of atrazine (the parent plus the chlorinated degradates deethyl-, deisopropyl-, and diamino- atrazine) and chloroacetanilides (alachlor, acetochlor, metolachlor, plus their ethane sulfonic acid (ESA) and oxanilic acid (OA) degradates). All have their primary use on corn. Atrazine is the most commonly used herbicide in Wisconsin. Its use began in about 1960, and by 1969, 1.5 million kg yr^{-1} were being applied in the state. Use peaked in about 1985 when 2.4 million kg yr^{-1} were used, and then declined. In 1996, 0.63 million kg were applied on 1.8 million Wisconsin acres. Atrazine residues have been known as ubiquitous groundwater pollutants in agricultural areas since the early 1990s (LeMasters and Baldock, 1995; Kolpin et al., 1993; Kolpin et al., 1996).

Alachlor, metolachlor, and acetochlor are also commonly used herbicides. In 1996, they were applied to 692,000; 972,000; and 351,000 acres of Wisconsin cropland, in the amounts of 0.5, 0.76, and 0.30 million kg, respectively. Alachlor and metolachlor have been in use for about 25 years while acetochlor only been used since 1994. All three metabolize into ESA and OA residues. Though the parent compounds are found relatively rarely and at low concentrations in groundwater, evidence indicates the ESA and OA metabolites are widespread groundwater pollutants (Kalkhoff et al., 1998; VandenBrook et al., 2002).

Pesticide residues in groundwater degrade drinking water quality (EC, 1998) and may harm aquatic life when pesticide residues are transferred from ground to surface water. The aquatic toxicity of many pesticide residues has been established at concentrations higher than those normally encountered in groundwater (about 1 mg L^{-1} and greater; Howe et al., 1998), but not at typical groundwater concentrations (a few $\mu g\ L^{-1}$ or less). Some effects suggested at the $\mu g\ L^{-1}$ level include impairment of amphibian young (Howe et al., 1998) and hermaphrodism in American leopard frogs (Hayes et al., 2002). This is an area of active research, and few of the possible substance-organism combinations have been investigated.

The status of pesticide residues in groundwater is more difficult to assess than that for NO_3, largely due to the availability of new products, the expense and difficulty of analyses, and the need to consider that multiple pesticide degradates may arise from each parent compound. A representative randomized survey of US groundwater (USEPA, 1990) found that 4.2% of US wells contain the residues of at least one pesticide, but these results need to be considered dated given the rise of new compounds and newly described degradates. Commonly used pesticides were detected in 28.4% of midwestern U.S. wells sampled in 1991 (Kolpin et al. 1993a; 1993b); a resampling of a 100-well subset in 1992 yielded a detection rate of 59% due to lower detection limits and expanded detection abilities (Kolpin et al., 1995). A sampling of Iowa wells found widespread detections of the ethanesulfonic acid (ESA) and oxanillic acid (OA) degradates of chloroacetanilide pesticides, with 75% of municipal wells sampled containing at least one pesticide residue (Kalkhoff et al, 1998).

Wisconsin has had several notable pesticide surveys (LeMasters and Baldock, 1995; Rheineck and Postle, 2000, VandenBrook et al., 2002). The most recent (VandenBrook et al. 2002) examined in particular the residues of atrazine, alachlor, metolachlor, acetochlor, cyanazine, metribuzin, and simazine and concluded that 38% of all Wisconsin wells contain the residues of at least one pesticide, most commonly those of atrazine, alachlor, and metolachlor. The two most commonly detected compounds were the metabolites alachlor ESA and metolachlor ESA, which occur in an estimated of 27.8 and 25.2% of Wisconsin wells. The proportion of Wisconsin wells containing atrazine residues (atrazine and three chlorinated metabolites) was 11.6%, and the estimated proportion of wells that exceeded the 3 ug/l enforcement standard for atrazine residues was 1.1%.

STUDY AREA

Wisconsin Central Sand Plain

The WCSP (Figure 1) is a 6400-km^2 area characterized by level topography and a mantle of coarse-grained Pleistocene sediment frequently more than 30 m thick overlying low permeability bedrock. Upland soils that developed in the Pleistocene sediment are sandy and extremely well-drained. Topsoil averages 93% sand and 1% organic matter, while subsoils average 98% sand and 0.1% organic matter (Otter and Fiala, 1978). The aquifer in the Pleistocene sediment supplies water for irrigation and industry, and both rural and municipal drinking water. Aquifer materials typically contain 92 to 95% quartz and less than 0.05% organic matter (Kraft, 1990). Groundwater is well oxygenated except for the deepest parts of the aquifer at a few locations and adjacent to some wetlands (Kraft et al., 1999). The climate is humid, temperate, and continental (Bartelme, 1977; Otter and Fiala, 1978). Winters are cold and snowy; summers are generally warm. The average frost-free growing season is 133 d (Bartelme, 1977). Annual precipitation averages about 790 mm. Approximately 60% of the annual precipitation falls in May through September. Of 790 mm precipitation, 510 to 560 mm goes to evapotranspiration, 230 to 255 mm recharges groundwater, and 250 mm runs off (Weeks et al., 1965; Holt, 1965).

Much of the upland WCSP is agricultural, which has profoundly impacted groundwater quality. In the Wisconsin Central Agriculture Statistics District, which includes much of the WCSP, drinking water wells had a 22% NO_3 MCL exceedence rate (the exceedence rate is > 70% at smaller scales), and a detection rate of atrazine, alachlor, and metolachlor residues of 18-23%, 36-51%, and 14%, respectively (LeMasters and Baldock, 1995; Vanden Brook et al., 2002). Other pesticides detected in WCSP groundwater include aldicarb, carbofuran, metribuzin, and ethylene dibromide (WDNR, 1997).

Irrigated vegetable production is a dominant agricultural form; others include irrigated and nonirrigated field corn and soybean, hay, and dairy. Irrigated acreage has been increasing since 1960, replacing dryland farming and forested lands. The irrigated vegetable system has received considerable attention because of its dominance and impacts on groundwater. The system employs a rotation generally consisting of 1 yr of potato and 2 to 3 yr of other crops, such as sweet corn, snap bean (*Phaseolus vulgaris* L.), field corn (*Zea mays* L.), soybean (*Glycine max* L.), or pea (*Pisum sativum* L.), in that order of frequency (D. Sexson, 1999, pers. commun.). Typical fertilizer-N applications to these crops are (respectively) 258, 200, 110, 180, 67, and 67 kg ha^{-1}. Annual NO_3-N loading to groundwater from this vegetable system is estimated to average about 147 kg ha^{-1} yr^{-1}, amounting to over half of applied N fertilizer (Kraft and Stites, 2003). Groundwater impacted by the irrigated vegetable rotation contains NO_3-N concentrations of about 15-40 mg L^{-1}. Some 40 different pesticides are used in this system with total application rates reaching 30 kg ha^{-1} yr^{-1} for some crops (USDA 1996). Pesticide impacts from this system have not been extensively evaluated, partly due to the lack of adequate capacities to analyze for the degradates of some pesticides. Under fields, Stites and Kraft (1999) commonly found atrazine, metribuzin, metolachlor, and carbofuran. Detections of each were usually < 2 μg L^{-1}, but ranged up to 6.4 μg L^{-1} for summed atrazine residues, 24.6 for metribuzin, 157 for metolachlor, and 20.6 for carbofuran. Downgradient of fields, Kraft et al. (1999) found the same pesticides but at smaller concentrations. Summed pesticide concentrations were generally < 1 μg L^{-1}, and ranged up to 8.0 μg L^{-1}. Notably, the analytical methodology of Stites and Kraft (2000) and Kraft et al. (1999) was only able to detect parent pesticide compounds and the three major degradates of atrazine. Hence the common alachlor and metolachlor ESA and OA degradates were not accounted for.

Less is known about the groundwater impacts of other irrigated and nonirrigated WCSP cropping systems. Generally, smaller amounts of fertilizer-N and pesticides (about 0.5 to 2 kg ha^{-1} yr^{-1}; USDA 1996) are applied to the nonirrigated crops (USDA, 1996), hence, smaller groundwater pollutant loads should usually result. Budget approaches suggest that NO_3-N loading amounts might range 30-100 kg ha^{-1} from row crops, with negligible amounts from permanent pasture and standing hay (Mechenich and Kraft, 1996). However, large groundwater NO_3 concentrations sometimes result, especially when manure applications and conversion out of hay to row crops are involved (Turyk and Shaw, 1992).

Stockton Study Area

The Stockton Study Area (Figure 1) is located in the Plover - Little Plover Rivers watershed (Wisconsin Watershed UW12-171) and is representative of much of the upland agricultural part of the WCSP. The Stockton Study Area lies generally along a groundwater flow line that originates on the groundwater divide separating the groundwater basins of the Tomorrow-Waupaca and Plover-Little Plover Rivers Watersheds. The area is bounded by groundwater flow lines that diverge with distance from the divide. Six groundwater monitoring locations are present, representative of up-, mid- and downgradient parts of the flow system. Geology consists of about 22 m of coarse grained unconsolidated Pleistocene deposits covering crystalline rock. The water table is at about 3-6 m. Groundwater velocity is estimated at roughly 0.5-1.0 m d^{-1}, based on typical values for hydraulic conductivity, aquifer porosity, and gradients.

The western part of the study area, containing most of the irrigated agriculture area, is a level glacial outwash plain. Farther east the topography becomes more hilly, as the Arnott and Hancock terminal moraines are encountered. Land uses at the downgradient-most extreme (near site A) are urban residential with municipal sewer and water, grading to low density rural residential with self-supplied water and onsite wastewater disposal (near site B). Farther upgradient, much of the land is in irrigated agriculture, with some nonirrigated agriculture, rural residential, and other land uses mixed in. On the moraines, land covers are forest with some nonirrigated agriculture and urban residential. Like much of the WCSP, land uses in the Stockton Study Area have evolved over the past 40 years, from dominantly dryland row crop, forage, and forest cover, to dominantly irrigated farmland with an emphasis on vegetable production.

