HYDROGEOLOGY OF PRE-ILLINOIAN TILL AT THE I-380 REST STOP SITE, LINN COUNTY

Iowa Geological Survey
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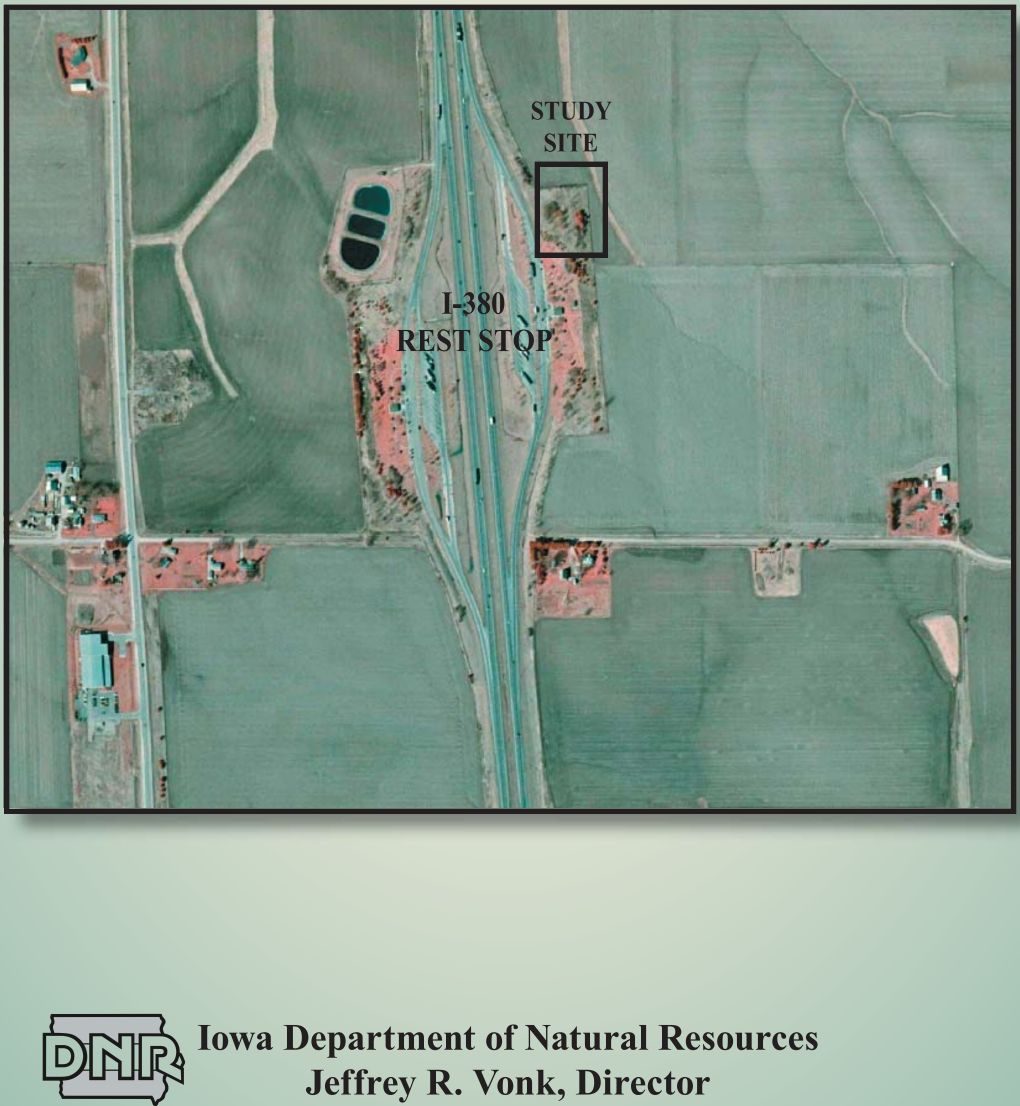

Iowa Department of Natural Resources
Jeffrey R. Vonk, Director
June 2006

COVER

Iowa Dept. of Natural Resources
color infrared photograph of the
I-380 rest stop and study site
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Iowa Geological Survey
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Prepared by

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HYDROGEOLOGY OF PRE-ILLINOIAN TILL AT THE I-380 REST STOP SITE, LINN COUNTY IOWA

Iowa Department of Natural Resources – Geological Survey
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Keith Schilling and Stephanie Tassier-Surine

ABSTRACT

Quaternary aquitards are often targeted for placement of contaminants because of exceedingly slow groundwater flow velocities. However, few hydrology studies have investigated glacial till older than Illinoian time (> 300,000 BP) despite these older tills overlying a large portion of North America. Comparatively little attention has been given to characterizing the hydrogeology and hydrogeochemistry of pre-Illinoian aquitards. This report presents the results of stratigraphic and hydrogeologic studies completed at the I-380 pre-Illinoian till hydrology site in southern Linn County Iowa from 2002 to 2004. An 8-well and 6-well monitoring well nest installed into a 31 m thick pre-Illinoian till sequence near Cedar Rapids, Iowa was characterized using traditional hydrologic and laboratory methods. The objectives of this study were to 1) determine the efficacy of using existing site monitoring wells as part of a new groundwater monitoring network in Iowa; 2) evaluate the water column geochemistry of aquitard wells and develop methods for obtaining representative samples from slowly recovering wells; 3) estimate the groundwater flow velocity through pre-Illinoian till which serves as the major aquitard unit protecting bedrock aquifers in eastern and southern Iowa; and 4) measure the background levels of nutrients, major and minor ions and metals to assess the potential for pre-Illinoian till to be a geochemical barrier and source of contamination to underlying aquifers. The aquitard system consists of about 9 m of fine-grained oxidized pre-Illinoian till overlying 22 m of unoxidized till and Devonian dolomite bedrock.

Downhole profiling and sampling of aquitard wells on three occasions was used to assess geochemical changes that occur in aquitard wells during water level recovery. Substantial water chemistry variations were observed in the standing water columns of till wells. Temperature decreased with depth, whereas pH and specific conductance increased with depth in the water column after 11 years of water level recovery. Less stable parameters such as dissolved oxygen (DO) and oxidation-reduction potential (ORP) showed strong zonation in the well column, with DO stratification occurring as the groundwater slowly entered the well. Oxidation of reduced till groundwater along with degassing of CO_2 from till pore water affects mineral solubility and dissolved solids concentrations. Recommendations for sampling slowly recovering aquitard wells include identifying the zone of DO and ORP stratification in the well column and collecting water samples from below the boundary to better measure unstable geochemical parameters.

Hydraulic conductivity ranged from 10^{-7} m/s in oxidized till to 10^{-10} m/s in unoxidized till. Hydraulic head relations indicated downward groundwater flow through the till profile with hydraulic gradients steepest near the unoxidized till/bedrock interface. Tritium and nitrate concentrations indicated recent (<50 years old) recharge to a depth of 9-12 m below land surface, whereas 18O and 2H results plotted near the local meteoric water line (MWL) and ranged between –6.2 to –7.9% and –38.0 to –50.9%, respectively. A 1 per mil shift toward less negative 18O values with depth may suggest a climate change signal contained in the till water but more data are needed to verify this trend. Vertical groundwater velocity through the unoxidized till was estimated to range from 0.4 to 5.7 cm/yr. The thickness of unoxidized pre-Illinoian till in Linn County was developed from available records and contoured as vertical travel times to evaluate the effectiveness of pre-Illinoian till to prevent nitrate migration to underlying bedrock aquifers.

Detailed sediment and water sampling indicated that the section consisted of a single till unit with distinct weathering zones likely comprising a member of the Wolf Creek Formation (500,000-730,000 years old). Groundwater in the oxidized zone contained higher dissolved oxygen, oxidation-reduction potential and measurable nitrate, whereas the unoxidized till showed an abrupt increase in sediment sulfur and ammonium, and decreased dissolved oxygen and redox potential in water. Denitrification occurring at the redoxcline in pre-Illinoian till via autotrophic denitrification suggests that unweathered pre-Illinoian till is a barrier to nitrate migration to aquifers. As a potential source of contamination, discharge of pollutants from pre-Illinoian till may contribute to existing problems but in general, does not appear to cause new problems to occur. Background concentrations of total N and P in till water exceed nutrient standards for streams and downward leakage of till water contributes As, Ba, F, NH_4, Fe and Mn to underlying aquifers but does not substantially affect aquifer concentrations.

INTRODUCTION

Quaternary aquitards deposited by continental glaciation underlie about 13 million km^2 in North America (Stephenson et al., 1988) and are the most common surficial deposit in agricultural areas of the northern United States and Canada (Rodvang and Simpkins, 2001). With groundwater flow rates on the order of 1 m per 1000 years (Hendry, 1988; Simpkins and Bradbury, 1992; Remenda et al., 1996; Parker et al., 2004) to <1 m per 10,000 years (Hendry and Wassenaar, 1999; Shaw and Hendry, 1998; Hendry et al., 2004), aquitard units are generally viewed as impermeable barriers to vertical contaminant migration to aquifers. As such, these units are often targeted for siting of landfills, hazardous waste transportation, storage and disposal (TSD) facilities, earthen waste storage structures for manure (Simpkins et al., 2002) and other ventures viewed as high-risk for groundwater impact.

Studies of till hydrology have primarily investigated younger tills deposited during the last glacial maximum (less than 12,000 BP), primarily because younger tills either incorporated older tills or buried them. However, a large area of North America is overlain by glacial till older than Illinoian time (greater than 300,000 years BP) (Figure 1). In these areas, “old’ glacial tills are at the land surface and provide the landscape on which societal activities are conducted. Moreover, as the oldest Pleistocene glacial deposits in North America, pre-Illinoian tills buried by younger tills are often found draped on the bedrock surface or in bedrock channels in close proximity to bedrock aquifers. Fracturing and weathering of old tills may be more extensive than younger glacial deposits. Hydrogeologic investigations of pre-Illinoian glacial till are needed to assess the ability of old tills to protect bedrock water resources.

Rodvang and Simpkins (2001) reviewed the occurrence of common agricultural contaminants in Quaternary aquitards and found that thick unweathered aquitards provide a barrier against migration of surficial contaminants to aquifers. They found that major differences in groundwater protection are afforded by unweathered and weathered zones within aquitards. Unweathered aquitards containing more organic carbon and reduced sulfer than weathered aquitards reduce nitrate concentrations from denitrification. On the other hand, weathered aquitard zones contained higher nitrate and phosphorus, often from agricultural

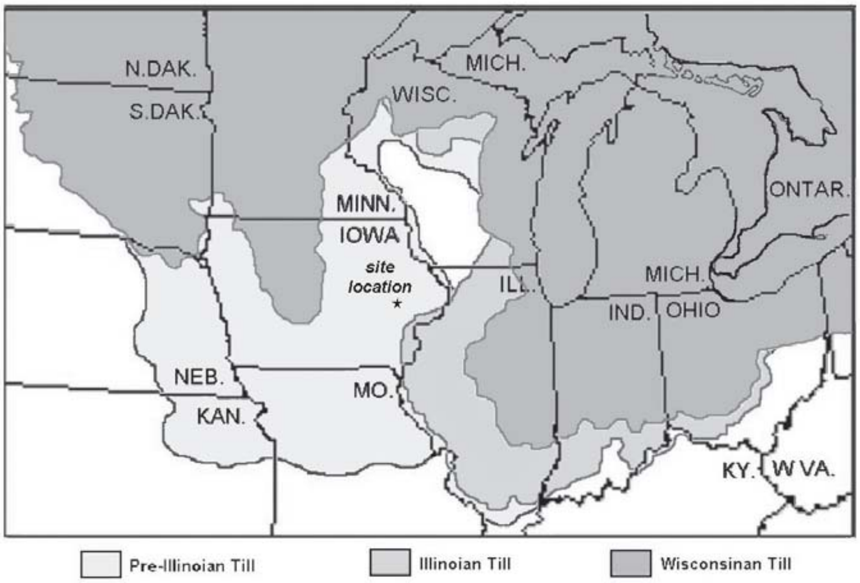

Figure 1. Extent of pre-Illinoian glacial drift in mid-continent of United States.

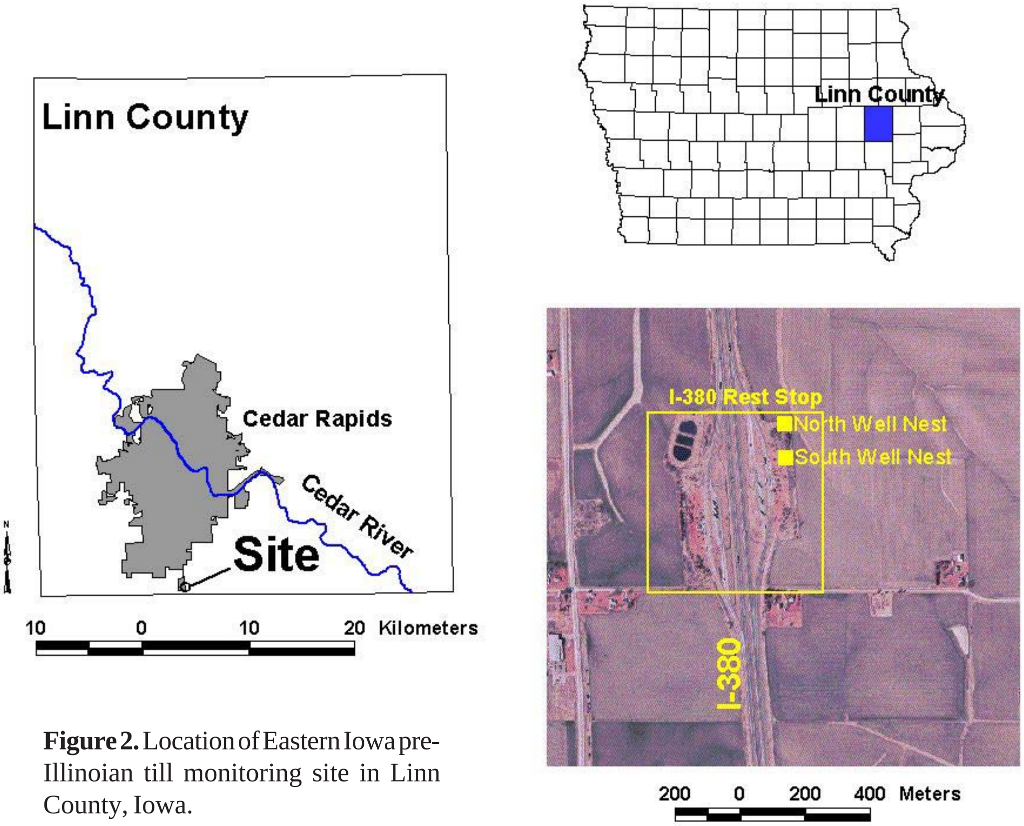

Figure 2. Location of Eastern Iowa pre-Illinoian till monitoring site in Linn County, Iowa.

origins. Late Wisconsin Quaternary deposits were noted to have greater denitrification potential than older pre-Illinoian till (Rodvang and Simpkins, 2001).