Figure 3 illustrates modeled flow paths to monitoring well locations as well as the land uses that might affect them. The model was relatively robust for depicting plan-view flowpaths, but times-of-travel and vertical flow were highly sensitive to model parameters (hydraulic conductivity, aquifer porosity, and aquifer bottom). Chemistry and age-date data indicate that the model underestimates times of travel by a factor of 1.5 to 2. A better understanding of the physical setting as well as a better distribution of reliable calibration targets might constrain the model and provide a better match to age-date data.

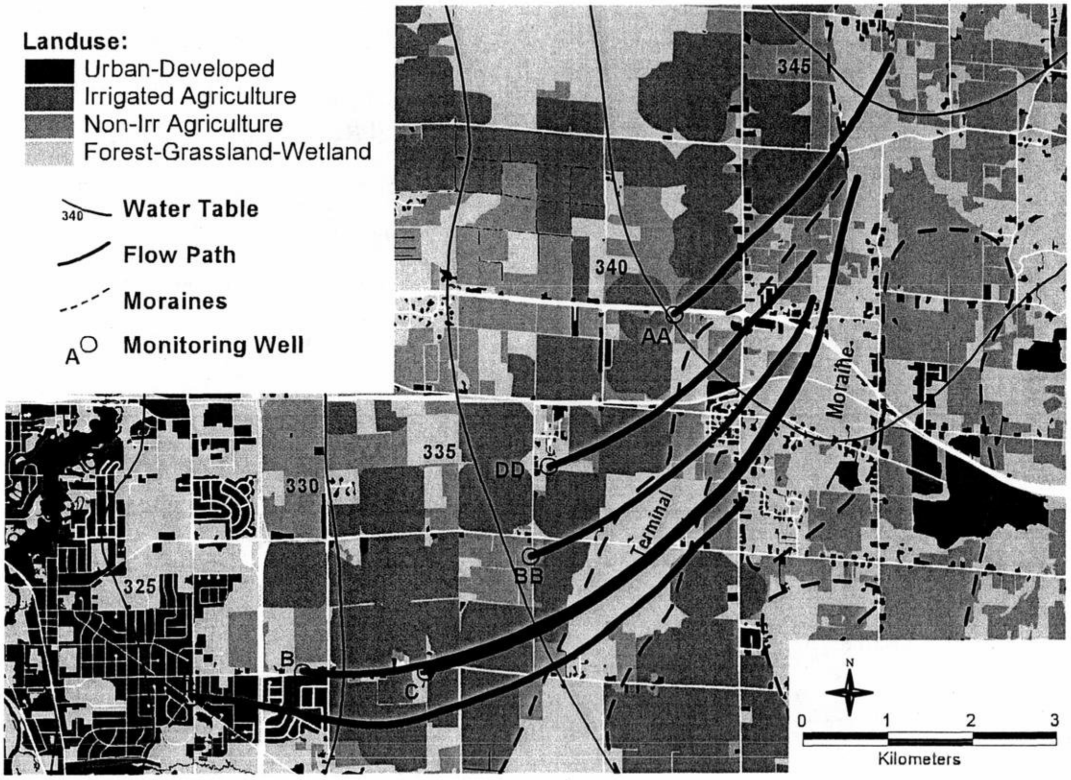

Figure 3. Groundwater flow paths to monitoring well locations.

METHODS

The premise of this study is that the pollutant loading and fate history are retained in the spatial structure of an aquifer. Loading and fate information can be extracted by acquiring samples from a groundwater flow system and subjecting them to groundwater dating and other appropriate analyses (e.g., Bholke and Denver, 1995). This information in turn will indicate the degree that an aquifer is in pollutant equilibrium with modern land use practices. For instance, an aquifer whose saturated thickness was completely penetrated by modern water and pollutants (or their byproducts) would be in equilibrium with modern practices, while a partially penetrated aquifer would not. In partially penetrated aquifers, average water quality would be expected continue to deteriorate over time, and pollutant exports would be expected to increase, until penetration is complete.

Conceptual Model of Hydrologic Systems and Pollutant Loading

Our conceptual model is that the study area groundwater system behaves in accordance with the groundwater hydraulics described by King (1899) and Hubbert (1940) (Figure 4). That is, the groundwater flow system is unconfined, receives areally-distributed recharge, and naturally discharges at line sinks (streams) or point sinks (wetlands, springs). In such systems, younger water generally overlies older water, with oldest water being deep and near discharge zones. Further, the conceptual model holds that NO_3 and pesticides originate as a diffuse source across the landscape, and that NO_3 loading history proceeded in three periods. In the pre-settlement period, NO_3 loading was virtually nonexistent; the ecological system efficiently scavenged available N and incorporated it into soil-plant systems, or lost it

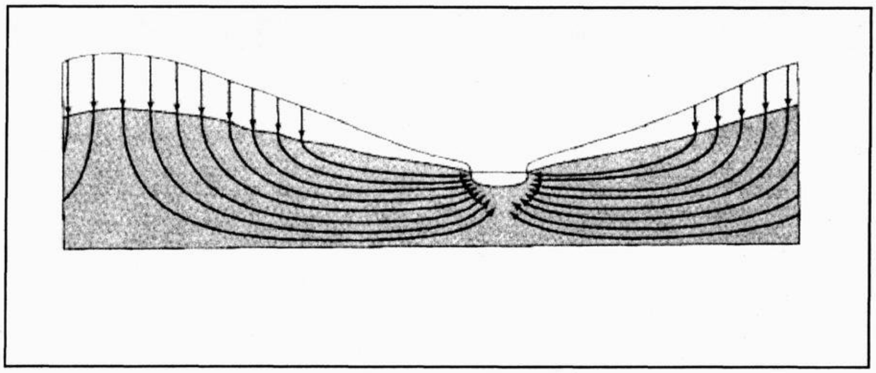

Figure 4. Illustration of groundwater flow patterns following King (1899). From Domenico and Schwartz, 1998.

to the atmosphere. In the post-settlement period, natural ecosystems were converted to agro-ecosystems. Cultivation initially resulted in a large release of N from soil organic matter oxidation, some of which was taken up by plants, but some that leached to groundwater. This release was at first rapid but then slowed, as the more labile organic matter was depleted, but still persists in modern times (Oberle and Keeney, 1990; Meisinger and Randall, 1991). During this period, a proliferation of N-fixing crops and increased livestock densities also occurred. The third and present loading period began about 40 years ago with the introduction and large increase of chemical fertilizer N and pesticide applications to the landscape. Though fertilizer-N and pesticide use leveled in the mid-1980s (Figure 2), we postulate that the amount of NO_3 and pesticides continues to accumulate in many agricultural area aquifers unless denitrification and degradation mechanisms exist, because aquifer residence times are much longer than the fertilizer-use period.

Monitoring Network

The groundwater monitoring network consisted of 22 wells nested at six sites (Figure 3; Appendix 1). Sites are roughly distributed along a flow line such that up-, mid-, and down-gradient parts of the groundwater system are represented. Well screens were distributed at individual monitoring sites so as to monitor the entire saturated thickness. Aquifer bottom was encountered at three of six sites. Wells were constructed of 26 to 35 mm inside diameter PVC casing fitted with 0.9 to 1.5 m long screens except for wells constructed of 35 mm galvanized pipe with 0.9 m screens.

Sampling Procedures

Samples for inorganic and pesticide analysis were collected using routine protocols (WDNR, 1996; http://dnr.wi.gov/org/water/dwg/gw/pubs/GW-SFM.PDF) for well purging, sample collection, and filtering and preservation as appropriate for individual analytes. Field measurements (temperature, pH, specific conductance, redox potential, dissolved oxygen, and total dissolved gas pressure) were obtained using a YSI 650 DMS sonde and a Common Sensing total dissolved gas pressure (P_T) monitor. Both instruments were equipped with flow cells to avoid exposure of sample to the atmosphere during measurement.

Dissolved gas samples were obtained by pumping induced ebullition (PIE; Browne, 2004). Groundwater was extracted from monitoring wells to the ground surface using a peristaltic pump attached to thin-wall copper tubing. The copper tubing extended from ground surface to slightly above the well bottom. Groundwater exiting the pump was delivered to a glass bottle that was allowed to continuously overflow. Water for gas extraction was collected through a tube that extended from the bottom of the overflowing bottle and into the PIE apparatus. During the process, a nominal gas yield of 0.02 mL s^{-1} was achieved at a water induction rate of 5.7 mL s^{-1}. Replicate gas samples (n=3) for CFC age-dating measurements (CFC11, CFC12, CFC113) were collected directly into an evacuated 30-ml stainless steel sampling loop (3 mm i.d.), after purging with one full volume of sample. The loop was sealed with gas-tight fittings for storage before analysis. Replicate gas samples (n=2) for other dissolved gases (Ar, N_2, O_2, CO_2, N_2O, CH_4) were collected and stored in 10-ml gas-tight syringes. All gas analyses were completed within two weeks of sample collection.

Analytical Procedures

Inorganics

Metals (Al, Ca, Mg, K, Na, Mn, Fe), Si, and S (reported as SO_4) were analyzed by inductively coupled plasma AES (APHA, 1995 methods 311B, 3111D, and 3129 B). Chloride, NO_2+NO_3-N, NO_2, NH_4, and total Kjeldahl N (TKN) were analyzed using automated colorimetry. ANC (acid neutralizing capacity) was analyzed by titration (APHA, 1995; method 2320B). These analyses were performed at the University of Wisconsin - Stevens Point Water and Environment Analysis Laboratory (WEAL), which is certified for these analyses by the State of Wisconsin.