Recent studies have also implicated Quaternary glacial deposits as sources of inorganic contamination of aquifers. In alluvial and glacial drift aquifers in the upper Midwest, high aqueous arsenic concentrations are widespread and associated with glacial till deposits (Welch et al., 2000; Warner, 2001). Elevated ammonium has been measured in Iowa's Quaternary aquifers at concentrations that interfere with disinfection of public water supplies (Schilling, 2002). Concentrations of total dissolved phosphorus in Iowa unconsolidated aquifers and aquitards have been found to exceed environmentally sensitive criteria (Burkart et al., 2004). However, it is difficult to assess the effectiveness of aquitards to prevent pollutant migration from source areas when the background concentrations of typical indicator parameters of inorganic contamination (eg., Cl, SO_4, NH_4, heavy metals, etc.) in the aquitard itself are unknown.

This report presents the results of stratigraphic and hydrogeologic studies completed at the I-380 till hydrology site in southern Linn County Iowa from 2002 to 2004. The study site is located at a rest stop for Interstate I-380 between Iowa City and Cedar Rapids (Figure 2). In the late 1980's, hydrologic investigations were initiated at the site and at another site in central Iowa as part of a statewide Aquitard Hydrology Project funded by the Iowa state legislature (Kanwar et al., 1993). The eastern Iowa (EI) site was chosen for investigation because the site is located on a thick, pre-Illinoian age till plain without significant loess cover. Previous investigations at the I-380 till hydrology site were led by the U.S. Geological Survey (Bowman, 1991, 1992).

In 1991, data collection at the Eastern Iowa site was halted due to funding constraints and the monitoring site was essentially abandoned. In 2002, staff from the Iowa Department of Natural Resources – Geological Survey resumed hydrologic investigation at the till hydrology site.

The objectives of this study were to 1) determine the efficacy of using pre-existing site monitoring wells as part of a new groundwater monitoring network in Iowa; 2) evaluate the water column geochemistry of aquitard wells and develop methods for obtaining representative samples from slowly recovering wells; 3) estimate the groundwater flow velocity through pre-Illinoian till which serves as the major aquitard unit protecting bedrock aquifers in eastern and southern Iowa; and 4) measure the background levels of nutrients, major and minor ions and metals to assess the potential for pre-Illinoian till to be a geochemical barrier and source of contamination to underlying aquifers.

REGIONAL SETTING

Pre-Illinoian glacial drift deposited between approximately 2.2 million to 500,000 years ago contains the oldest record of continental glaciation in North America (Boellstorff, 1978; Hallberg, 1980). The term "pre-Illinoian" is used to describe till units older than Illinoian time (300,000 yr old) since research conducted in western Iowa and Nebraska (Boellstorff, 1978) and eastern Iowa (Hallberg, 1980) identified as many as seven till sheets older than Illinoian. Hence, the older two-tiered Kansan-Nebraskan terminology is no longer adequate for describing the complexity of "pre-Illinoian" till units. In east-central Iowa, pre-Illinoian stratigraphy consists of Wolf Creek Formation (500,000-730,000 yr old) and Alburnett Formation (>730,000 yr old) with differentiation between the two formations based primarily on clay mineralogy (Hallberg, 1980). Both tills are loams that contain 30-50% sand, 30-45% silt and 20-25% clay. Bulk densities are 1.76 to 2.11 Mg/m^3 and 1.97 to 2.11 Mg/m^3 for Wolf Creek and Alburnett Formation tills, respectively (Kemmis et al., 1992).

In the vicinity of the study site, 60-120 m of Devonian and Silurian carbonate rocks form the primary bedrock aquifer in Linn County (Wahl and Bunker, 1986). Approximately 90 percent of the total pumpage in the Cedar Rapids and Linn County area is from Silurian, Devonian and Quaternary aquifers. In 1980, total pumpage in Linn County was about 41 million gallons per day (Wahl and Bunker, 1986).

METHODS AND MATERIALS

Hydrogeologic Investigation

A total of 22 observation wells were installed at five locations in 1988-89 at the EI site (Bowman, 1992). Two methods of drilling were used to drill boreholes for observation wells; boreholes less than 45 feet in depth were drilled using hollow-stem auger whereas hydraulic rotary drilling was used for deeper wells (Bowman, 1992). A bedrock observation well was constructed with 6-inch steel casing (EI-1). All other observation wells were constructed with 5-cm diameter polyvinyl chloride (PVC) casing and 1-m length PVC screens. Dry bentonite was poured into the borehole annulus to a depth of about 0.5 m below the ground surface. The wells were enclosed in a locked steel protective casing set in a concrete footing. Use of the wells was abandoned in August 1991 prior to the present study.

In 2002, hydrologic investigation resumed at 14 of the 22 wells located in two main well nests located in the southern and northern portion of the site (Figure 3). The well nests consisted of an 8-well and a 6-well nest, respectively. Drilling notes and grain size data from previous study provided a rudimentary understanding of the site stratigraphy and glacial history. However, soil cores for analysis were not available from previous work, thus, a soil core (near EI-2) was collected from the southern well nest from the ground surface to

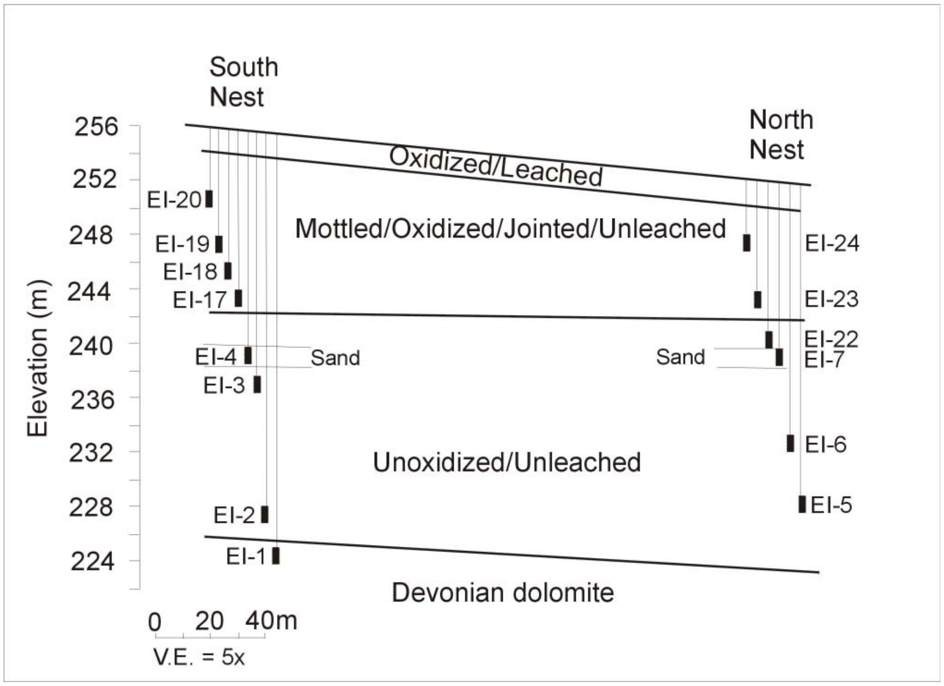

Figure 3. Cross-section of monitoring well network.

bedrock (31 m depth). Continuous 7.6 cm core was collected using a hydraulically driven 1.5-m split spoon barrel to a depth of 16.1 m. The drilling method was switched to slide hammer after 16.1 m because of auger refusal in the dense till. Thereafter, a 0.6-m long, split spoon sample was collected every 1.5 m to the base of the core at the Devonian bedrock surface encountered at a depth of 28.6 m. Site lithology was developed from a combination of recent core drilling and previous work.

The hydraulic conductivity (K) of the saturated zone was measured by either monitoring the water level recovery in the wells after purging (deep wells only) or by conducting slug tests in shallow wells. Recovery data was obtained from daily water level measurements reported by Bowman (1992) assuming that the unoxidized till wells were purged dry prior to recovery. The recovery data were analyzed as a rising head slug test with the entire water column evacuated. Rising head slug tests were conducted in other wells by removing a 1.9-L bailer of water from the well and monitoring the recovery of water to static conditions. Results of the recovery tests and slug tests were analyzed with the method of Hvorslev (1951), a commonly used method for estimating K in till wells (Hendry, 1982; Simpkins and Bradbury, 1992; Shaw and Hendry, 1998).

Hydraulic heads in the wells were measured four times prior to well purging in 2002 using an electronic water level indicator and recorded to the nearest 0.25 mm. It was assumed that the static water level in the wells after more than a decade of inactivity represented the true static hydraulic head in the till. Without a sufficiently long period for hydraulic head recovery in aquitard wells, true hydraulic head conditions are rarely measured. Many studies of low K aquitards report non-equilibrium achieved during slow water recovery following installation or purging (Shaw and Hendry, 1998; Wassenaar and Hendry, 1999). For the shallower, oxidized till wells, water levels generally recovered to static conditions within a single day to a week. Hydraulic gradients between nested wells were calculated as the difference in total hydraulic head between wells divided by the distance of sandpack elevations.

Water Sampling and Analysis

In October 2002, following more than 11 years of inactivity, a Hydrolab MiniSonde™ multiprobe was slowly lowered through the standing water column in 14 aquitard wells. The multiprobe simultaneously measured temperature, pH, specific conductance (SC), dissolved oxygen (DO) and oxidation-reduction potential (ORP) and were continuously recorded at 10 second intervals on a laptop computer. MiniSonde readings were taken at the water surface in the well casing and at approximate 3-m intervals through the standing water column with a final reading taken at the midpoint of the well screen. The MiniSonde readings were allowed to stabilize at each depth before being slowly lowered to the next depth increment (Figure 4). Accuracy of the measurements was ±0.10 C for temperature, ±0.2 pH units for pH, ±0.1% for SC, ±0.2 mg/l for DO and ±20 mv for ORP. Calibration of the MiniSonde was established by Hydrolab at the factory prior to rental shipment with pH calibration maintained in the field using standard buffer solutions.

Following downhole profiling, water samples were collected from the top and bottom of the standing water column using a Waterra inertial lift pump. In the case of the upper water column sample, the tubing and foot valve were lowered into the well and removed, with the tubing and valve serving as a bailer. For the lower water column samples, the foot valve and tubing were lowered to the bottom of the well and pumped sufficiently to lift a water sample from the bottom of the well to the ground surface. Admittedly, the method of sample collection was rather crude and the water quality data should probably be considered semi-quantitative; however the results do provide another line-of-evidence for interpreting geochemical changes in the standing water column. Following water column sampling, the standing water columns were purged using a submersible pump.

On December 2, 2003, after approximately 14 months of water level recovery and well inactivity, downhole water chemistry logging with the MiniSonde was conducted again. The profiling procedures were the same as described above, with the intention of repeating the same depth intervals each time. The standing water column was again purged, and one week later (December 8, 2003), the MiniSonde downhole logging procedure was conducted a third time in all the wells.

On December 8, 2003, water samples were collected from the southern and northern well nest for isotope and chemical analysis. Water samples were collected by slowly lowering a bailer through the standing water column to the well screen. Water samples were filtered in the field by passing the water through a 0.45 micron filter. Subsamples of the filtered water samples were acidified to pH<2 for analysis of cations and metals. All samples were stored at 4º C and delivered to University of Iowa Hygienic Laboratory for analysis of major and minor ions and alkalinity. Water samples for isotopic analysis of 18O, 2H and 3H were collected and delivered to the University of Waterloo Environmental Isotope Laboratory. The isotope analyses were conducted using methods described by Epstein and Maeda (1953), Drimmie et al. (1991), Drimmie et al., (1993). Tritium results had a detection limit of 0.8 tritium units (TU). Stable isotope data were expressed as the difference between 18O/16O and 2H/1H abundance ratios of the samples and Vienna Standard Mean Ocean Water (VSMOW) in permil notation (2D% and 18O%).

EFFECTS OF SLOW RECOVERY RATES ON WATER COLUMN GEOCHEMISTRY

Water sampling of aquitard wells presents a challenge due to the slow recovery times for water recharging the wells. Unlike more

Table 1. Summary of monitoring well information and water level recovery data.

Well ID	Well Depth (m)	Geologic Unit	Static Water Level Depth (m)	% Recovery from Previous Purging 11-year	14 month	1 week	Measured Recovery Rate (m/day)	Time Needed for 100% Recovery (days)
EI-2	28.3	Unoxidized p-I till	3.15	100%	96.1%	16.5%	0.06	437
EI-5	23.7	Unoxidized p-I till	4.99	100%	90.6%	12.2%	0.04	464
EI-6	18.8	Unoxidized p-I till	3.23	100%	65.5%	5.9%	0.02	641
EI-22	11.2	Oxidized p-I till	1.74	100%	100%	98%	1.33	7
EI-19	8.5	Oxidized p-I till	2.45	100%	100%	100%	6.85	1

permeable formations where multiple well casing volumes can be removed prior to sampling that ensure collection of groundwater samples representative of formation water (Barcelona et al., 1985), removal of a single casing volume in an aquitard well will often bail the well completely dry. Water sampling can only be completed after sufficient volume of water has recharged the well for collection, which can take as long as weeks, months or years to recharge depending on the sample volume needed. An accurate assessment of aquifer geochemistry is therefore problematic given that unstable parameters such as pH, DO and ORP may change in the water column over time.