Pesticides

Pesticide residues were also analyzed by the UW-Stevens Point WEAL facility. Atrazine, atrazine metabolites, and other parent herbicide residues were analyzed by GC/MS (modified EPA method 8270) with an extraction method developed by the Wisconsin State Laboratory of Hygiene to isolate the more water soluble atrazine metabolites. The laboratory is State of Wisconsin certified for these procedures. Chloroacetanilide herbicide metabolites were determined using solid-phase extraction and high performance liquid chromatography/diode array detection as described by Zimmerman et.al (USGS open-file report 00-182). No certifications are available for this method. Approximately 60% of the samples were confirmed by liquid chromatography/mass spectrometry at the Wisconsin Department of Agriculture, Trade and Consumer Protection's Bureau of Laboratory Services or the Syngenta Crop Protection Laboratory.

Stable Isotopes

Samples were analyzed for ^{15}N-NO_3 and ^{18}O-NO_3 as described by Silva et al. (2000) at the Illinois Geological Survey Laboratory. These data were used to help assess potential origins of NO_3 in groundwater and as supporting evidence for denitrification (Kendall and McDonnell, 1998; McMahon and Bohlke, 1996).

Dissolved Gases

Dissolved gasses were analyzed at the University of Wisconsin - Stevens Point Trace Gas Analysis Laboratory. Mole fractions (X_i) of individual gases within gas samples were determined by gas chromatography. A pulse discharge detector (PDD) in the helium ionization mode (Wentworth et al., 1994) was used to detect N_2, Ar, O_2, N_2O, CO_2, and CH_4; a ^{63}Ni electron capture detector (N_2 carrier gas) was used to detect CFCs (CFC11, CFC12, CFC113). Helium was the carrier gas for all PDD measurements; other chromatographic conditions (columns, temperatures, carrier gas flow rates) were similar to those described in (USGS DGL) for N_2, Ar, and O_2, McMahon et al. (2000) for CH_4, CO_2 and N_2O, and in Busenburg and Plummer (1992) for CFC11, CFC12, and CFC113

Gas standards and samples were injected into the GC using a gas sample loop on a ten-port valve. The loop was preceded by a $Mg(ClO_4)_2$ moisture trap. Six point calibration curves (dry gas mole fraction versus peak area) were performed by injection of gas dilutions prepared by mixing aliquots of blank gas and standard gas. In load position, the sample loop was maintained at ambient lab temperature and pressure prior to injection.

Partial pressures (P_i) of individual gases within the groundwater samples were determined by:

$$P_i = X_i P_t / F_i$$

where P_t is the total dissolved gas pressure measured in the field and F_i is an analyte-specific fractionation coefficient reported in Browne (2004). Concentrations (C_i) of individual dissolved gases were determined using Henry's Law:

$$C_i = K_{Hi} P_i$$

where K_{Hi} is the Henry's Law constant calculated for the field temperature from temperature dependent solubility data reported in Busenberg and Plummer (1992, CFCs) or Wilhelm et al. (1977, all other gases).

Denitrified N

Dissolved N_2O-N, and dissolved N_2-N in excess of atmospheric concentrations ("denitrified N_2-N"), were used to account for denitrified NO_3. Denitrified N_2-N was quantified (Heaton, 1981; Martin et al., 1995) using the following Henry's Law relationship:

$$\text{Denitrified } N_2\text{-N} = C_{N2} - (K_{H,N2,r}\, P_{atm,N2})$$

where C_{N2} is the total concentration of dissolved N_2, $P_{atm,N2}$ is the partial pressure of N_2 in the atmosphere, and $K_{H,N2,r}$ is Henry's Law constant calculated for the temperature during groundwater recharge. Argon was used as a non-biogenic, atmospheric reference gas concentration to determine the temperature of groundwater during recharge.

CFC Age Date Assignments

Due to solubility of gases within atmospheric moisture, CFCs have accumulated in the hydrosphere in conjunction with their accumulation in the atmosphere. Because their rapid atmospheric accumulation has been well documented from about 1940 to the present, and because detection at part per trillion concentrations is possible using common laboratory instrumentation (GC ECD), CFCs have become valuable tracers for groundwater recharge age-dating (Busenberg and Plummer, 1992; 2000; Puckett et al., 2002). The premise of CFC age-dating is that the mole fraction of CFC dissolved in groundwater reflects the atmospheric mixing ratio of CFCs during the year of groundwater recharge (Appendix III).

The mole fractions of CFC11, CFC12 and CFC113 measured within the gas harvested from groundwater, adjusted to the temperature of groundwater recharge using Henry's Law relationships, were compared to historic records of CFC atmospheric mixing ratios (USGS, 2003) to determine the year of groundwater recharge (the "apparent CFC recharge age-date"). The minimum age-date estimate of each CFC was bounded by its practical laboratory detection limit. The practical detection limits were: CFC 11 - 4 pptv (parts per trillion by volume); CFC 12 - 9 pptv; CFC 113 - 1.3 pptv. These correspond to the following minimum age-dates: CFC 11 - 1955; CFC 12 - 1951; CFC 113 – 1959. For CFC 11 and CFC 113, the atmospheric-mixing ratio vs. time curve flattens substantially and then falls between about 1990 and present. Hence, a given atmospheric-mixing ratio does not correspond to a unique age-date. Therefore, we report an age-date of 1995 for CFC 11 and 113 samples with atmospheric-mixing ratios corresponding to 1990 to 2001, recognizing an uncertainty of about ± 5 years.

CFC 11, 12, and 113 yield up to three independent observations of apparent age for each well. However, three valid and agreeing observations are not usually obtained unless conditions are ideal. The most frequent cause of invalid and disagreeing observations include:

1. An anthropogenic source of CFCs (e.g., pesticide carrier matrix) produces a concentration in groundwater for one or more CFCs in excess of equilibrium with the atmosphere at the time of recharge. These samples are deemed "environmentally contaminated."

2. Biological degradation of one or more CFCs (in order of susceptibility CFC11 >> CFC113 > CFC12) under reducing conditions causes a lower concentration of CFC11 than CFC113 and CFC12, a lower concentration of CFC113 than CFC12, or both.

3. Mixing of groundwater (shallow and deep) containing different relative mixing ratios of the four indicator gases produces, for example, a younger apparent age-date by CFC113 than by CFC12. This tends to be a fairly subtle and complex condition, requiring somewhat subjective speculation. As a practical matter, we did not consider it in our data analysis.

The assignment of "best" apparent age-date for each well was based on the following guidelines modified from the Unites States Geological Survey (http://water.usgs.gov/lab/dissolved-gas):

1. Any observation with a ground water concentration in excess of that in equilibrium with the modern atmosphere was considered contaminated and therefore invalid. These occurrences are left blank in Table 2.

2. When substantial disagreement existed between two or more CFCs, the most stable (least susceptible to biological degradation) was selected as the valid observation. In this hierarchy CFC12 trumps both CFC113 and CFC11 and CFC113 trumps CFC11. Observations invalidated on this basis are indicated in gray in Table 2.

3. Where near agreement among multiple age-dating gases was evident, the observations were averaged.

Besides CFC techniques, prior work allows the assignment of age-dates to wells intersecting the water table. Recharge precipitation and conservative solutes migrate from the soil surface to the water table within months in the WCSP (Kung, 1990; Stites and Kraft, 2000). Hence, we assigned an age-date of 2001 to monitoring points intersecting the water table.

RESULTS AND DISCUSSION

Inorganic Analyses

Study area groundwater chemistry is similar to that of the WCSP as a whole (Rothschild 1982; Hindall 1978). Groundwater is the Ca – Mg – HCO_3 type, with anthropogenic NO_3-N, SO_4, and Cl, supplanting HCO_3 as the natural dominant anion. These constituents each had median of concentrations 5.4 to 61.2 mg L^{-1} (Table 1, Appendix 2). The median pH, ANC, and dissolved organic C (DOC) were 7.56, 3.0 meq L^{-1}, and 1.2 mg L^{-1}.

Table 1. Summary of water analyses. All units in mg L^{-1} except pH (standard units) and ANC (meq L^{-1}).

Analyte	Median	Minimum	Maximum
Ca	61.2	30.4	120.5
Mg	27.9	14.5	57.9
Na	5.4	3.4	97.6
K	1.2	0.7	17.5
NO_3-N	19.8	4.4	41.0
Cl	30.5	5.5	206.0
ANC	3.0	1.2	9.0
SO_4	22.3	4.5	136.4
pH	7.6	6.8	8.0
Dissolved O_2	10.0	0.5	12.4
Fe	0.007	< 0.002	0.043
Mn	0.024	< 0.001	0.352
Dissolved organic C	1.17	0.47	4.4*

* Neglects one value presumed spurious.

Most groundwater was well oxygenated (median dissolved oxgyen (DO) = 10 mg L^{-1}), with the exception of well B3, a deep well with a DO of 0.52 mg L^{-1}. Other indications of reducing conditions (e.g., elevated Fe and Mn) were mostly absent. One water table well (BB1) contained an anomalously confused redox signal. Oxidizing conditions were indicated by a fairly large DO for groundwater (4.4 mg L^{-1}), elevated NO_3-N (22.7 mg L^{-1}) and small Fe (0.018 mg L^{-1}) concentrations. However, compared to other wells, the DO was small; Mn, CO_2, and N_2O were greatest; and denitrified N_2-N was present. DOC was also elevated. The well was immediately adjacent to a cattle-grazed pasture, and we attribute the anomaly to nearby manure deposition.