In a recent study, Wassenaar and Hendry (1999) monitored temporal changes in pH, temperature, ORP, DO and specific conductance in slowly recovering aquitard piezometers over a 3-year period. Using downhole instrumentation, they observed changes in geochemical conditions in the standing water column, particularly with respect to pH, ORP and DO measurements. Wassenaar and Hendry (1999) recommended that there should be 2 to 10 m of standing water in the piezometer before in-situ temperature, pH, ORP and DO measurements are obtained. Moreover, they noted that measuring water quality parameters as the well is slowly recovering from bailing would likely produce misleading results.

Results presented in this section build on the previous work of Wassenaar and Hendry (1999) by considering how geochemical parameters in standing water columns of aquitard wells vary since the time the wells were last purged. Downhole profiling and sampling of aquitard wells conducted after more than an 11 year period since the wells were last purged and sampled are combined with more recent purging and downhole profiling after 1-year and 1-week intervals to assess the geochemical changes and rate of change that occur in aquitard wells during slow recovery.

Results from five of the 14 wells are reported herein. The five wells include two wells from the south well nest (EI-2 and EI-19) and three wells from the northern well nest (EI-5, EI-6, and EI-22). Wells EI-2, EI-5 and EI-6 are screened across unoxidized pre-Illinoian till at depths of 28.3 m, 23.7 m, and 18.8 m, respectively. Shallower wells EI-19 and EI-22 were installed in oxidized pre-Illinoian till at depths of 8.5 m and 11.2 m, respectively. Data from these five wells were selected for presentation because the wells represent typical water quality conditions and trends observed in the other aquitard wells. A summary of the downhole measurement results for all monitoring wells is included in Appendix A.

Water Level Recovery Rates

If assumed that the static water level in the wells after an 11-year period of inactivity represents the true static hydraulic head in the aquifer, the water recovery rates following purging can be estimated (Table 1). In the case of the unoxidized till wells, water levels in the well casing recovered to 65.5% to 96.1% of static water level after 14 months of recovery (~420 days). In contrast, the water levels in the oxidized till wells recovered completely to previous static levels during this time interval. After one week following purging, water levels in the unoxidized till wells were slow to recover, only recovering 5.9% to 16.5% of static. Considering the slow water level recovery rates in the unoxidized till wells, as much as 1.2 to 1.7 years would be needed for the water levels in the wells to fully recover from complete well purging. For the shallower, oxidized till wells, water levels generally recovered to static conditions within a single day to a week (Table 1).

Vertical Variations in Water Chemistry

Substantial variation in standing water geochemistry developed in all aquitard wells with different time intervals since they were last purged (Figures 4 to 9). A closer look at the geochemical profiles considers each parameter individually.

Temperature

Vertical variation in water temperature developed in all wells during the 11-year period of inactivity. In the deeper till wells, water temperature gradually decreased from 12-14 °C in the upper 10 m of standing water column to a consistent 10.3 to 10.4 °C in the lower portion of the well column. In the shallower wells, temperature also decreased in the water column with depth and reached its lowest level at the bottom of the well. During the subsequent two purging intervals (14-month and

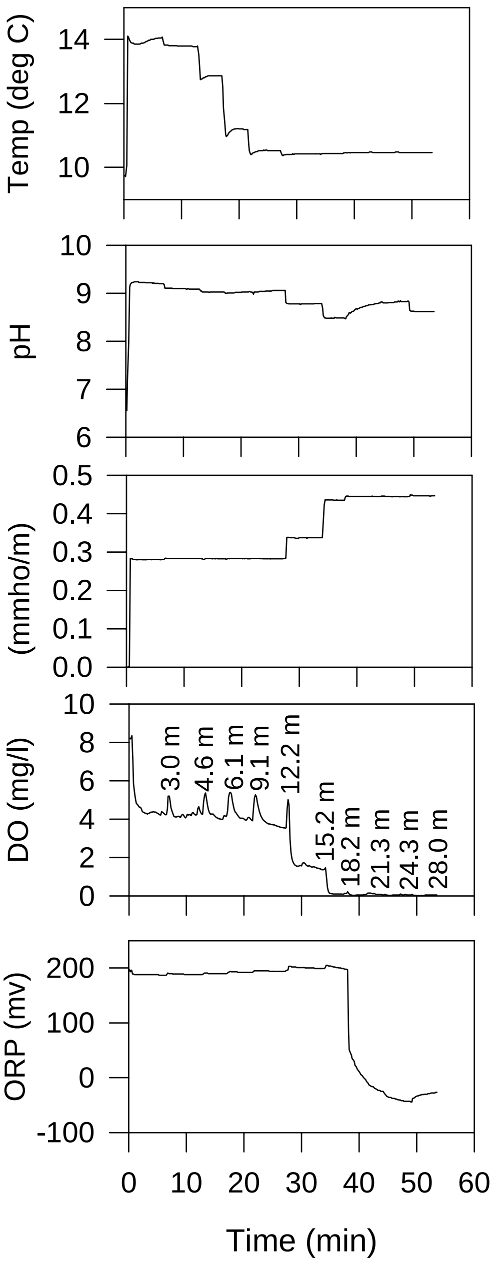

Figure 4. Readings of temperature, pH, specific conductance, dissolved oxygen and ORP taken at 10 second intervals with MiniSonde when lowered in well EI-2 in October 2002.

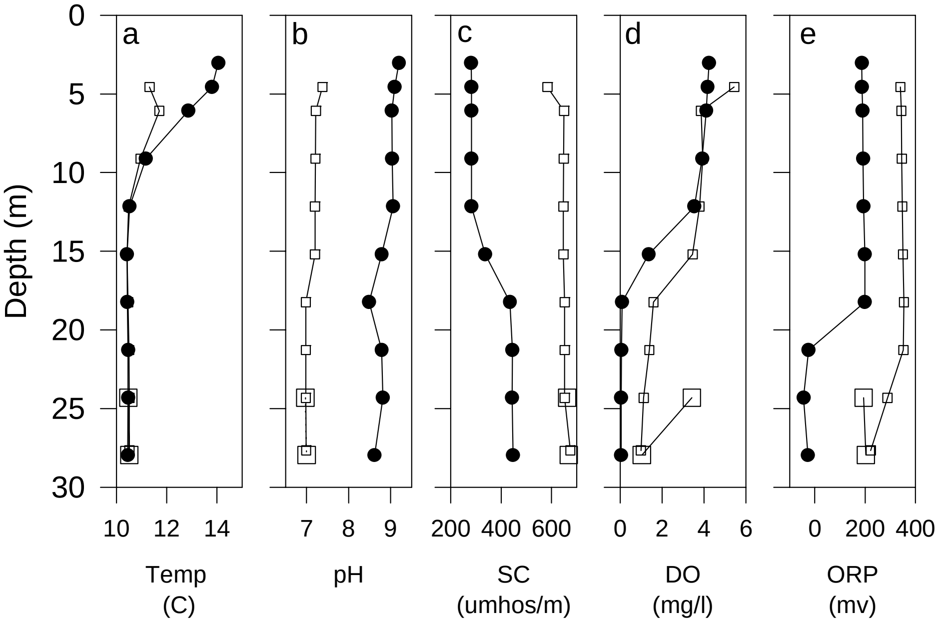

Figure 5. Stabilized parameters of a) temperature, b) pH, c) specific conductance, d) DO, and e) ORP taken during lowering of MiniSonde in EI-2 in October 2002 (dark circles), December 2, 2003 (small open squares) and December 8, 2003 (large open squares).

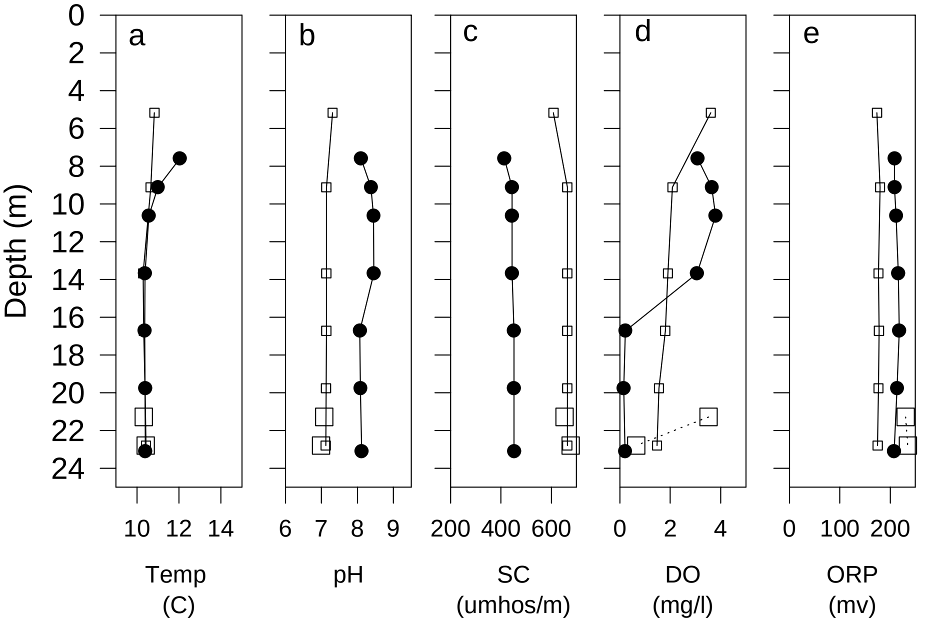

Figure 6. Geochemical parameters measured in the standing water column of EI-5 (symbols same as Figure 3).

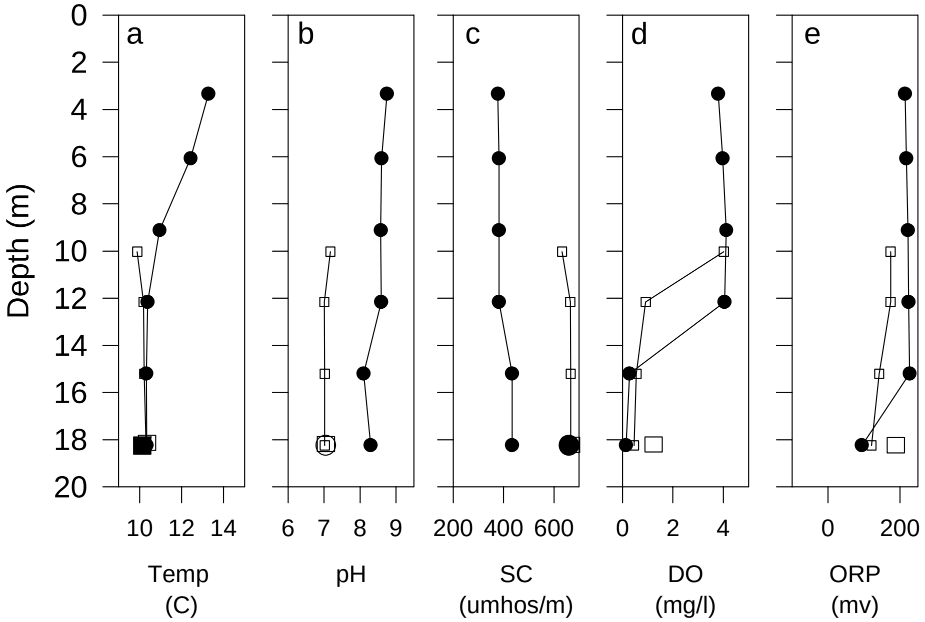

Figure 7. Geochemical parameters measured in the standing water column of EI-6 (symbols same as Figure 3).

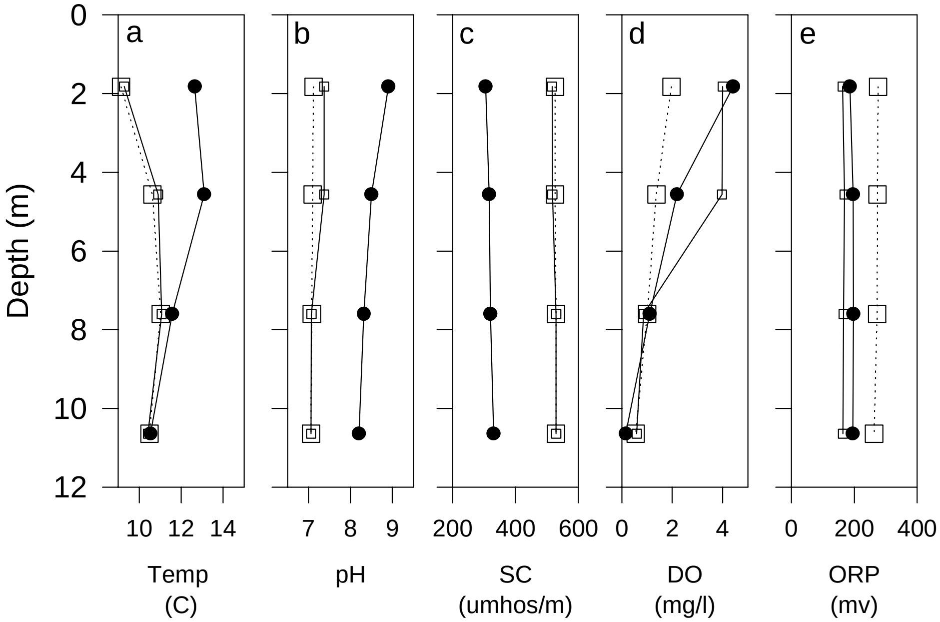

Figure 8. Geochemical parameters measured in the standing water column of EI-22 (symbols same as Figure 3).