Groundwater Age-Dates

CFC-based age dates could be inferred for 19 of 22 wells (Table 2). Three age date estimates (i.e., all CFCs were uncontaminated) were obtained in five wells, two were obtained in four wells, and one was obtained in 10 wells, for an average of 1.4 estimates per well. No CFC age date estimates were available for wells A2, BB1, and AA1, but an estimate of 2001 for the latter two could be made because the well screens intersect the water table (see Methods).

CFC 113 provided the largest amount of age-date information (17 of 22 wells). CFC 12 provided uncontaminated samples for only about one-third of wells. This is consistent with previous work (Kraft and Browne, 2002) that indicates CFC 12 is a widespread contaminant over much of the Wisconsin landscape. The specific sources of contamination are unclear. Results from agricultural areas in Wisconsin (Browne, unpublished data) and elsewhere (Plummer et al. 2000) suggest that agricultural chemicals (e.g., pesticide carrier matrices) may be prevalent sources. CFC 12 and 113 age-date estimates agreed well for the six wells where both yielded age-date estimates. CFC 11 yielded the least amount of useful age-date information. Ten wells yielded concentrations indicative of uncontaminated conditions, but CFC 11 age dates were biased older in seven of eight cases where comparisons could be made with CFC 12 and 113. Hence, we disgarded CFC 11 age-dates when others were available. CFC 11 yielded the only available age date estimates for wells DD1 and A2, 1978 and 1986 respectively. The estimate for DD1 was rejected because it is older than underlying water and because it is a water table well expected to yield water < 1 year old. For A2, the CFC 11 age-date is plausible, and no directly contradicting evidence is available, and we cautiously accept it as a minimum age-date.

Groundwater in the study area was unexpectedly young. Age-dates spanned 1969 to 2001, but most recharged before 1986 and only three of 19 samples pre-dated 1980. Though groundwater age increased with depth (Figure 5) at any one location, pre-1975 groundwater was observed only in the deepest parts of the aquifer in mid flow system (Figure 6), while younger water penetrated the entire aquifer thickness in both the up- and downgradient positions.

Table 2. Results of age date analyses. Observations shaded gray were invalidated (see Methods).

Well	CFC11	CFC12	CFC113	Best CFC	Assigned
A-1	1986			1986	1986*
A-2					
A-3			1980	1980	1980
AA-1					2001**
AA-2			1990	1990	1990
AA-3			1985	1985	1985
AA-4			1984	1984	1984
B1	1976		>1990	1995	1995
B2			>1990	1995	1995
B3			1984	1984	1984
BB1					2001**
BB2	1980		1986	1986	1986
BB3	1969	1977	1978	1977	1977
BB4	1967	1969	1971	1969	1969
C1	1979	1992	>1990	1992	1992
C2	1978	1990	1987	1988	1988
C3		1985	1986	1985	1985
C4	1972	1979	1982	1980	1980
DD1	1978			1978	2001**
DD2			>1990	>1990	1995
DD3	1980		1987	1987	1987
DD4			1977	1977	1977

* Value is suspect; based on CFC11 only

** 2001 assigned because well intersects water table.

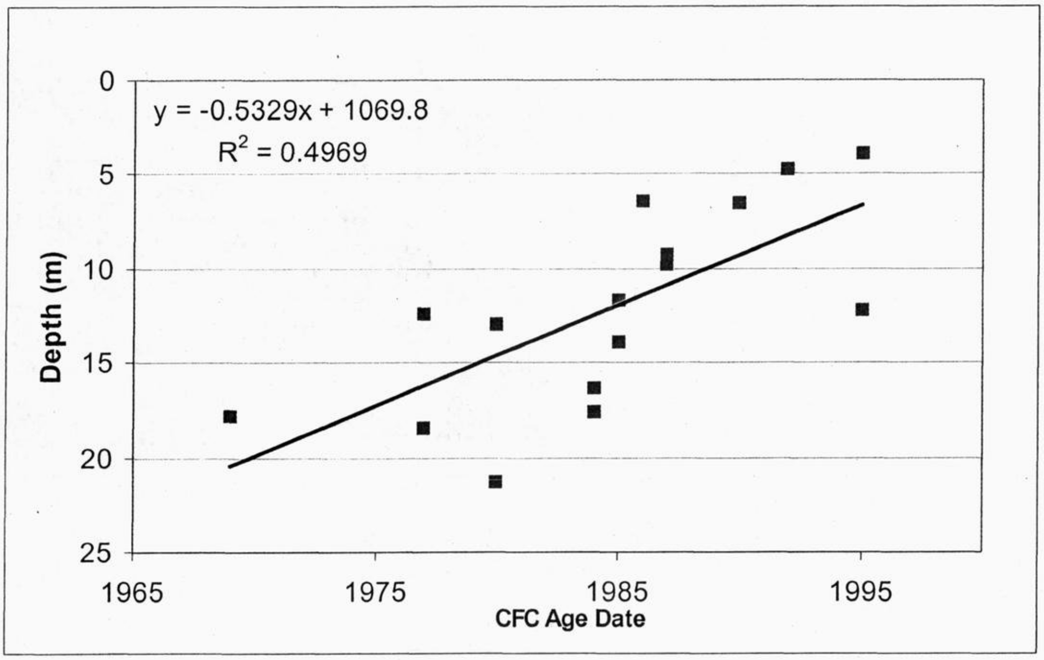

Figure 5. Relation between depth below water table and CFC derived age date.

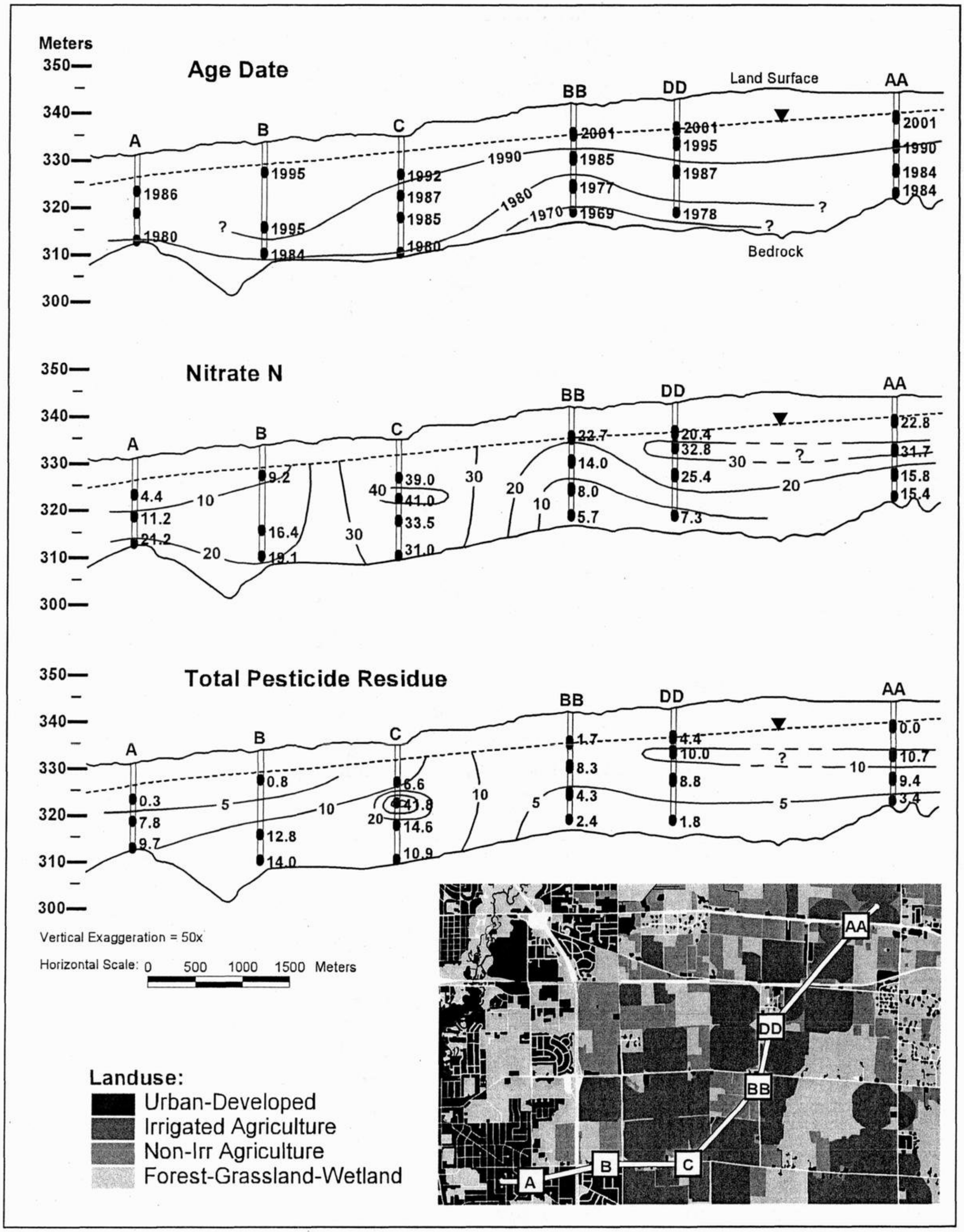

Figure 6. Cross sections through the Stockton Study Area with groundwater age-data, nitrate, and total pesticide residue concentrations.

Nitrogen

Nitrate was the dominant form of groundwater N (Table 3). Nitrate-N averaged 20 mg L^{-1}, and ranged 4.4 to 41 mg L^{-1}. Most groundwater (17 of 22 wells) exceeded the drinking water MCL and Wisconsin groundwater enforcement standard of 10 mg L^{-1} NO3-N. Concentrations < 10 mg L^{-1} were found only (1) near the water table immediately downgradient of nonagricultural land covers (urban, rural residential) and (2) in the deep mid portion of the flow system coincident with older groundwater in wells locations BB and DD (Figure 6). The latter probably originated upgradient of the present irrigated area and under what is now mapped as forested and nonirrigated cropland land-covers. The greatest concentrations were associated with irrigated fields. Total Kjeldahl, NH_4, and NO_2-N were negligible, and usually below detection limits (Appendix 2).

Denitrification

Denitrification products N_2O and denitrified N_2 were determined in 21 groundwater samples. N_2O-N was detected in all samples, but concentrations were negligible (median and maximum of 0.01 and 0.15 mg L^{-1}) compared with NO_3. Denitrified N_2-N was detected (≥ 0.20 mg L^{-1}) in five of 21 samples, at concentrations ranging 0.67 to 3.9 mg L^{-1}. In the five samples, denitrification accounted for the elimination of 1.7 to 17% of the original NO_3-N load (Table 4).

Dissolved oxygen was significantly smaller (means of 5.0 vs 10.6 mg L^{-1}, $P < 0.01$) in groundwater with detectable denitrified N_2-N compared to groundwater with none. One well (BB4) with denitrification had a large DO (10.2 mg L^{-1}). Perhaps the old and deep water tapped by this well underwent mixing with more highly oxygenated water after denitrification occurred, either in the vadose zone or in the aquifer. Differences in other redox indicators (NO_3, Fe, Mn) were not observed, nor were differences in DOC, an electron donor source for NO_3 reduction. In three of four cases where both isotopic and excess-N_2 information is available, manure was the most likely NO_3 source (see Nitrate Isotopic Composition). This included well BB1, suspected of being directly impacted by manure (see Inorganic Analyses). In the single case where a manure source was not strongly indicated (well C1), denitrification was relatively unimportant, amounting to only 0.67 mg L^{-1} or 1.7% of the NO_3 load.

Nitrate isotopic composition

^{15}N and ^{18}O isotopes of NO_3 were analyzed for 20 of 22 wells. The isotopes are reported as δ ("delta") values which are expressed as parts per thousand (‰) relative to a standard of known

Table 3. Summary of N analyses.

N Analysis	% Detects	Detection Limit	Median	Maximum
		--------- mg L^{-1} N	------------	
NO_3+NO2	100	0.1	19.8	41
Total Kjeldahl	27	0.08	< 0.08	0.67
NH4	18	0.01	< 0.01	0.21
NO2	14	0.005	< .005	0.03
Denitrified N_2	25	0.20	<0.20	3.9
N_2O	100	0.001	0.01	0.15

Table 4. Excess N_2 gas for samples in which denitrification was indicated.

Well	NO_3-N	Denitrified N_2	Denitrified $N_2 + NO_3$	Fraction Denitrified N_2-N
	------------- mg L^{-1} -N	--------------		
B2	16.4	1.4	17.8	0.08
B3	19.1	3.9	23.0	0.17
C1	39	0.67	39.6	0.017
BB1	22.7	1.6	24.3	0.07
BB4	5.7	1.1	6.8	0.16

composition:

$$\delta = (R_x/R_s - 1) \cdot 1000$$

where R is the ratio of lighter to heavier isotope, and R_x and R_s are the ratios in the sample and standard, respectively. ^{15}N is expressed relative to ^{14}N in the atmosphere ($^{15}N/^{14}N = 10^{-2.44}$) and ^{18}O relative to ^{16}O in seawater ($10^{-2.698}$ VSMOW; VSMOW = Vienna Standard Mean Ocean Water). Ratios of NO_3 $\delta^{15}N$ and $\delta^{18}O$ in water samples provide clues as to the origins of groundwater NO_3 (as NH_4 fertilizer, NO_3 fertilizer, soil N, manure, and septage) and to the degree that denitrification or mixing may have occurred (Kendall and McDonnell, 1998; Figure 7). Note substantial overlap in parts of Figure 7 of most interest in this study: fertilizer NH_4-N, soil-N, and septage/manure-N.

$\delta^{18}O$ vs $\delta^{15}N$ patterns and NO_3 sources. Isotope values were in a narrow range (Figure 8); 0.90 to 9.80 for $\delta^{15}N$, and 3.49 to 10.50 for $\delta^{18}O$, and lay along a trendline defined as $\delta^{18}O = 0.54 \cdot (\delta^{15}N) + 4.5$

($r^2 = 0.41$). Older groundwater tended to be both more enriched and variable in NO_3 $\delta^{15}N$ and $\delta^{18}O$ (Figure 10).

$\delta^{18}O$ vs $\delta^{15}N$ values fell into four potential source clusters (Figure 9): A) fertilizer NH_4 and manure; B) fertilizer NH_4, soil N, and manure; C) soil N and manure; and D) manure only. From a practical standpoint we eliminated septage and precipitation N as a potential N sources because they are small in the study area relative to other sources (e.g., Mechenich and Kraft, 1999; Stites and Kraft, 2001). Though soil N also contributes relatively little to the available soil N pool (about 45 kg ha^{-1} yr^{-1}, Andraski and Bundy, 1999) in this setting relative to fertilizer and manure when they are applied, we included it in Figure 9 to distinguish between clusters C and D. A distinct NO_3 fertilizer cluster is not apparent, possibly because ammoniacal fertilizer predominates over other N forms (Kraft et al., 1996).

Potentially fertilizer-affected clusters A and B comprised the majority (15 of 20) of groundwater samples. These were mostly shallow and young (mean age date 1989). In only one case (C1) was evidence of denitrification observed, and then only mildly (1.7% of the NO_3 load). Fertilizer-excluding clusters C and D comprised five groundwater samples that shared subsets of several traits: three (BB1, BB4, B3) display larger degrees of denitrification (7-17%) and all but one (BB1) contained older groundwater (mean age-date of 1978) from the deepest well at their respective locations.

Is the NO_3 in clusters A and B more likely fertilizer or manure derived? Several lines of evidence indicate fertilizer sources would be more prevalent:

- Most groundwater in clusters A and B is young and hence more reflective of current nutrient sources.
- Fertilizer inputs presently dominate manure inputs in the study area.
- Whereas three of five groundwater samples in fertilizer-excluding clusters C and D exhibit signs of denitrification, only one in 14 from clusters A and B do so, and then only mildly (1.7% of the NO_3 load was denitrified).

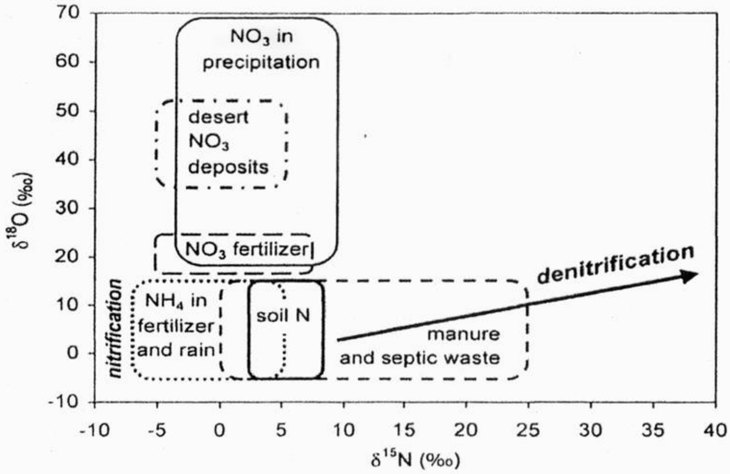

Figure 7. Schematic of typical ranges of 18O and 15N values of NO3 from various sources (from Kendall and McDonnell, 1998).

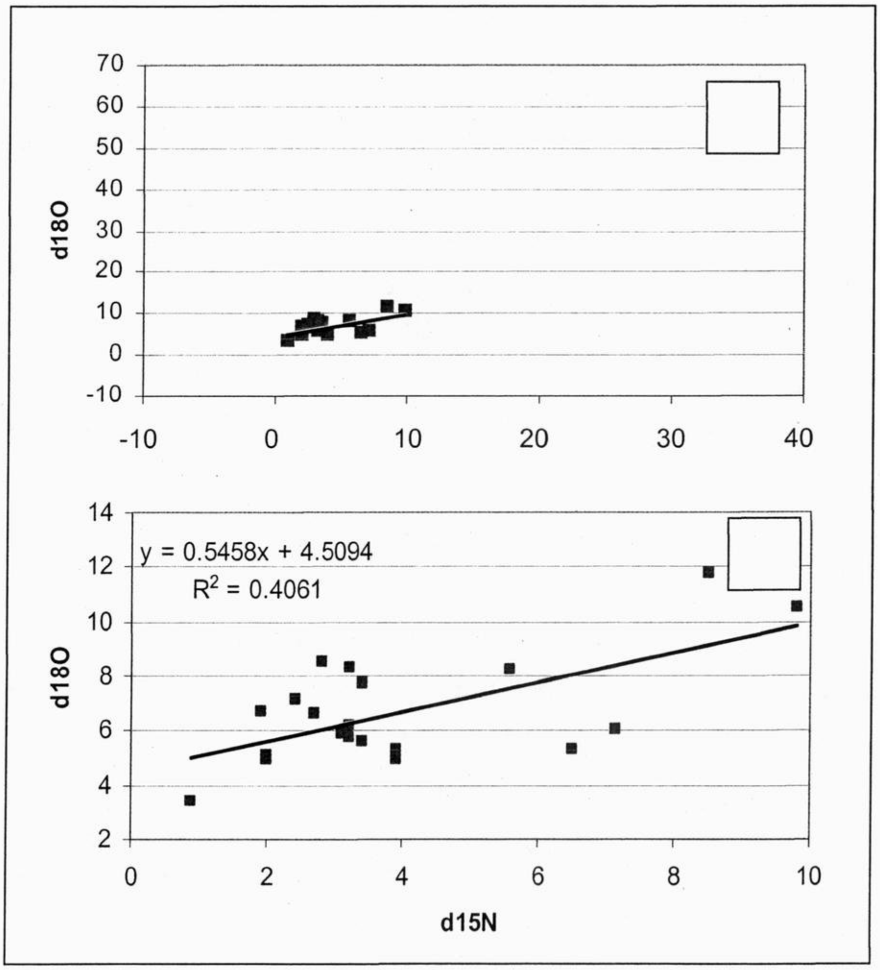

Figure 8. δ^{18}O and delta δ^{15}N of NO3 from study area plotted (a) at same scale as Kendall and McDonnell (1998, Fig. 7) and (b) at an expanded scale.