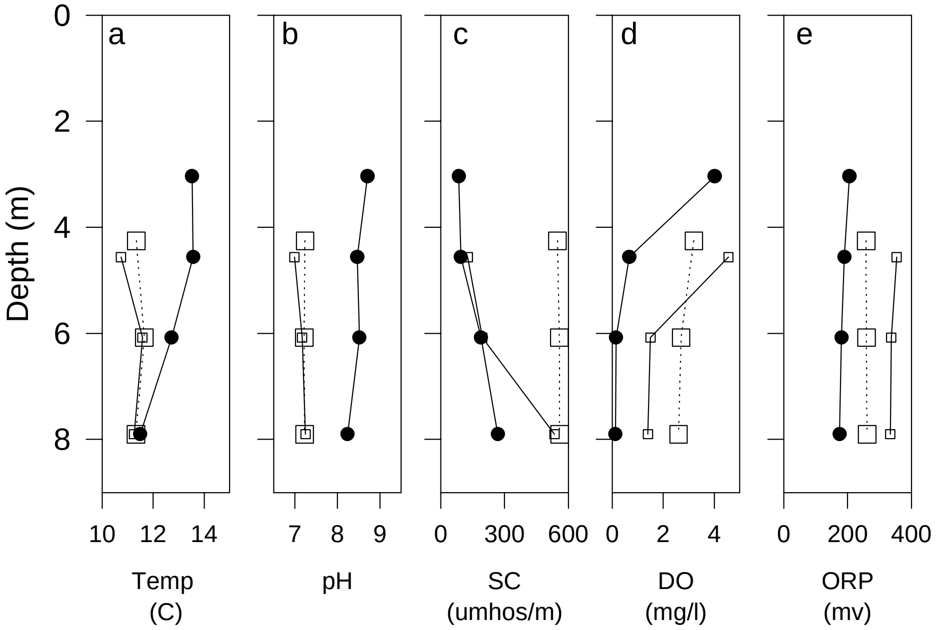

Figure 9. Geochemical parameters measured in the standing water column of EI-19 (symbols same as Figure 5).

1 week periods), vertical temperature variations in the well columns were not as apparent. Temperature in EI-2 decreased from 11.7 to 10.5 °C after a 14-month inactive period, but stayed relatively constant at the bottom of the well at 10.5 °C during slow water recovery after one week of purging (Figure 5a). Similarly, water temperature in the standing water column was generally consistent between 14-month and 1 week purging intervals despite incomplete water level recovery in the other unoxidized till wells. In the two oxidized till wells, water temperature at the bottom of the well was consistent among purging events, but was cooler at the top of the water column during the 14-month and 1 week purging intervals. This was most likely due to lower ambient surface air temperatures in December during the latter two well purging episodes compared to the initial October 2002 purging.

pH

Vertical profiles in pH did not exhibit much variation in the standing water columns in the different purging time intervals, but did show much higher overall pH after water was sitting in the well columns for 11 years (Figures 5b-9b). The pH in the water columns ranged from 8.1 to 9.2 in all wells after the long inactive period. After the wells were purged and allowed to recover for 14-months, the pH in all the wells ranged from 6.98 to 7.37, and stayed in this range after one week of recovery.

Elevated pH in the water columns after an extended period of time probably reflects degassing of CO_2 from till pore water recharging the well (Wassenaar and Hendry, 1999). Clay-rich aquitards of North America are typically charged with CO_2 above atmospheric levels (Keller, 1991, Simpkins and Parkin, 1993). Degassing of CO_2 from the till groundwater would drive dissolved CO_2 in water normally present as bicarbonate (HCO_3^-) to gaseous CO_2, thereby consuming hydrogen ions and raising water column pH:

$$HCO_3^- + H^+ = H_20 + CO_{2(g)}\uparrow$$

The effects of degassing CO_2 in all the wells apparently occurred between the 1.2 and 11 years of recovery time since all wells showed a pH shift after 11 years but none showed increased pH after 14 month and 1-week periods. Moreover, the pH in the water columns after 14 month and 1-week periods was consistently neutral during these two periods suggesting that little change in CO_2 equilibria occurred during the first 1.2 years of water level recovery. This is contrary to conditions reported by Wassenaar and Hendry (1999) who observed that CO_2 degassing occurred rapidly in their aquitard wells within the first 30 days after well installation. One water sample had a pH of 9.23 after 30 days, with the well column water pH later stabilizing to values around 7.9 from day 200 to 1089 (Wassenaar and Hendry, 1999). An important difference between this study and that of Wassenaar and Hendry (1999) was that the latter study evaluated water column geochemistry following new well installation techniques (using an Ar gas pocket in the sand pack) whereas this study evaluated well column geochemistry associated with purging existing, older wells installed with traditional methods.

The geochemical program PHREEQC (Parkhurst, 1995) was used to evaluate the effect of variable pH conditions on carbonate mineral equilibria and P_{CO2}(Table 2). Because groundwater samples for complete geochemical analyses were only taken from the wells after the third purging time, only a single set of water analyses was available for input into the model. Although some water quality samples were collected for redox sensitve species from the top and bottom of the standing water columns, the list of analytes was not sufficient for PHREEQC modeling. Therefore, the model was run to assess what effects pH changes due to CO_2 degassing would have had on the static water geochemistry in the well column. Comparisons are made between water column geochemistry at the bottom of each well after an 11-year water recovery period versus a one-week recovery period (Table 2).

Table 2. Saturation indices for carbonate minerals and PCO2.

Well ID	Recovery Time	Log P_{CO2}	log SI Calcite	log SI Dolomite
EI-2	11-year	-3.37	1.51	2.57
	1-week	-1.50	-0.23	-0.92
EI-5	11-year	-2.59	0.93	1.44
	1-week	-1.45	-0.18	-0.79
EI-22	11-year	-2.76	1.10	1.82
	1-week	-1.62	0.01	-0.35
EI-19	11-year	-2.83	0.83	1.30
	1-week	-1.81	-0.16	-1.81

Results suggest that given the aquitard water geochemistry, the high pH of the water after an 11-year recovery period would have resulted in saturation indices of calcite and dolomite greater than 0.83, with most values between 1 and 2 (Table 2). These saturation indices suggest that the water in the wells was oversaturated with respect to calcite and dolomite. Log P_{CO2} values at this time ranged between –2.59 to –3.37. In contrast, pH conditions measured in the well after a week of water level recovery indicated that the groundwater was near saturation or slightly undersaturated with respect to calcite and dolomite. LogP_{CO2} values ranged between –1.45 to –1.81. The P_{CO2} and saturation indices for calcite and dolomite measured after one week of water level recovery are similar to results reported at other till hydrology sites in Alberta (Hendry et al., 1986), Iowa (Simpkins and Parkin, 1993) and Saskatchewan (Wassenaar and Hendry, 1999). The differences in saturation indices and PCO2 between 11-year and 1-week recovery times suggests that degassing of CO2 from the till pore water strongly affected carbonate mineral equilibria in the standing water column in aquitard wells.

Specific Conductance

In all wells, SC was lower in the standing water column after the 11-year period than the 14-month and 1-week purging intervals (Figures 5c-9c). In the unoxidized till wells, SC values ranged from 281 to 453 umhos/m in October 2002 but ranged between 584-675 umhos/m in December 2003. In the oxidized till wells (EI-19 and EI-22), SC values were twice as high during this time period from 85-330 umhos/m to 516-535 umhos/m. Vertical variations in SC were noted in the standing water columns of EI-2 and EI-19. In EI-2, SC increased with depth below the water level surface after the 11-year inactive period, with increasing SC occurring between a zone about 12 to 18 m below the water surface. This zone appears to align with a zone of decreasing DO in the water column (Figure 4d). In EI-19, SC increased with depth after both 11-year and 14-month recovery periods, but varied little following one week of water level recovery. The SC at the lowermost depth interval measured at the 14-month recovery time was nearly the same as measured after one-week of water level recovery (535 and 560 umhos/m, respectively).

The differences in SC between the 11-year recovery period and more recent 14-month and 1-week recovery times may be related, in part, to the pH changes caused by degassing of CO_2 from the till groundwater. As pH increased in the well casing water over time, PHREEQC modeling suggests oversaturation of other minerals in the water column besides calcite and dolomite, such as goethite, hematite and rhodochrosite (not shown). It is conceivable that precipitation of minerals from the well casing water occurred, effectively lowering the amount of ions in solution and lowering SC values. In well EI-2, geochemical modeling of water at the top of the water column versus the bottom of the water column after the 11-year period suggests greater saturation of calcite would occur at the top of the well (SI of calcite at 3.15) compared to bottom of the well (SI of 1.57). Considering the higher pH and water temperature at the top of EI-2, perhaps greater loss of aqueous mineral species occurred in upper well casing water compared to lower well water. Clearly without detailed water analysis of the standing water columns after the various recovery times, much of this analysis is speculative; however, the in-well geochemistry and modeling do hint at potentially significant geochemical changes occurring in the well casing water over time.

Dissolved Oxygen

DO showed the most variation, both vertically within the standing water columns of each well, and among the different water level recovery periods (Figure 5d-9d). In the unoxidized till wells, sharp zonation in DO was particularly apparent in the standing water columns after the 11-year recovery period. In well EI-2, DO changed from 3.54 to 1.37 to 0.1 mg/l in the span of 6 m from 12.2 to 18.2 m. Similarly, DO concentrations decreased from 3-5 mg/l in the upper water column to less than 0.2 mg/l at the well bottom in the other till wells. Although the boundary between high and low DO was less defined, DO stratification also developed after the 14-month recovery periods in all wells.

After one week of water level recovery, DO concentrations measured at the top of the rising water columns in wells EI-2 and EI-5 were markedly higher than concentrations taken from their well screens (Figures 5d, 6d). In EI-2, DO was measured at 3.42 mg/l at a depth of 16 m (top of the water column) and 1.04 mg/l at the well screen, and in EI-5 DO was 3.52 mg/l at a depth of 70 m but 0.65 mg/l at 21 m. The pattern was not as apparent in unoxidized till well EI-6 (Figure 7d) where a single measurement taken at the well screen was 1.23 mg/l, still much higher than DO concentrations measured at the well screen after 11-years and 14-months of recovery. In oxidized till wells EI-19 and EI-22, DO concentrations increased slightly from the well bottom to the top of the standing water column after one week of water level recovery (Figures 8d, 9d). Less DO stratification developed in the well casing water of the oxidized till wells after the one week period.

Reasons for DO variation in the standing water columns of wells have been postulated (Wassenaar and Hendry, 1999). A simple explanation would revolve around the sampling methodology used in this study, implying that the lowering of the MiniSonde probe into the well casing water brought high dissolved oxygen concentrations down to lower casing water. While it is clear that some flow around the instrument occurred during lowering that temporarily increased DO concentrations (Figure 4), in all cases, DO readings quickly stabilized after the agitation and leveled out into uniform values in a span of several minutes. Moreover the rapid change in DO in the well casing water was strongly decreasing, not increasing, so if anything, actual DO stratification may have been more prominent than measured.

Could downward diffusion of oxygen from the atmosphere account for the DO stratification observed in the wells? Assuming a DO concentration at the water table surface to be 10 mg/l and the DO at the bottom of the well to be zero, a maximum rate of diffusion can be established using the equation (Crank, 1956):

$$C_i\ (x,\ t) = C_0\ \mathrm{erfc}\ [x/2\ x\ (D^*t)^{0.5})]$$

Where C_i is the solute concentration at depth x at time t, C_0 is the original concentration, erfc is the complimentary error function and D* is the effective diffusion coefficient. Assuming the diffusion coefficient of oxygen in water to be $1 \times 10^{-9}\ m^2/s$, the concentration of oxygen at a depth of 2 m after 11 years would be less than 0.2 mg/l. Hence, it is evident that downward diffusion of oxygen in the well column could not account for the DO stratification in the well water that developed at depths 5-15 m below the water surface.

The appearance of DO stratification in the standing water column after only 1 week of water level recovery suggests that the processes contributing to DO stratification occurred as groundwater slowly entered the well. Aquitard wells are typically purged dry, after which the entire headspace in the well casing is air. Assuming that till groundwater entering the well casing would contain little or no dissolved oxygen, the recharging water would be immediately exposed to the atmosphere as the rising water level in the well is continually exposed to air at the water surface. Atmospheric oxygen would partition in the slowly recharging water and dissolve into groundwater according to Henry's Law, resulting in apparently "elevated" dissolved oxygen levels in the till casing water. With increasing water level recovery in the well, the recharging water at the well screen would be further removed from the air-water interface. Thus, the inflow to the well would then retain the natural low dissolved oxygen signal from the aquitard groundwater. In the slowly recovering unoxidized till wells, a balance appeared to have been achieved between the slow water level rise in the well and the partitioning of oxygen into the rising water column. Hence, the stratification zone between high and low DO water was about midway in the well casing. In the oxidized till wells, the higher aquitard K allowed the recharging water to occur faster than the partitioning of oxygen into the water and thus permitted a greater proportion of the standing water column to retain the low DO signal of the aquitard. The depth of the DO stratification line appeared to be largely controlled by the K of the aquitard.

Reduced groundwater entering the well casing would rapidly undergo oxidation that would consume DO. Till groundwater containing ammonium (NH_4) entering the well would undergo nitrification in the reaction:

$$2O_2 + NH_4^+ = NO_3^- + 2H^+ + H_2O$$

Oxidation of iron and manganese would further consume DO in the reactions:

$$O_2 + 4Fe^{2+} + 4H^+ = 4Fe^{3+} + 2H_2O$$
$$O_2 + 2Mn^{2+} + 2H_2O = 2MnO_2 + 4H^+$$

and oxidation of hydrogen sulfide (HS^-) would produce sulfate in the reaction:

$$2O_2 + HS^- = SO_4^{2-} + H^+$$

These reactions would affect the balance between the influx of DO at the rising water level surface versus the loss of DO in the standing water column as aqueous minerals are oxidized.

ORP

Stratification of ORP occurred in wells EI-2 and to a lesser degree in EI-6, but was not apparent in EI-5 or oxidized till wells (Figures 5e-9e). In EI-2, after 11 years of water level recovery, ORP decreased rapidly in the well column from approximately 200 mv at a depth of 18.2 m to –25.3 mv at 21 m (Figure 4 and 5e). The shift in ORP at 18.2 m was approximately 6 m lower in the standing water column compared to the DO decline. In EI-6, ORP decreased from 227 mv at 15.2 m to 94 mv at the well bottom (Figure 7e), also occurring at a lower depth than the DO stratification. After purging the wells and allowing for 14-months of water level recovery, the ORP in EI-2 and EI-6 showed a slight shift toward reduced ORP with depth, but it was not particularly pronounced. ORP measured after one week of recovery was similar to the ORP measured after 14-months in all wells.