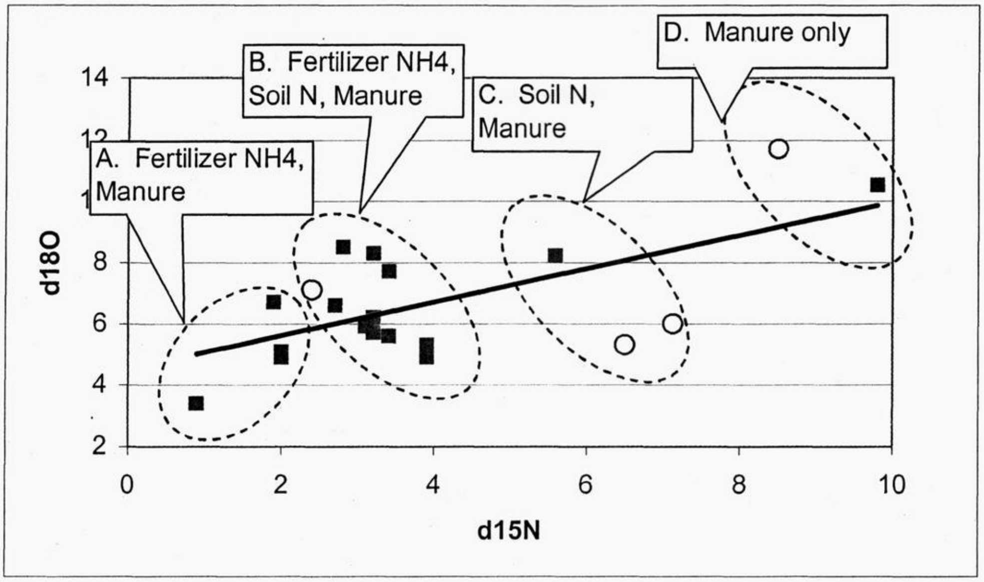

Figure 9. $\delta^{18}O$ and delta $\delta^{15}N$ of NO_3 from study area wells grouped according to potential sources, according to Figure 7. Note that manure is a potential source for all wells. Samples where denitrification was measured are in open circles.

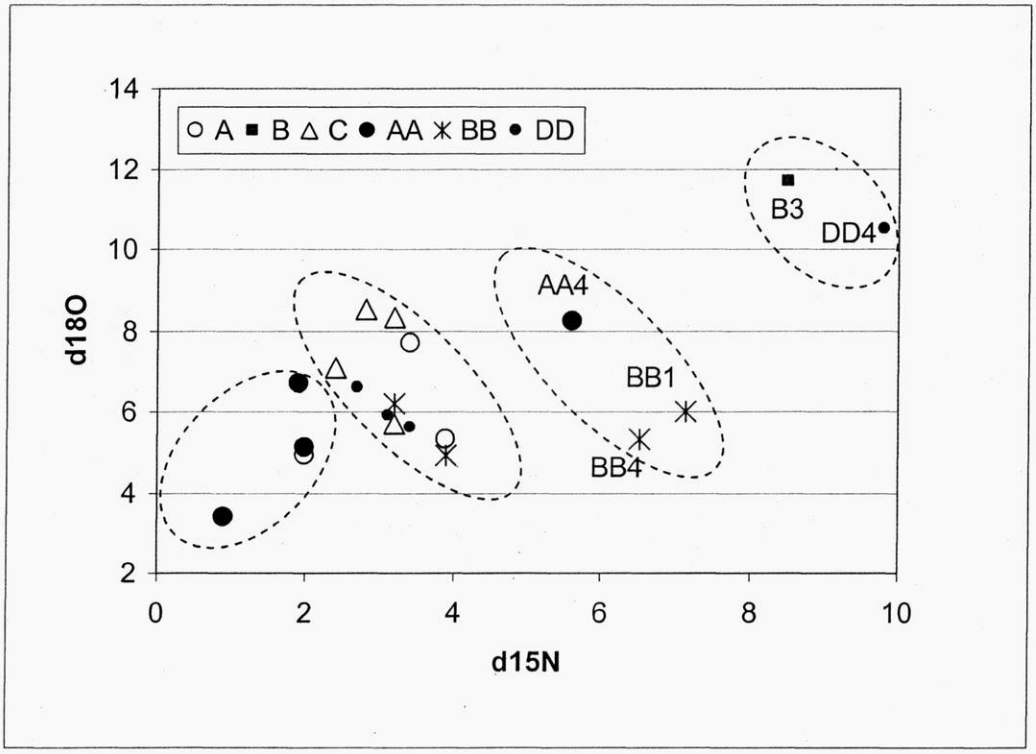

Figure 10. $\delta^{18}O$ and delta $\delta^{15}N$ of NO_3 from study area wells, with well clusters shown and potentially manure-affected wells labelled.

Accounting for denitrification in the isotopic signature. Though denitrification processes alter the original isotopic signature, accounting for denitrification (see below) does not substantially alter the source cluster observations.

Denitrification increases the $\delta^{15}N$ and $\delta^{18}O$ content of residual NO_3. $\delta^{15}N$ increases according to the Rayleigh equation:

$$\delta^{15}{}_{R}N = \delta^{15}{}_{o}N + \varepsilon \ln C/C_o$$

where $\delta^{15}{}_{R}N$ is the residual $\delta^{15}N$ at some time, $\delta^{15}{}_{o}N$ is the starting $\delta^{15}N$, ε is the enrichment factor (negative to make the algebra work), and C and C_o are the concentrations at some time and at time zero, respectively. $\delta^{18}O$ enrichment with denitrification proceeds at a rate equal to about half that for $\delta^{15}N$, e.g., if denitrification increased residual NO_3 $\delta^{15}N$ from 5 to 10‰, $\delta^{18}O$ would be expected to increase from 6 to 8.5‰. This effect is shown by the "denitrification" line in Figure 7. It might be tempting to hypothesize that the trendline in Figure 8 is due to denitrification from an isotopically common NO_3 pool, as the slope (0.54) is quite close to the expected denitrification slope (~0.5). However, this hypothesis fails when confronted with the fact that denitrification was observed in only five wells. Could accounting for denitrification in the five move them to a different cluster? An accounting can be done utilizing the Rayleigh equation, solving for $\delta^{15}{}_{o}N$ by using:

C = current NO_3-N concentration;

C_o = original NO_3 concentration = C + denitrified N

$\delta^{15}{}_{R}N$ = sample $\delta^{15}N$

According to Kendall and McDonnell, a large range denitrification ε (-40 to -5 ‰) has been calculated, determined in laboratory experiments, measured in soil, and observed in marine studies. However, a narrow range, -5 to -8 ‰, is common for groundwater, while more extreme values are associated with (1) aquifers prone to diffusion processes into dead-end pores (e.g., chalk) and (2) extremely slow denitrification processes, perhaps on the order of centuries or more. Invoking ε values in the common range produces a change of source cluster for only one well (B3), moving it from D to C. An extreme ε of -20 would moves B3 from cluster D to C, and a second well (BB4) from cluster C to B. Hence, accounting for denitrification does not alter observations of source and age substantially.

Pesticide Residues

Twenty-one of 22 wells contained the residues of at least one pesticide detectable by the methods used in this study. Residues of five pesticides were detected: atrazine, alachlor, metolachlor, metribuzin, and pendamethalin (Table 5). No alachlor parent compound was found. Neither were any acetochlor residues, in line with regulatory restrictions that prohibit acetochlor use on sandy soils. Summed pesticide residues in individual groundwater samples were typically 5 to 15 μg L^{-1}, but reached 41.7 μg L^{-1} in one well due to large concentrations of metolachlor degradates.

Alachlor and metolachlor ESA and OA (13 to 18 wells; Table 5) were the most commonly detected residues. Atrazine residues were also common (11 wells), though atrazine parent compound was detected rarely (two wells) and at small concentrations ($\leq$ 0.23 μg L^{-1}). Deethylatrazine was the predominant atrazine degradate. One well (AA3) exceeded the Wisconsin groundwater enforcement standard (ES, 3.0 μg L^{-1}) for summed atrazine residues with a concentration of 5.2 μg L^{-1}. Ten wells exceeded the Wisconsin preventive action limit (PAL) standard for summed atrazine residues (0.3 μg L^{-1}), two exceeded the metolachlor PAL (1.5 μg L^{-1}), and one exceeded that for alachlor (0.2 μg L^{-1}).

Table 5. Detected pesticide residues.

Pesticide residue	**Detects (No.)**	**Detection Limit**	**Median Detection**	**Maximum Detection**
		----------------	μg L^{-1}	---------------
Atrazine	2	0.1	0.2	0.2
Deethylatrazine	8	0.2	1.2	3.8
Deisopropylatrazine	2	0.2	0.7	0.8
Diaminoatrazine	1	0.3	1.4	1.4
Total	11	0.1-0.3	1.1	5.2
Alachlor	0	0.1		
Alachlor ESA	18	0.2	1.6	6.0
Alachlor OA	13	0.1	1.3	3.4
Total	19	0.1	1.6	8.6
Metribuzin	7	0.1	0.4	0.9
Metolachor	4	0.1	0.2	0.2
Metolachlor ESA	13	0.12	2.0	21.7
Metolachlor OA	15	0.2	1.4	17.7
Total	17	0.2	1.6	39.6
Pendimethalin	2	0.1	0.5	0.8
Summed residues	21	0.1-0.3	8.0	41.7

None of the detected pesticides have reported standards or guidelines for the protection of aquatic ecosystems (USEPA, 2002). Aquatic standards become a concern in areas where groundwater discharges to surface water.

Pesticide residues penetrated the entire saturated thickness at five of six monitoring sites (Figure 6). Similar to NO_3, small ($< 2\ \mu g\ L^{-1}$) concentrations of pesticides were observed only near the water table immediately downgradient of nonagricultural land covers (urban, rural residential), and in the deep mid portion of the flow system coincident with older groundwater in locations BB and DD. Pesticide residue and NO_3 concentrations increased together (Figure 11), with the exception of two high NO_3-N (> 20 mg L^{-1}) wells (AA1 and BB1) with small residue concentrations. This is explained for BB1 because its nitrate is linked to a manure source (see "Inorganic Analytes" and "Nitrate isotopic composition") from cattle pasturing, a land use which would be expected to exhibit little pesticide residue. An explanation for AA1 is not readily apparent.

Residue concentrations related poorly to depth below the water table, but well to age-date. Except for the youngest (2001) groundwater linked to nonagricultural land covers, post-1980 groundwater almost always contained 5-15 $\mu g\ L^{-1}$ of pesticide residues.

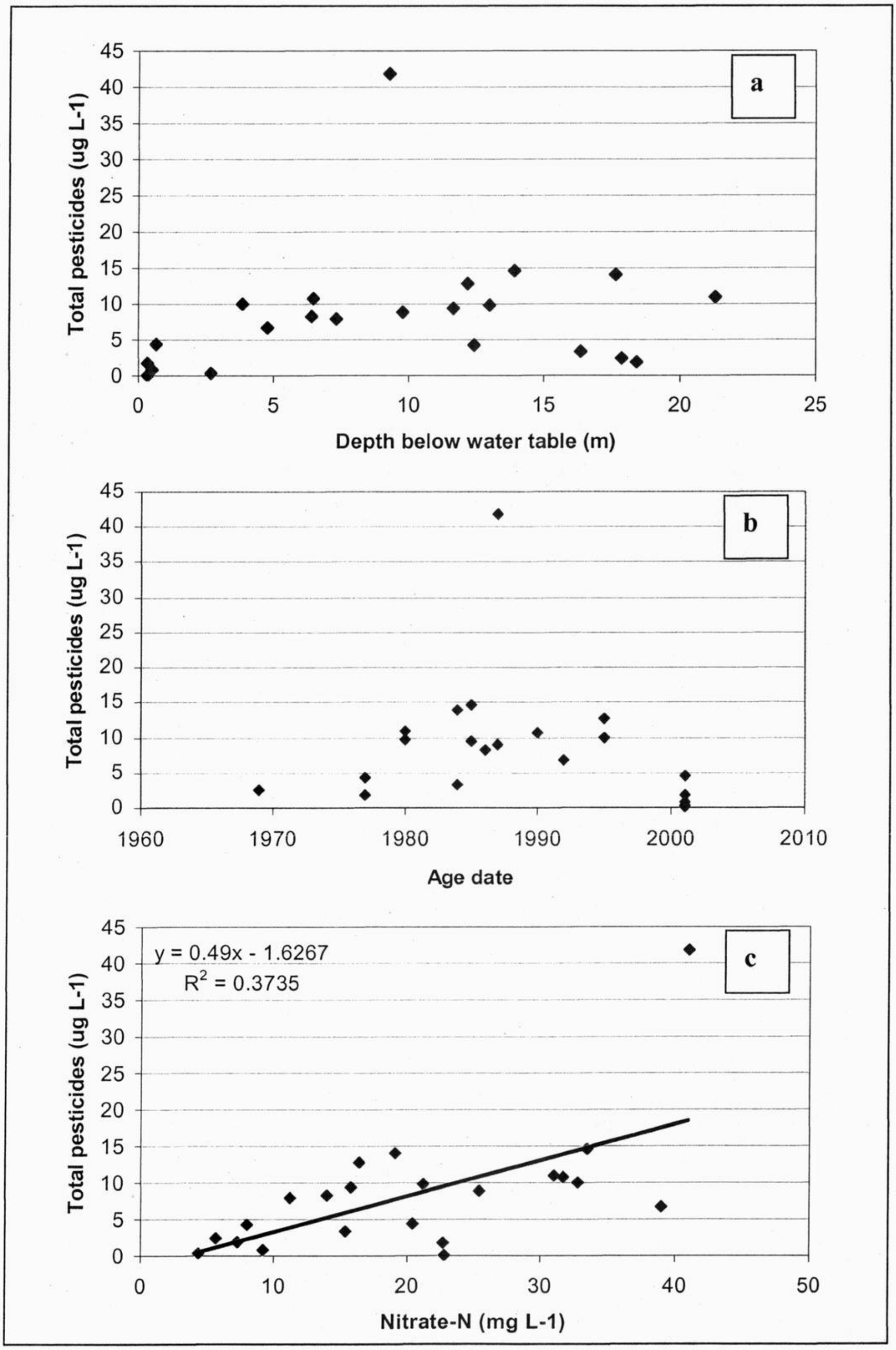

Figure 11. Total pesticide residues with (a) depth below water table, (b) age-date, (c) NO3 concentration.

DISCUSSION

Large concentrations of NO_3 and pesticide residues consistent with modern high-input agricultural practices have penetrated the entire saturated thickness of the Stockton Study Area aquifer. Exceptions include small areas of shallow groundwater downgradient of nonagricultural land uses and (e.g., locations A and B) and deeper groundwater in the mid flow system (i.e., locations BB and DD). Smaller NO_3 and pesticide residue concentrations downgradient of nonagricultural areas are readily explained by smaller loading rates from nonagricultural land uses. But do concentrations in the deeper, mid-system groundwater result from old land uses that have since been displaced by higher input land uses, or from forest and non-irrigated landuses that still persist? The short distances from BB and DD upgradient to forest and nonirrigated land uses (Figure 3) support the notion that the low NO_3 and pesticide residue groundwater likely originated from the low-input land uses that still persist on the modern landscape. Hence the "bubble" of low pollutant groundwater could persist indefinitely if the land use is not changed.

CONCLUSION

Stockton Study Area groundwater chemistry was similar to that of the WCSP as a whole (Rothschild 1982; Hindall 1978). Groundwater is the Ca – Mg – HCO_3 type, with anthropogenic NO_3-N, SO_4, and Cl, supplanting HCO_3 as the natural dominant anion. Groundwater was most often well oxygenated.

Nitrate and pesticide residues penetrated most of the study area aquifer. Nitrate-N usually exceeded the drinking water MCL and Wisconsin Enforcement Standard of 10 mg L^{-1}, averaging 20 mg L^{-1} and ranging 4.4 to 41 mg L^{-1}. Small concentrations (< 10 mg L^{-1}) were only found near the water table immediately downgradient of nonagricultural land covers (urban, rural residential) and in the deep mid portion of the aquifer coincident with older groundwater (pre-1980). A fourth of wells demonstrated a manure NO_3 source, with the remainder probably originating from fertilizer. Organic, NH_4, and NO2-N concentrations were negligible.

Denitrification was not an appreciable sink for NO_3. Denitrification product N_2O-N was ubiquitous, but at concentrations miniscule with respect to NO_3-N. Denitrified N_2-N was observed in one-fourth of groundwater samples, where it accounted for only 1.7 to 17% of the original NO_3-N load. Groundwater where denitrification to N_2-N was observed was usually well-oxygenated (mean of 5.0) but was less so than compared with groundwater where no denitrification was observed. Denitrification to N_2-N was usually tied to a manure NO_3 source.

Pesticide detection patterns generally followed NO_3: high frequencies and large concentrations were prevalent except downgradient of nonagricultural land uses and in deep, old groundwater. Residues of five pesticides were detected: atrazine, alachlor, metolachlor, metribuzin, and pendamethalin. No acetochlor residues were detected, in line with a regulatory prohibition of acetochlor use on sandy soils, nor was any alachlor parent compound detected (found in one well as noted above). Summed pesticide residues in individual wells were typically 5 to 15 μg L^{-1}, but reached 41.7 μg L^{-1} in one well due to large concentrations of metolachlor degradates. Like Wisconsin and the WCSP as a whole, alachlor and metolachlor residues, mainly the OA and ESA degradates, were the most common. The maximum / median detection of summed alachlor and metolachlor residues were 8.6 / 1.6 and 39.6 / 3.0 μg L^{-1}, respectively. Atrazine parent compound was rare, but its degradates were also common. Summed atrazine residue maximum / median concentrations were 5.2 / 1.1 μg L^{-1}. One well exceeded the

Wisconsin groundwater enforcement standard of 3.0 $\mu g\ L^{-1}$ of summed atrazine residues. Metribuzin and pendamethalin were infrequently detected and at concentrations $< 1\ \mu g\ L^{-1}$.