Water Quality Results

Water quality data from 1991, November 2002 and December 2003 for several redox sensitive species shed light on chemical processes that may occur in the standing water columns of aquitard wells (Table 3). While chloride, a non-reactive species, changed little during the sampling periods, other inorganic species showed substantial variation. Differences were particularly evident when comparing water quality measured in the top of the water column compared to the well bottom in November 2002. In the unoxidized till wells and EI-22, NO_3-N was present in the upper portion of the water column but not at the bottom where NH_4 concentrations were present at concentrations ranging from 0.31 to 0.82 mg/l. Organic N concentrations were present in all wells but at variable concentrations ranging up to 26 mg/l in EI-22. In the shallowest well EI-19, co-occurrence of nitrate and ammonium was observed, but this could have been the result of cross-communication during sampling. Iron and manganese concentrations were significantly higher at the bottom of the well compared to the top, with iron concentrations varying from 0.27 to 1.2 mg/l at the top and bottom of EI-2, respectively, and from 0.62 to 27 mg/l in EI-5. Manganese concentrations showed similarly large differences (Table 3). Concentrations of Fe and Mn were generally consistent between 1991 and December 2003 sampling period, showing much lower levels than the November 2002 period. Sulfate concentrations showed decreasing concentrations between sample periods in a few wells but did not exhibit the same water column variability as N, Fe and Mn.

The presence of nitrate at the top of the water column and ammonium at the bottom of the water column suggests that nitrification has converted naturally-occurring ammonium in till pore water to nitrate in the well casing. Ammonium is routinely detected in Quaternary aquifers in Iowa and the Midwest at concentrations greater than 1 mg/l (Schilling, 2002). Most likely nitrification occurred when the water levels in the till wells were slowly recovering and when DO levels were high at the water column surface. Hence, caution must be used to generalize about the occurrence of nitrate in aquitard wells, especially those that have been bailed dry, because nitrification

Table 3. Summary of water quality results for select constituents during three time periods, in 1991 (last time sampled before present investigation), 2002 (top and bottom of standing water column before purging), and 2003 (after one week of water level recovery). All concentrations in mg/l.

Well	Sample Date	Well Sample Location	Cl	SO4	NO3-N	NH4-N	TKN	Fe	Mn
EI-2	Aug-91	bottom	4.6	48	0.74	0.01	-	0.01	0.26
	Nov-02	top	4.2	33	0.7	<0.05	0.34	0.27	<0.02
	Nov-02	bottom	3.4	40	<0.1	0.62	0.98	1.2	0.57
	Dec-03	bottom	2.9	36	<0.5	0.29	0.26	0.04	0.23
EI-5	Aug-91	bottom	8.6	230	0.34	0.31	-	0.02	1.7
	Nov-02	top	3.6	66	0.6	<0.05	0.09	0.62	0.11
	Nov-02	bottom	2.7	49	<0.1	0.31	3.2	27	3
	Dec-03	bottom	1.5	25	1.4	0.08	0.78	<0.02	0.11
EI-6	Aug-91	bottom	13	-	0.53	0.35	-	1.4	2.1
	Nov-02	top	4.6	120	0.2	<0.05	0.17	1.5	0.03
	Nov-02	bottom	3.4	86	<0.1	0.36	0.7	3.9	1.6
	Dec-03	bottom	4.3	120	0.2	0.28	0.77	0.1	0.64
EI-22	Aug-91	bottom	3.7	71	0.07	0.2	-	0.02	1.54
	Nov-02	top	1.1	9.6	0.6	<0.05	0.42	1.7	0.25
	Nov-02	bottom	<1	7.4	<0.1	0.82	26	24	0.82
	Dec-03	bottom	0.7	5.2	<0.1	0.17	0.5	<0.02	0.37
EI-19	Aug-91	bottom	2.6	41	2	0.02	-	0.004	0.02
	Nov-02	top	1.8	7.7	2.9	0.17	0.63	2.4	0.03
	Nov-02	bottom	1.8	8.7	3.8	1	1.8	4.7	0.07
	Dec-03	bottom	2.7	30	2.3	<0.05	0.23	<0.02	<0.02

- not analyzed

processes may have converted ammonium to nitrate as the well was slowly recovering.

Higher concentrations of Fe and Mn at the bottom of the wells after the 11-year recovery period suggests that a combination of either: a) water at the well bottom has not been oxidized and the measured concentrations represent true values, or b) additional iron (III) and manganese (IV) reduction has occurred. Oxidation of organic matter (CH_2O) in the well column via iron reduction (Freeze and Cherry, 1979):

$$CH_2O + 4Fe(OH)_3 + 7H^+ = 4Fe^{2+} + HCO_3^- + 10\ H_2O$$

and manganese reduction:

$$CH_2O + 2MnO_2 + 3H^+ = 2Mn^{2+} + HCO_3^- + 2\ H_2O$$

would result in higher dissolved Fe and Mn concentrations in the water column than actually present in the till pore water. The occurrence of high organic N concentrations at the well bottom (suggesting the presence of organic matter), and the overall higher Fe concentrations in water column in November 2002 compared to 1991 and 2003 levels provide indication that some Fe reduction was occurring in the standing water column. However, it is possible that low concentrations of Fe and Mn measured in aquitard wells in 1991 and 2003 are lower than true values due to oxidation processes occurring in the wells as the water level slowly recovered.

Recommendations for Aquitard Sampling

Results from this study indicate that substantial geochemical change may occur within the standing water columns of aquitard wells as water levels slowly recover after purging. By evaluating in-situ geochemical parameters with downhole instrumentation at three different time scales, constraints on the timing of geochemical changes are provided by this study. Changes in pH and specific conductance appeared to occur sometime between 14-months and 11 –years after purging. Less stable parameters such as DO and ORP, appeared to change as the groundwater slowly entered the well. DO showed stratification in the standing water column after only one week since purging and well bottom DO concentrations after one week were higher than 14-month and 11-year DO levels.

The geochemical picture that emerges from monitoring water column geochemistry of slowly recovering aquitard wells is rather complex. Under short timeframes of days to weeks after an aquitard well is purged dry, reduced till groundwater enters an air-filled well, reacts with oxygen and oxidizes ammonium, iron, manganese and sulfur contained in the till water. Over longer timeframes, (1.2-11 years), degassing of CO_2 from till pore water raises the pH of the standing water column and affects mineral solubility and dissolved solids concentrations. Reduction of N, Fe, Mn and SO_4 may also occur in the standing water column over longer periods of time.

Recommendations for sampling slowly recovering aquitard wells are generally consistent with those offered by Wassenaar and Hendry (1999). Downhole instrumentation is preferred for monitoring unstable geochemical parameters in-situ and identifying the zone of DO and ORP stratification that may have developed in the well. Rather than specifying how much standing water should be in the well before sampling, results from this study point to identification of the DO or ORP boundary as the determinate for identifying the proper depth of sampling. Water samples should be taken from below the boundary to better measure unstable geochemical parameters. In slowly recovering wells, it is not unusual for water levels to require years to recover to static conditions. Water quality samples from wells that require a long time for recovery present a challenge because the long time needed to achieve static water level recovery will likely allow in-well geochemical changes to occur. A balance must be achieved between collecting water quality samples that are truly representative of aquitard groundwater and measuring a hydraulic head in an aquitard well that accurately reflects site conditions. Depending upon which objective is deemed most important for a project, specific water level measurement or sampling procedures can be established.

HYDROGEOLOGY OF PRE-ILLINOIAN TILL

Geology

A stratigraphic description derived from the soil core revealed a Pre-Illinoian till unit typical of eastern Iowa (Appendix A). The upper 1.5 m was oxidized and leached of carbonates (OL) with a weak soil profile (BA horizon) developed in the surface. The OL zone was underlain by 12.2 m of yellowish-brown (10YR5/6) oxidized and unleached (OU) silty clay loam with common light gray mottles (2.5Y 6/2). The OU till was fractured and jointed with Fe and Mn accumulations common on joint faces. Very dark gray (5Y 3/1), unoxidized and unleached (UU) silt loam occurred from the base of the oxidized till to the bedrock surface at 31 m. The UU till was massive and very firm with a trace of fine gravel consisting mainly of quartz and igneous rock clasts. Three sand zones within the till were identified in the EI-2 core (7 to 9 m, 13.1 to 14 m, and 14.6 to 15.8 m), but it is unclear whether the sand units are continuous across the site. One sand unit was noted in previous drilling notes from the northern well nest (Figure 3).

Grain size data collected from previous site drilling indicate relative uniformity of texture within the till unit. From 32 soil samples collected from a depth of 2.2 m to 28.6 m, the till averages (and standard deviation) 19.2% clay (2.3), 18.2% fine silt (2.8), 18.9% coarse silt (3.0) and 43.7% sand (3.0). Based on the uniformity of the till (color, texture, consistency, etc.) and lack of weathering zones identified, we believe that only one till unit is present at the EI site. Although not conclusively identified without clay mineralogy, the till is likely an undifferentiated member of the Wolf Creek Formation.

Fractures common in the upper OU portion of the till are likely similar to those described by Helmke and Simpkins (2004) for Wolf Creek Formation till at a quarry located 30 km south of the study site. Average fracture spacing was less than 5 cm at shallow depths and fracture spacing averaged 10.4 cm with a fracture density of 221 fractures per m^2 at deeper sample depths (Helmke and Simpkins, 2004). Whereas fracturing was not observed in UU till cored at the study site, fractures may have become too widely spaced to be detected by a vertical core.

Hydraulic Head and Vertical Gradients

The water table depth in 2002 averaged approximately 2.2 m and 1.8 m at the southern and northern well nests, respectively, typical of water table conditions monitored previously between 1988 to 1991 (Bowman, 1992). Groundwater occurs under unconfined conditions in the till and under confined conditions in the Devonian bedrock aquifer and in an inter-till sand at the north nest (Figure 10). The potentiometric surface of the bedrock aquifer is approximately 5-10 m above the top of the bedrock surface. The potentiometric surface in the sand unit at EI-7 is 0.5 m above the land surface and would be flowing if not for the well casing.

Vertical hydraulic gradients were downward from the water table to the Devonian bedrock aquifer at both well nest sites. Assuming that the potentiometric surface of the Devonian aquifer remained relatively constant between the nests, since hydraulic head was only measured at the south nest in EI-1, the average vertical gradient across the entire pre-Illinoian till section was similar at both sites, averaging approximately 0.95 downward. The vertical gradient through the unoxidized till, from the base of the oxidized till to the Devonian bedrock, was also similar at both nests, averaging 1.2 (Figure 10). Within the till section, variation in hydraulic gradient was evident (Figure 10). At the south nest, the vertical gradient was considerably lower in the oxidized till (0.03) than the overall gradient, and 0.09 in the unoxidized till. Indeed, most of the total head loss in the till section occurred at the base of the till section between the unoxidized till and Devonian bedrock contact. It is hypothesized that the head difference between the till and bedrock aquifer represents an underdrain phenomena, where groundwater in the unoxidized till was drained to the Devonian aquifer faster than recharge through the till replenished it. Vertical groundwater flow through 11 m of unoxidized till was not sufficient to keep pace with drainage from the bottom of the unoxidized till section to the lower aquifer.

At the north well nest, an upward hydraulic head was measured from the sand lense to the ground surface and a downward hydraulic gradient was maintained from the sand unit through the unoxidized till (Figure 10). The upward gradient at the north nest may be due to topographic effects since the land surface slopes to the north (Figure 3). In the unoxidized till, the downward vertical gradient at the north nest was nearly an order of magnitude greater than the vertical gradient in unoxidized till at the south nest (0.8 compared to 0.09) but the north nest vertical gradient was similar to the overall gradient from the base of the oxidized till to bedrock aquifer measured at both sites. It is possible that a similar underdrain zone above the bedrock surface may be present at the north nest. An estimate of the bedrock surface elevation and Devonian potentiometric head at the north nest hints that a similar loss of

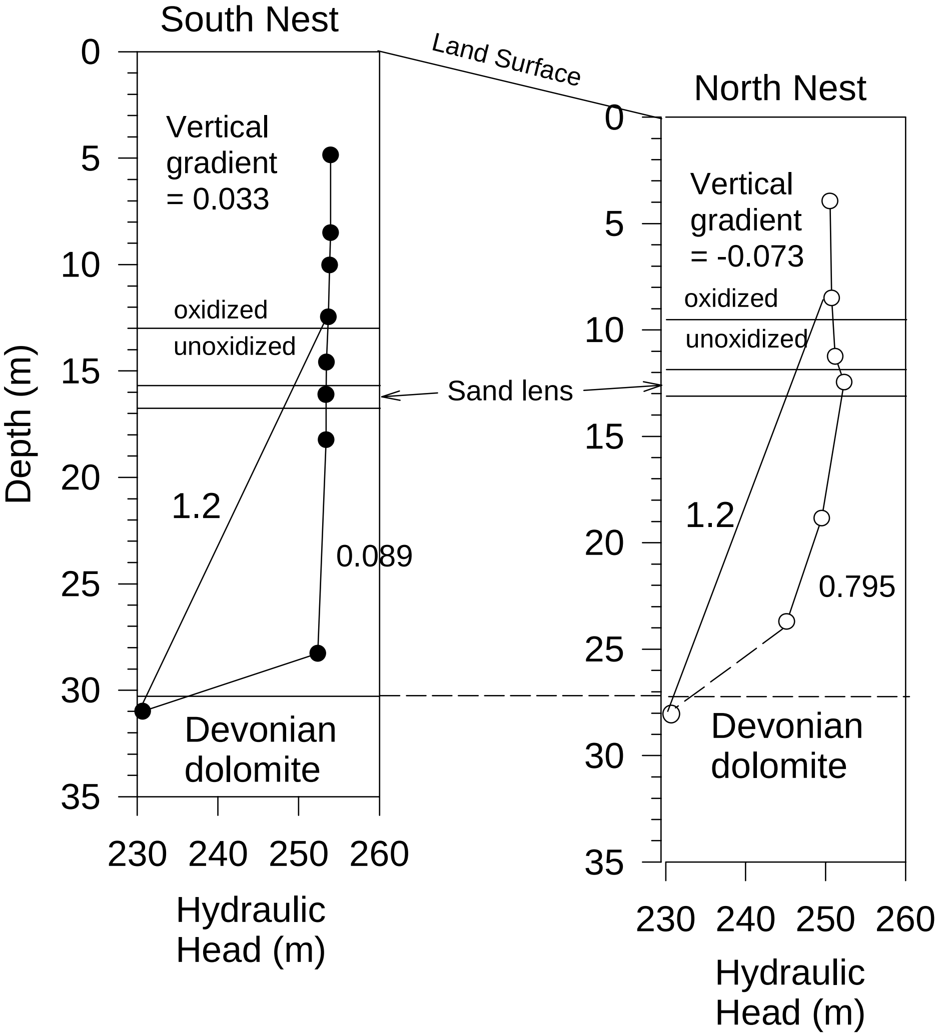

Figure 10. Summary of hydraulic head measurements and vertical gradients at the southern and northern well nests.

hydraulic head may be present at the base of the till section at this location (Figure 10). However, additional wells in the unoxidized till and Devonian bedrock aquifer are needed to confirm this condition.