Most groundwater in the Stockton Study Area was of recent origin - 1985 to present - and carried pollutant concentrations consistent with and current land uses. Very little groundwater was older (1969-1980). Older groundwater had lower pollutant concentrations, possibly likely because it originated from relatively low-input land uses that are still present on the modern landscape. Hence a "bubble" of low pollutant groundwater could persist indefinitely if the land uses in this area do not change. However, from an aquifer viewpoint, too little older groundwater exists in the aquifer to affect the overall quality.

The Stockton Study Area appears to be largely in equilibrium with current land uses; i.e., modern groundwater with modern pollutant loads have mostly penetrated the entire saturated thickness. Hence, water quality and pollutant export are also close to equilibrium. Additional work is needed to confirm whether these findings are generally applicable to the WCSP.

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APPENDIX I

MONITORING WELL INFORMATION

Monitoring Well Construction Information

Site Symbol	Site name	Well no.	WUWN	Lithology	Typical water depth	Well top elevation (m)	Well material	Well length (m)	Screen length (m)
A	Airline	1	EG390	19.2 m medium sand; rock at 19.2 m	5.2 m	331.4	32 mm PVC	8.4	0.9
		2	EG388			331.4	32 mm PVC	13.3	0.9
		3	EG387			331.39	32 mm PVC	19.2	0.9
B	Sankey	1	EG401	24.1 m med sand; rock not encountered	5.6	333.9	32 mm PVC	6.6	0.9
		2	EG403			333.9	32 mm PVC	18.3	0.9
		3				333.75	45 mm steel	23.7	0.9
C	Pavelski	1	EG406	25 m med sand, rock not encountered	3.4	335*	32 mm PVC	8.6	0.9
		2	EG405			335*	32 mm PVC	13.1	0.9
		3	EG407			335*	32 mm PVC	17.8	0.9
		4				335*	45 mm steel	25.1	0.9
AA	Pehoski	1		21.6 msand, rock at 21.6	4.9	344.4*	25 mm PVC	6.0	1.5
		2				344.4*	25 mm PVC	12.1	1.5
		3				344.4*	25 mm PVC	17.3	1.5
		4				344.4*	25 mm PVC	21.7	0.9
BB	Lutz	1		25 m med sand, rock at 25 m	5.2	342*	25 mm PVC	6.3	1.5
		2				342*	25 mm PVC	12.4	1.5
		3				342*	25 mm PVC	18.4	1.5
		4				342*	45 mm steel	23.6	0.9
DD	Zurawski	1		25 m med sand, rock not encountered	5.7	343*	25 mm PVC	7.1	1.5
		2				343*	25 mm PVC	10.4	1.5
		3				343*	25 mm PVC	16.3	1.5
		4				343*	45 mm steel	24.6	0.9

*Accurate to within 0.9 m

APPENDIX II

ANALYTICAL RESULTS

1 Table A2-1. Values of field parameters.

Well	Temp °C	SpCond µS/cm	DO mg/L	pH	ORP
A1					
A2	------ Instrument failure, no measurement ----				
A3					
B1	9.8	593	9.2	7.7	90.4
B2	10.5	730	3.7	7.9	78.4
B3	10.4	652	0.5	7.6	57.8
C1	9.6	618	6.0	8.0	119.2
C2	9.9	615	9.7	8.0	123.5
C3	9.4	604	9.3	7.5	122.9
C4	9.3	549	9.3	7.5	124.4
BB1	8.7	990	4.4	6.9	120.3
BB2	10.3	589	8.6	7.5	87.9
BB3	9.5	145	10.7	7.6	94.1
BB4	9.9	310	10.2	7.6	87.0
DD1	8.4	627	12.4	7.5	115.0
DD2	9.3	595	11.7	7.4	106.9
DD3	9.0	595	11.5	7.4	
DD4	8.9	410	11.8	7.7	
AA1	8.5	457	12.0	7.9	109.2
AA2	9.8	1088	10.0	6.8	79.7
AA3	9.4	435	11.6	7.7	92.2
AA4	9.8	417	10.5	7.6	38.8

Table A2-2. Miscellaneous anions, TKN, reactive-P, and dissolved organic carbon (mg L^{-1}).

Well	Reactive P	DOC	ANC	TKN	NH4-N	NO2+NO3 N	NO2-N	Cl	SO_4
A1	---	0.8	94	<.08	<0.01	4.4	---	31.0	9.9
A2	---	1.2	112	<.08	<0.01	11.2	<.005	40.5	17.3
A3	---	1.2	113.2	<.08	<0.01	21.2	---	29.5	23.1
B1	0.005	2.0	204	0.21	<0.01	9.2	<.005	45.8	21.9
B2	0.009	1.1	116	0.11	<0.01	16.4	<.005	161.0	22.7
B3	0.014	2.1	149	0.22	<0.01	19.1	---	136.0	38.1
C1	0.025	1.2	105	0.14	<0.01	39.0	<.005	32.4	45.4
C2	0.039	1.1	61	<.08	<0.01	41.0	0.030	36.0	54.6
C3	0.035	0.8	150	<.08	<0.01	33.5	<.005	26.5	32.3
C4	0.05	1.0	155	0.09	0.04	31.0	---	24.3	28.0
AA1	0.02	23.5	145	0.13	<.01	22.8	---	9.5	5.6
AA2	0.029	1.3	114	<0.08	<.01	31.7	<.005	206.0	8.1
AA3	0.051	0.5	154	0.16	<.01	15.8	<.005	16.5	11.0
AA4	0.019	4.4	138	0.67	0.21	15.4	---	22.0	10.8
BB1	0.014	3.8	451	0.58	<0.01	22.7	0.006	28.0	30.0
BB2	0.037	0.5	191	0.12	<0.01	14.0	<.005	38.0	21.1
BB3	0.035	0.5	167	0.15	<0.01	8.0	<.005	13.5	12.7
BB4	0.044	2.7	202	0.25	0.01	5.7	---	5.5	4.5
DD1	0.015	1.0	188	0.24	<.01	20.4	<.005	30.0	29.8
DD2	0.014	1.8	148	<0.08	<.01	32.8	<.005	48.5	39.9
DD3	0.029	0.9	223	<0.08	<.01	25.4	<.005	34.0	136.4
DD4	0.007	1.8	149	0.21	0.08	7.3	---	11.0	11.5

Table A2-3. Metals and cations (mg L^{-1}).

Well	Al	Ca	Mg	K	Na	Mn	Fe	Si
A1	0.006	30.4	14.5	3.0	12.3	<.001	0.005	4.05
A2	0.002	41.8	19.4	1.2	18.9	<.001	0.002	4.78
A3	0.003	54.4	28.5	1.5	3.6	<.001	0.003	6.03
B1	0.004	59.7	23.9	2.6	31.0	<.001	0.005	3.71
B2	0.004	75.2	30.7	2.1	46.5	<.001	0.005	4.25
B3	0.005	51.4	24.0	1.9	97.6	0.004	0.008	3.04
C1	0.006	74.4	26.9	0.8	11.2	<.001	0.008	5.67
C2	0.004	62.8	31.5	0.7	5.6	<.001	0.004	5.04
C3	0.006	66.6	36.2	1.0	4.1	<.001	0.004	6.00
C4	0.027	63.3	35.7	1.0	3.8	0.004	0.013	6.43
AA1	0.02	56.7	21.1	3.8	7.3	0.016	0.016	4.07
AA2	0.006	81.8	39.5	1.9	67.3	0.023	0.007	4.06
AA3	0.005	51.0	27.2	0.9	4.1	0.001	0.004	6.45
AA4	0.023	48.6	25.7	1.2	4.0	0.300	0.025	5.75
BB1	0.013	120.5	57.9	17.5	10.0	0.352	0.018	6.94
BB2	0.297	62.7	35.2	1.4	6.7	0.098	0.043	7.72
BB3	0.014	48.0	25.2	0.9	3.4	0.003	0.016	7.39
BB4	0.013	35.0	18.6	1.2	3.9	0.025	0.007	5.62
DD1	0.024	69.0	38.2	1.2	3.8	0.046	0.023	5.00
DD2	0.008	76.1	43.2	1.4	4.2	0.180	0.005	5.25
DD3	0.008	73.0	41.2	1.0	5.1	0.002	0.006	6.37
DD4	0.003	34.3	25.2	1.0	3.7	0.094	0.002	4.16

Table A2-4. Pesticide analyses. Only detections (table 5) shown ($\mu g\ L^{-1}$).

Well	Atrazine	Deethylatrazine	De isopropylatrazine	Diaminoatrazine	Alachlor ESA	Alachlor OA	Metolachor	Metolachlor ESA	Metolachlor OA	Metribuzin	Pendimethalin
A1					0.32						
A2			0.69		3.13	1.38		1.49	1.15		
A3		0.9			5.32	1.65		0.83	0.37		
B1								0.77			
B2						0.29		9.19	3.05		0.20
B3					6.00	0.35		5.20	2.41		
C1	0.2	1.8					0.20		4.47		
C2		1.2			0.75		0.11	21.74	17.74	0.21	
C3		1.1			1.42	1.37	0.22	5.58	4.42	0.365	
C4	0.2				2.28	1.13		4.03	3.19		
AA1											
AA2		1.1			1.86			4.53	3.23		
AA3		3.8		1.41	0.65			1.90	1.36	0.21	
AA4		1.6			0.59			0.67	0.44		
BB1					1.24					0.46	
BB2					4.54	1.62		1.60	0.44		
BB3			0.76		0.43	0.19		1.99	0.83		
BB4					0.86	0.42			0.27		0.80
DD1					2.49	1.30				0.55	
DD2					5.19	3.41	0.10		0.39	0.85	
DD3		0.8			5.17	2.42				0.40	
DD4					1.21	0.62					

APPENDIX III

CFC and SF6 Atmospheric Mixing Ratio Histories

(http://water.usgs.gov/lab/cfc/background/Chapter.html#history)