Hydraulic gradients measured in pre-Illinoian till are similar to vertical gradients measured in pre-Illinoian till in central Iowa and younger Wisconsin-age tills in Iowa, Wisconsin, and Canada. In central Iowa, the vertical gradient through a deeper pre-Illinoian till unit buried by younger loess and till was greater than 1, whereas younger Wisconsin till at the same site had vertical gradients less than 0.06 (Simpkins et al., 1993). In Wisconsin, overall vertical hydraulic gradients at five sites ranged from 0.11 to 0.76, with steeper gradients apparent with depth (up to 1.1) (Simpkins and Bradbury, 1992). Wisconsin-age Battleford till in Saskatchewan, Canada had a vertical gradient of 0.014 (Shaw and Hendry, 1998) whereas gradients in weathered and unweathered tills in

Alberta ranged from 0.02 to 0.03 and 0.7 to 1.5, respectively (Hendry, 1988). Hence, the range of vertical gradients measured in oxidized and unoxidized pre-Illinoian till are consistent with those measured at other till monitoring sites.

Hydraulic Conductivity

The K test results with depth indicate that K decreases substantially from oxidized to unoxidized till (Figure 11). Oxidized pre-Illinoian till had a K ranging from 8 x 10^{-8} m/s to 5 x 10^{-7} m/s with a geometric mean of 1.2 x 10^{-7} m/s. In contrast, K measured in four unoxidized till wells ranged from 3 x 10^{-9} to 2 x 10^{-10} m/s with a geometric mean of 4.5 x 10^{-10} m/s, a mean more than two orders of magnitude lower than oxidized and fractured till. Similarly, unoxidized pre-Illinoian till in central Iowa was found to have a K of 3 x 10^{-11} m/s (Simpkins et al., 1993). The presence of fractures and textural heterogeneity (sand seams) contribute to higher K in the OU till. The higher K values in oxidized till and lower K in unoxidized till is consistent with measured hydraulic heads that showed a refraction of hydraulic gradient across the oxidized/unoxidized till boundary. Interbedded sand lenses had higher K's than the till, with K in both north and south units between 1-2 x 10^{-6} m/s (Figure 11). Devonian carbonate bedrock had a K of 6.1 x 10^{-7} m/s.

Average Linear Velocity

The average linear velocity (V) of groundwater through pre-Illinoian till was calculated using Darcy's Law:

$$V = - Ki/n$$

where K and i are field measured hydraulic conductivity and hydraulic gradient of oxidized and unoxidized till and n is porosity. Recent work of Helmke et al. (2004) measured porosity of Iowa till units and reported n of weathered and unweathered pre-Illinoian till ranging from 0.29 to 0.31. Herein, a porosity of 0.3 was assumed for pre-Illinoian till consistent with laboratory-measured values. Effective porosity was not considered in this study, which would have resulted in higher groundwater flow velocities. At the south well nest, the average downward groundwater velocity through oxidized till was calculated to be 0.38 m/yr based the geometric mean K of oxidized till, average i of 0.03 and estimated n of 0.3. The estimated groundwater age at the base of the oxidized till at the south nest was approximately 34 years.

Groundwater velocity through unoxidized pre-Illinoian till was estimated using specific hydraulic gradients determined at each well nest and the overall unoxidized till gradient estimated at both nests. At the south nest, the average downward groundwater velocity was calculated to be 0.4 cm/yr based on the geometric mean K of unoxidized till, average i of 0.09 and

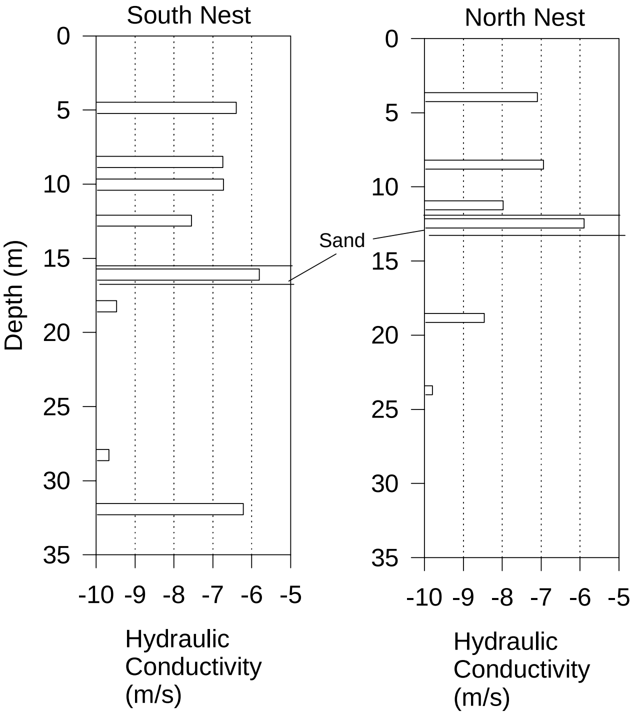

Figure 11. Summary of hydraulic conductivity measurements in pre-Illinoian till monitoring wells.

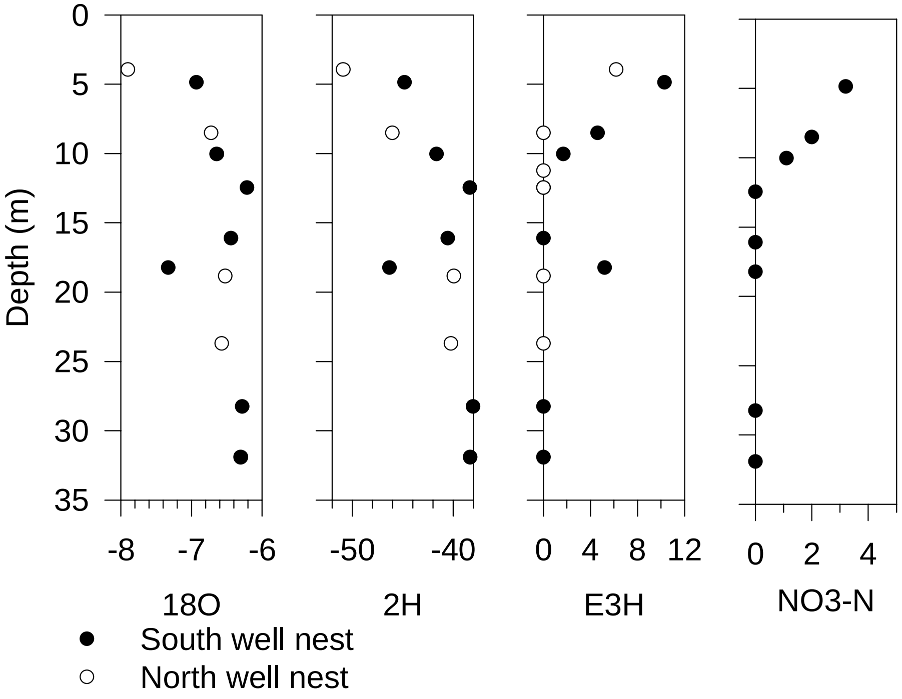

Figure 12. Isotopes of 18O, 2H, and 3H and nitrate concentrations measured in south and north well nests.

estimated n of 0.3. At the north nest, a larger downward hydraulic gradient of 0.8 resulted in a higher groundwater flow velocity of 3.8 cm/yr. Considering an average hydraulic gradient of 1.2 from the base of oxidized till to Devonian bedrock aquifer at both nest sites, the average downward groundwater velocity through the unoxidized pre-Illinoian till was 5.7 cm/yr. From the thickness of unoxidized till at both sites (approximately 17 m), the estimated groundwater age at the base of the till ranged from approximately 3,950 years to 298 years under vertical hydraulic gradients of 0.09 and 1.2, respectively. The differences in estimated groundwater age at the base of oxidized and unoxidized till suggest that groundwater circulation through oxidized and fractured till is more active and reflects relatively recent recharge (<50 years) whereas groundwater flow through unoxidized till is much slower and reflects recharge centuries to millennia old.

Isotopic and Chemical Tracers

Environmental isotopes of hydrogen (2H, 3H) and oxygen (18O) and occurrence of nitrate-nitrogen in groundwater provide constraints on groundwater flow velocities estimated with Darcy's Law.

Tritium

While tritium data (3H) alone are not sufficient for definitive age determinations (Simpkins and Bradbury, 1992), they provide an estimate of the amount of time since precipitation recharged groundwater. Atmospheric testing of nuclear weapons from 1953 to the early 1960's produced a large amount of tritium (several thousand tritium units or TU) in the atmosphere that has since declined from radioactive decay to background levels of 20-30 TU. Groundwater recharged at the height of bomb testing in 1962

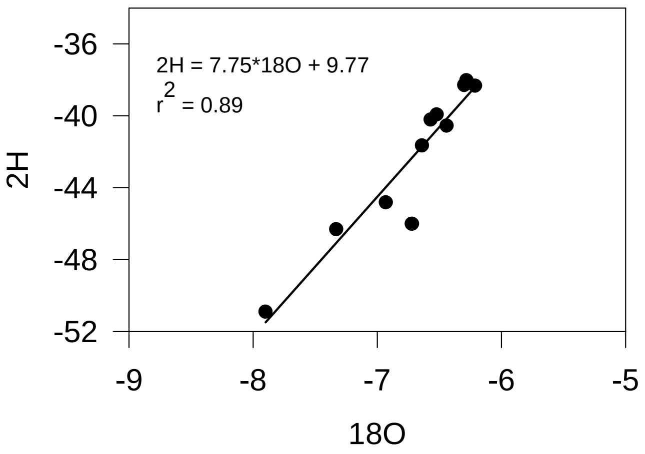

Figure 13. Local meteoric water line determined from December 2, 2003 groundwater samples.

would be expected to have a tritium concentration greater than 100 TU today. Due to the short half life of tritium (12.4 years) water that entered groundwater system before 1953 would have tritium concentrations less than 2 TU now. Hence, in many groundwater studies, concentrations of tritium are used to identify “pre-bomb” vs “post bomb” water, that is, water recharged before or after about 1953 (greater or less than 50 years old).

Tritium concentrations were detected in five wells at the till study site, declining with depth at the south nest from 10.3 TU at EI-20 to 1.7 TU at EI-18 (Figure 12). Concentrations were less than the detection limit of 0.8 TU at a depth of 11.5 m at EI-17. Tritium values in the 10-12 TU range in Iowa were reported by Tomer and Burkart (2003) to represent water aged less than 20 years old, whereas water with tritium activity between 2 and 10 TU were likely samples with recent or mixed-age waters. Tritium activities less than 1 TU were considered indicative of pre-bomb water. However, a tritium concentration of 5.2 TU was observed in the unoxidized till in well EI-3 indicative of post-bomb water. Recent recharge water in this well may represent groundwater flow through fractures or other secondary porosity in the unoxidized till or vertical transport through the well annular space. At the north nest, a single sample from the shallowest till well (EI-24) had a tritium concentration of 6.2 TU, whereas all other till water samples had concentrations less than 0.8 TU.

Tritium data from the south nest suggest that groundwater at a depth of 9.1 m was recharged less than 50 years ago, representing a velocity of about 0.2 m/yr. This velocity estimate is similar to that calculated for oxidized till from hydraulic data. At the north nest, the upward hydraulic gradient measured in the oxidized till may be retarding downward groundwater transport of tritium in recharge water. Other solute transport factors, such as matrix diffusion, may also complicate groundwater age determinations using tritium (Simpkins and Bradbury, 1992).

Stable Isotopes

Stable isotope concentrations ranged from –6.2 to –7.9‰ for 18O and from –38.0 to –50.9‰ for 2H and averaged -6.7‰ and -42.3‰, respectively (Figure 12). Values of 18O and 2H plot on a local meteoric water line (LMWL) (Figure 13). The LMWL equation is similar to those developed in central Iowa by Simpkins (1995) (D = 7.518O + 5.1) and western Iowa by Tomer and Burkart (2003) (D = 8.2 18O + 9.1) and the average isotope values are also similar to published values. The regression of the LMWL is significant ($p<0.05$; $r^2 = 0.89$). The distribution of the stable isotope data around the LMWL suggests that no substantial evaporative enrichment of groundwater relative to local precipitation occurred since recharge.

Stable isotope profiles indicate a shift toward less negative 18O values with depth (Figure 12). Most shift in isotopic composition occurs within the upper 10 m of the profile and within the oxidized till zone. With exception of a south well nest sample at 17 m (EI-3), the isotope profiles in unoxidized till varied little with depth, averaging approximately -6.4 to -6.6‰

for 18O. Assuming the values in the water table wells at both nest sites to be indicative of modern precipitation (-6.9 to –7.9‰), the oxygen isotope value in EI-3 (-7.3‰) also appears to be modern. This would confirm the tritium data and suggest that modern water has migrated into the unoxidized till at EI-3 through either fractures or well casing. The isotopic composition of modern recharge inferred from water table values is about 1 per mil more negative compared to unoxidized till water and suggests that modern recharge is isotopically different than recharge occurring centuries to millennia ago. A 1 per mil decrease in 18O was measured in lacustrine calcite at Lake Mendota (Wisconsin) over the last century and correlated to changing regional climate patterns and increased precipitation (Smith and Hallander, 1999). It is unknown whether the 1 per mil difference in 18O in unoxidized till water is attributable to changing climatic conditions over timeframes ranging from the last 100 years to the mid-Holocene. Increased resolution of the stable isotope precipitation record since the mid to late Holocene is needed to resolve a possible climate signal contained in the till water profile. Nonetheless, the stable isotope record documents a modern climate signal confined to the oxidized zone and supports the interpretation of recent groundwater circulation in this zone compared to deeper unoxidized till water.

Nitrate-Nitrogen

Occurrence of nitrate-nitrogen (nitrate) in wells is often used as a proxy for identification of groundwater zones vulnerable to recent contamination. Rodvang and Simpkins (2001) reviewed the occurrence of common agricultural contaminants in Quaternary aquitards and reported that agricultural nitrogen contamination from fertilizers and manure is greater in weathered oxidized zones than unoxidized zones. Thick unweathered aquitards were found to provide a barrier against migration of surficial contaminants to aquifers. In Iowa, a rural well water survey reported that nitrate concentrations varied with well depth. The percentage of wells with nitrate above 3 mg/l was considerably greater in shallow wells (<50 ft deep) than wells >50 feet deep (Kross et al., 1990). Although geochemical processes may affect nitrate concentrations in groundwater (e.g., denitrification), occurrence of nitrate in till water is often related to weathering zones and well depth and suggests zones of recent groundwater circulation may be identified by nitrate contamination. In the pre-Illinoian till water, nitrate concentrations were detected in three samples at the south nest at depths less than 9.1 m (Figure 12). The concentration profile decreased with depth and followed the same depth profile as tritium. Both nitrate and tritium decreased below detectable concentrations between 9.1 and 11.6 m in the oxidized till (Figure 12). Nitrate was not detected in shallow groundwater at the north nest.

Implications for Aquifer Protection by Pre-Illinoian Till

Groundwater velocity determinations derived from hydraulic gradient and slug test measurements and isotopic and chemical sampling indicates that the pre-Illinoian till section at the study site is comprised of two distinct groundwater zones. The upper oxidized zone above 11.5 m is a zone of recent groundwater recharge (<30 to 50 years old). Groundwater flow velocity in oxidized pre-Illinoian till was estimated to range from 0.2 to 0.4 m/yr. In contrast, the groundwater age of water in unoxidized pre-Illinoian till may be on the order of centuries to millennia old with flow velocities ranging from 0.4 to 5.7 cm/yr. Thus, it is evident that protection of underlying bedrock aquifers from surficial contamination in pre-Illinoian landscapes must be dependent upon the thickness of unoxidized zone if protection for periods longer than 50 years is required.

The feasibility of mapping the extent of unoxidized pre-Illinoian till in Linn County was assessed to determine if thickness of unoxidized

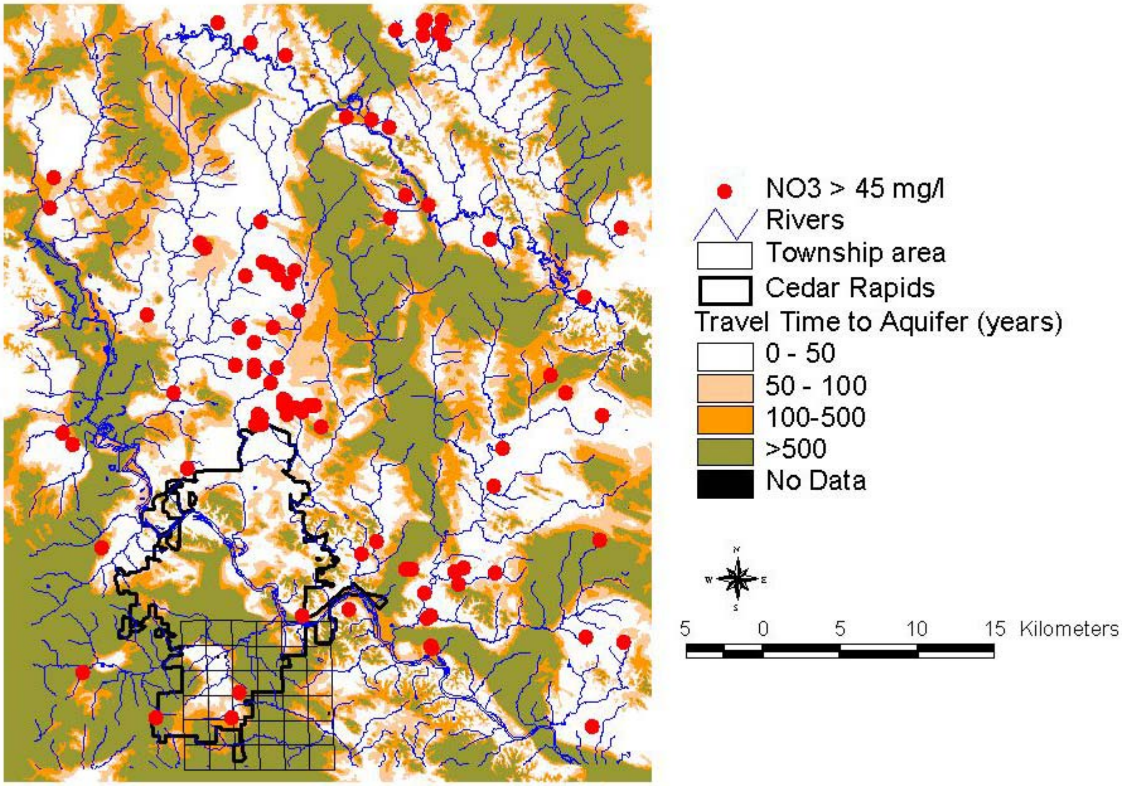

Figure 14. Estimated vertical travel time from the ground surface to bedrock aquifer in Linn County. Nitrate concentrations detected greater than 45 mg/l in private wells are shown.

till could be obtained from readily available data. If thickness could be assessed, a second goal was to evaluate the effectiveness of unoxidized till thickness to prevent surficially derived contamination from entering local bedrock aquifers. Lithologic logs were obtained from the Iowa Geological Survey's Geosam database (http://gsbdata.igsb.uiowa.edu/geosam/) for the township area (93.2 km2) of Linn County that contained the study site (Figure 14). Logs were selected for analysis if the driller noted the depth of the contact between oxidized and unoxidized till (often described by a color difference). From a total of 26 logs that met selection criteria in the township, the depth to bedrock, total till thickness and the thickness of unoxidized till was recorded. Total till thickness was determined by removing the loess thickness from the depth to bedrock thickness and any other coarse-grained zones noted in the lithologic log. Significant linear relations were developed relating the unoxidized till thickness to bedrock depth and total till thickness (Figure 15). Results indicated that unoxidized till did not occur at sites where the bedrock depth was less than approximately 12 m or where the total till thickness did not exceed 15 m. The thickness of oxidized till determined in this manner was very similar to conditions measured independently at the study site through core drilling. We estimated the thickness of unoxidized pre-Illinoian till in Linn County by subtracting the bedrock surface from the land surface elevation in a geographic information system (GIS) and using the relation of unoxidized till thickness to bedrock depth. The

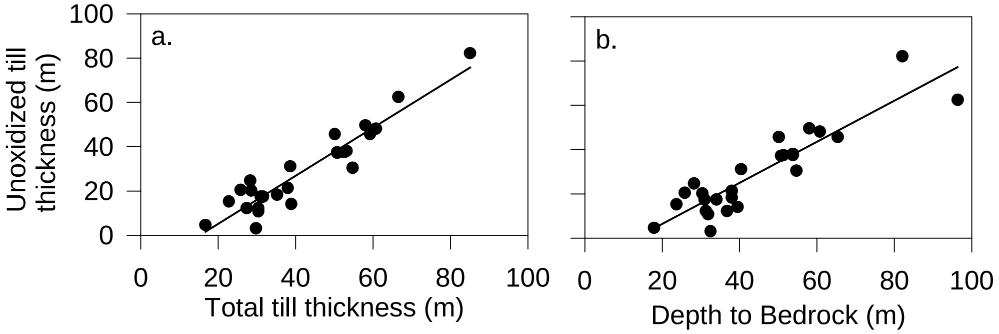

Figure 15. Relation of unoxidized pre-Illinoian thickness to (a) total till thickness and (b) depth to bedrock in township area containing till hydrology site.

thickness of unoxidized till in Linn County was then contoured using the estimated velocity of 5.7 cm/yr. Thus a map of Linn County was produced that showed the estimated vertical travel time through the unoxidized till to the bedrock aquifer (Figure 14). Any bedrock area overlain by less than 12 m of overburden material was considered vulnerable to contamination with vertical travel times less than 50 years.

To evaluate the effectiveness of the map to identify protected and vulnerable bedrock aquifers, private well nitrate results from shallow bedrock wells from Linn County were plotted (Figure 14). The results indicated a close relationship between vulnerable bedrock aquifer regions and the absence of substantial thickness of unoxidized pre-Illinoian till. Nitrate concentrations in excess of drinking water standards were clustered in regions with little or no unoxidized till cover. Likewise, water supply wells were protected from surficial contamination in thick unoxidized till zones in Linn County.

HYDROGEOCHEMISTRY

Sediment Geochemistry

Typical matrix properties of pre-Illinoian Wolf Creek Formation deposits have been established in eastern Iowa and indicate a clay mineral composition dominated by expandable clay minerals (i.e., smectites) (62%) with less illite (17%) and kaolinite + chlorite (21%) (Hallberg, 1980). Sand fraction lithologies have typically shown more variation within the Wolf Creek Formation than clay minerals, but consist largely of crystalline grains (quartz plus feldspar, igneous and metamorphic grains) with equal amounts of carbonate and sedimentary grains (15-27%) (Hallberg, 1980). Calcite/dolomite (C/D) ratios in the till matrix are also variable, but are typically dominated by calcite with ratios ranging from 1 to greater than 15 (Hallberg, 1980). In general, sand fraction lithologies and C/D ratios have been most useful for distinguishing among members of the Wolf Creek Formation.

In this study, concentrations of major ions and metals (Table 4) and nutrients (Table 5) measured in the pre-Illinoian till at our study site showed variability in some constituents and relative consistency in others. Sulfate concentrations in sediment increased substantially from OU to UU till, with the lower portion of UU till having SO4 concentrations nearly two orders of magnitude higher than upper OU till (2400 mg/kg; Table 4). Other than leached calcium from the OL zone, other major ion concentrations in soil were relatively consistent throughout the till section. Arsenic was detected in pre-Illinoinan till at concentrations ranging between 3.2 to 7.4 mg/

Table 4. Sediment solids concentrations in pre-Illinoian till collected from core EI-2.

Depth		**Solids Concentration (mg/kg by dry wt)**																	
(m)	**WZ**	**Fl**	**Cl**	**Br**	**SO4**	**Ca**	**Fe**	**Mg**	**Mn**	**Na**	**K**	**As**	**Ba**	**Cd**	**Cr**	**Pb**	**Hg**	**Se**	**Ag**
1.1	OL	<10	<10	<10	10	2700	22000	2000	400	<50	0.1	4.8	77	<2	20	<10	<1	<1	<1
4.1	OU	<10	<10	<10	11	38000	17000	10000	200	58	0.1	5.4	40	<2	14	<10	<1	<1	<1
7.0	OU	<10	<10	<10	<10	27000	14000	7000	200	<50	<1	3.2	40	<2	10	<10	<1	<1	<1
10.0	OU	<10	<10	<10	32	36000	19000	9000	230	100	0.12	4.8	63	<2	14	<10	<1	<1	<1
11.7	OU	<10	<10	<10	98	38000	18000	10000	230	130	0.14	4.8	51	<2	15	<10	<1	<1	<1
14.3	UU	<10	<10	<10	210	48000	16000	11000	270	120	0.14	5.3	58	<2	13	<10	<1	<1	<1
17.6-22.8	UU	<10	<10	<10	2400	29000	19000	6300	380	140	0.11	7.4	49	<2	21	<10	<1	<1	<1
22.8-29.8	UU	<10	<10	<10	2100	24000	17000	4400	370	110	0.11	6.8	42	<2	19	<10	<1	1	<1

WZ = weathering zone

kg (Table 4) with slightly higher concentrations found in UU till. Barium (40-77 mg/kg) and chromium (10-21 mg/kg) were similarly detected in all till samples, but with the exception of selenium detected at 1 mg/kg in the lowest UU sample, no other heavy metals were found above laboratory detection limits (Table 4).

Concentrations of N in pre-Illinoian till showed vertical variation in terms of ammonium and organic nitrogen (Kjeldahl nitrogen) (Table 5). Ammonium concentrations increased significantly in UU till from less than 5 mg/kg in OL and OU samples to 210-1100 mg/kg in UU till. Conversely, organic N concentrations decreased with depth from 930 –1900 mg/kg in OL and OU till to 250-780 mg/kg in UU till. No concentrations of oxidized N (nitrite and nitrate nitrogen) were detected above 10 mg/kg in any pre-Illinoian till samples. Total phosphorus in all soil samples ranged from 260 to 960 mg/kg, whereas total organic carbon (TOC) concentrations ranged from 490 to 7800 mg/kg. TOC concentrations nearly doubled from OU to UU till.

Aqueous Geochemistry

Aqueous concentrations of major and minor ions and metals, and nutrients, in pre-Illinoian till and Devonian bedrock are shown in Tables 6 and 7, respectively. With exception of elevated Ca^{2+} in EI-20 and EI-22 (120 mg/l), concentrations of major cations, Ca^{2+}, Mg^{2+}, K^{+},

Table 5. Nutrient concentrations in pre-Illinoian till collected from core EI-2.

Depth	Weathering	**Solids Concentrations (mg/kg by dry wt)**				
(m)	Zone	NH3	NO2+NO3	Kjed N	Total P	TOC
1.1	OL	<5	<10	1900	450	1000
4.1	OU	<5	<10	1100	960	490
7.0	OU	<5	<10	1600	260	2900
10.0	OU	<5	<10	1100	370	4300
11.7	OU	<5	<10	930	420	4100
14.3	UU	13	<10	780	300	6700
17.6-22.8	UU	1100	<10	250	360	7800
22.8-29.8	UU	210	<10	260	330	7300

Table 6. Water concentrations measured in pre-Illinoian till monitoring wells and upper Devonian bedrock. All concentrations in mg/l, except alkalinity which has units of mg/l as CaCO3. Wells EI-20 to EI-1 are located at south well nest and EI-24 to EI-5 are located at north well nest site.

Well No.	Depth (m)	Weathering Zone	Alk	Ca	Mg	K	Na	Fe	Mn	SO4	Cl	F	Br
EI-20	4.9	OU	510	120	31	3.7	9.6	<0.02	<0.02	49	16	<0.5	<0.5
EI-19	8.5	OU	270	58	18	1.7	35	<0.02	<0.02	30	2.7	<0.5	<0.5
EI-18	10.0	OU	280	66	22	1.8	15	<0.02	0.03	17	1.8	0.5	<0.5
EI-17	12.5	OU	300	61	19	2.1	33	<0.02	<0.02	22	1	0.7	<0.5
EI-4	16.1	UU	390	65	19	2.8	15	0.68	0.8	10	1.2	0.7	<0.5
EI-3	18.2	UU	300	85	19	3.5	15	<0.02	<0.02	21	8.7	<0.5	<0.5
EI-2	28.3	UU	330	75	19	3.5	39	0.04	0.23	36	2.9	<0.5	<0.5
EI-1	31.9	Bedrock	340	85	24	4.8	38	8.9	0.19	89	2.3	<0.5	<0.5
EI-24	4.0	OU	370	98	26	3.4	8.7	<0.02	<0.02	22	4.4	<0.5	<0.5
EI-23	8.5	OU	300	69	23	2.6	19	<0.02	0.14	9.2	0.8	0.7	<0.5
EI-22	11.2	UU	300	120	37	2.5	26	<0.02	0.37	5.2	0.7	0.7	<0.5
EI-7	12.5	UU	290	66	20	2.4	14	<0.02	0.08	5	0.7	0.7	<0.5
EI-6	18.8	UU	310	78	22	3.5	28	0.1	0.64	120	4.3	<0.5	<0.5
EI-5	23.7	UU	360	69	18	3.4	53	<0.02	0.11	25	1.5	<0.5	<0.5

Well No.	Depth (m)	Weathering Zone	Ba	Cr	Se	Pb	Cd	As	Hg	Sil
EI-20	4.9	OU	0.14	<0.01	<0.01	<0.01	<0.01	<0.001	<0.00005	<0.001
EI-19	8.5	OU	0.2	<0.01	<0.01	<0.01	<0.01	<0.001	<0.00005	<0.001
EI-18	10.0	OU	0.31	<0.01	<0.01	<0.01	<0.01	<0.001	<0.00005	<0.001
EI-17	12.5	OU	0.18	<0.01	<0.01	<0.01	<0.01	<0.001	<0.00005	<0.001
EI-4	16.1	UU	0.22	<0.01	<0.01	<0.01	<0.01	0.001	<0.00005	<0.001
EI-3	18.2	UU	0.13	<0.01	<0.01	<0.01	<0.01	0.002	<0.00005	<0.001
EI-2	28.3	UU	0.08	<0.01	<0.01	<0.01	<0.01	0.002	<0.00005	<0.001
EI-1	31.9	Bedrock	0.08	<0.01	<0.01	<0.01	<0.01	0.002	<0.00005	<0.001
EI-24	4.0	OU	0.17	<0.01	<0.01	<0.01	<0.01	<0.001	<0.00005	<0.001
EI-23	8.5	OU	0.26	<0.01	<0.01	<0.01	<0.01	0.001	<0.00005	<0.001
EI-22	11.2	UU	0.46	<0.01	<0.01	<0.01	<0.01	<0.001	<0.00005	<0.001
EI-7	12.5	UU	0.23	<0.01	<0.01	<0.01	<0.01	<0.001	<0.00005	<0.001
EI-6	18.8	UU	0.12	<0.01	<0.01	<0.01	<0.01	0.002	<0.00005	<0.001
EI-5	23.7	UU	0.09	<0.01	<0.01	<0.01	<0.01	0.002	<0.00005	<0.001

Na^+, were within a relatively narrow range of values throughout the till water profile (Table 6). Dissolved Mn^{2+} was found in most UU wells at detected concentrations ranging between 0.08 to 0.8 mg/l, whereas Fe^{2+} was detected in EI-4 (0.68 mg/l), EI-2 (0.04 mg/l) and EI-6 (0.1 mg/l) only. Highest ferric iron was detected in Devonian limestone well EI-1 at 8.9 mg/l; however, it must be noted that the well casing for this well consists of 8-inch diameter iron pipe which may have biased the Fe concentration. Highest Fe^{2+} and Mn^{2+} concentrations in the pre-Illinoian section were found in a UU sand layer within the UU till at the south well nest (EI-4; Table 6).

Alkalinity and sulfate were the dominant anions in the till section, with both constituents exhibiting a wide range of values (Table 6). Highest alkalinity was detected in EI-20 (510 mg/l as $CaCO_3$), but other wells ranged within a narrower field of 270-390 mg/l as $CaCO_3$. Sulfate concentrations ranged from 5 to 120 mg/l, and a similar vertical concentration pattern was evident at both well nests. Sulfate generally

Table 7. Water nutrient concentrations (in mg/l) measured in pre-Illinoian till monitoring wells and upper Devonian bedrock. Wells EI-20 to EI-1 are located at south well nest and EI-24 to EI-5 are located at north well nest site.

Well No.	Depth (m)	Weathering Zone	NH4	NO3-N	NO2-N	Org.N	OrthoP	Tot. P	TOC
EI-20	4.9	OU	<0.05	3.2	<0.5	1.3	<0.02	0.08	6.3
EI-19	8.5	OU	<0.05	2	<0.5	0.23	<0.02	0.06	1.9
EI-18	10.0	OU	<0.05	1.1	<0.5	0.2	0.03	0.04	1.6
EI-17	12.5	OU	<0.05	<0.5	<0.5	0.13	0.03	0.05	1.5
EI-4	16.1	UU	0.23	<0.5	<0.5	0.16	<0.02	0.04	1.8
EI-3	18.2	UU	<0.05	<0.5	<0.5	0.43	0.02	0.05	4
EI-2	28.3	UU	0.29	<0.5	1.1	0.26	-	0.03	2
EI-1	31.9	Bedrock	3.6	<0.5	<0.5	1.4	<0.02	0.04	5.5
EI-24	4.0	OU	<0.05	<0.5	<0.5	1.4	0.03	0.07	7.4
EI-23	8.5	OU	<0.05	<0.5	<0.5	0.68	0.02	0.04	3.7
EI-22	11.2	UU	0.17	<0.5	<0.5	0.5	<0.02	0.03	2.6
EI-7	12.5	UU	0.18	<0.5	<0.5	0.85	<0.02	0.03	4.1
EI-6	18.8	UU	0.28	0.7	<0.5	0.77	-	<0.02	3.8
EI-5	23.7	UU	0.08	1.4	<0.5	0.78	<0.02	<0.02	3.5

decreased from higher values at the water table to lowest values measured in an interbedded UU sand, then increased again with depth in the UU till. Highest sulfate concentration (120 mg/l) was detected in a UU till water sample at 18.8 m (EI-6; Table 6). Chloride was detected within a narrow range of values in all wells (0.7-8.7 mg/l), except EI-20 (16 mg/l), whereas fluoride was found at concentrations slightly above the detection limit in six wells (0.5-0.7 mg/l).

Arsenic and barium were the only heavy metals found above laboratory detection limits (Table 6). In the south nest, arsenic was detected in UU till at 0.001 to 0.002 mg/l, and in the north nest arsenic was found in UU till and a single OU till water sample at similar levels. Barium concentrations were ubiquitous in all water samples at concentrations ranging between 0.08 to 0.46 mg/l. Concentrations of chromium, selenium, lead, cadmium, mercury and silver were not detected in any pre-Illinoian groundwater above detection limits.

Differentiation in groundwater in OU versus UU till was particularly evident in nitrogen speciation in till water (Table 7). Ammonium was exclusively detected in unoxidized till water at concentrations between <0.05 to 0.29 mg/L and not detected in oxidized till (<0.05 mg/l). A single detection of nitrite was also measured in EI-2 at 1.1 mg/l. In contrast, nitrate was found at the south well nest in oxidized till only to a depth of 10 m. At the north nest, nitrate was only detected in UU wells EI-5 and EI-6, but this was most likely an artifact of slow water recovery rates in the well water column. Ammonium in these wells was probably converted to nitrate during water level recovery as ammonium-rich groundwater slowly entered the well column and gained exposure to the atmosphere, oxidizing to nitrate. Considering the apparent NO_3-N concentration produced in EI-5 and EI-6, ammonium concentrations may have exceeded 1 mg/l in the UU till at this location. Highest organic N concentrations were measured in shallow water table wells (1.3-1.4 mg/l), with largely consistent values measured deeper through the till profile (0.13-0.85 mg/l).

Total phosphorus and orthophosphorus concentrations were generally clustered near their detection limits of 0.02 mg/l (Table 7). Detected orthophosphorus concentrations were measured in five wells at values between 0.02 and 0.03 mg/l, whereas total phosphorus concentrations were measured in all but two UU wells (EI-5 and EI-6) at 0.03 to 0.08 mg/l. Highest TOC values were again measured in the two shallowest wells, but concentrations were fairly low throughout the till section between 1.5 and 4.1 mg/l (Table 7).

Pre-Illinoian Till as a Geochemical Barrier to Contamination

The boundary between oxidized and unleached till (OU till or weathered zone) and unoxidized and unleached till (UU till or unweaterhed zone) has been termed a “redoxcline” (Postma et al., 1991) and is useful when describing differences between oxidized and reduced zones (Robertson et al., 1996; Rodvang and Simpkins, 2001). Loss of nitrate from denitrification often occurs at the redoxcline in aquitards. From sediment core classification of weathering zones, a redoxcline occurred at a depth of 12.2 m at the south nest and 8.7 m at the north nest in the pre-Illinoian till. Sediment samples collected from the south well nest support the observational data. Sediment sulfur and ammonium content increased substantially in the unweathered till (Tables 4 and 5). Sharp increase in sediment sulfur at the redoxcline has been observed by others (Postma et al., 1991; Robertson et al., 1996) and reflects leaching of reduced sulfur from weathered till sediment. Pyrite is common in unweathered Quaternary aquitards (Rodvang and Simpkins, 2001; Hendry and Wassenaar, 2000) and in Iowa till (Simpkins and Parkin, 1993). Given the length of time since deposition of pre-Illinoian till occurred (>500,000 years), most of the original disseminated sulfur in the pre-Illinoian till was probably oxidized and leached from the weathered zone as evidenced by sediment SO_4 concentrations increasing from <10 mg/kg in weathered till to 2400 mg/kg in unweathered till. Furthermore, an abrupt increase in ammonium concentrations in pre-Illinoian sediment at the redoxcline boundary suggests that oxidation of available ammonium has proceeded to near completion in the weathered zone. Ammonium concentrations in weathered till were less than the detection limit of 5 mg/kg. In unweathered till, mineralization (ammonification) of organic nitrogen by microorganisms may still be occurring as evidenced by the associated loss of organic N with high ammonium in sediment.

Total organic carbon (TOC), also referred to as solid organic carbon (Robertson et al., 1996; Rodvang and Simpkins, 2001) or particulate organic carbon (Simpkins and Parkin, 1993), increased slightly below the redoxcline in pre-Illinoian till. The trend in sediment TOC was subtle compared to sulfur and ammonium and may indicate that most of the TOC remaining in the till consists of higher molecular weight organic compounds resistant to oxidation (Robertson et al., 1996). In younger Wisconsin till and loess in central Iowa, high dissolved carbon concentrations (up to 54 mg/l) are attributable to degradation of wood and labile organic carbon disseminated in the glacial materials (Simpkins and Parkin, 1993). In the considerably older pre-Illinoian till, much of the labile organic carbon was likely oxidized and removed from the till section. It is unknown if TOC concentrations in unweathered UU till ranging up to 7300 mg/kg represent relict TOC levels in pre-Illinoian till. However, given the age of the till it is more likely that TOC concentrations in sediment were reduced substantially since till deposition and probably consisted of TOC concentrations typical of more recent glacial sediments.

Water samples collected from the till profile indicate that water quality differences have developed at the redoxcline due to denitrification. Rodvang and Simpkins (2001) point out that the loss of nitrate at the redoxcline is accompanied by decreased dissolved oxygen, increasing Fe^{2+} and decreasing redox potential in unweathered till. Furthermore, they reference an increase in Mn^{2+}, NH_4^+ and As^{3+} below the redoxcline in Alberta tills (Rodvang et al., 1998 in Rodvang and Simpkins, 2001). These conditions were all detected in pre-Illinoian till water at both south and north well nests. Nitrate was observed in the upper 10-12 m of OU till whereas NH^{4+} and nitrite were detected in UU till water. DO concentrations decreased below 1 mg/l at the redoxcline and ORP was found to be highly reducing (<0 mv) in UU wells that were allowed to recover from purging for long periods of time. Measured ORP in UU water samples less than 100 mv are consistent with moderately reducing ORP conditions that favor denitrification (Robertson et al., 1996). Fe^{2+}, Mn^{2+} and As^{3+} were all detected in UU water samples at levels exceeding OU concentrations.

However, Rodvang and Simpkins (2001) suggested that older pre-Illinoian tills typically show no evidence for denitrification owing to insufficiently labile organic carbon compared to younger tills. It was evident that TOC concentrations in pre-Illinoian till water at the eastern Iowa site were not particularly high (less than 7.4 mg/l) and that given the age of the till, remaining TOC in water and sediment would appear to be inadequate as an electron donor for significant heterotrophic denitrification. This would argue that TOC may not be the preferred electron donor but rather like Wisconsin till in southern Ontario (Robertson et al., 1996) reduced sulfur in the till sediment may support autotrophic denitrification in the reaction:

$$5FeS_2 + 14NO_3- + 4H^+ = 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_20$$

Supporting this hypothesis, an abrupt increase in sedimentary sulfur was observed at the redoxcline and relatively little change in TOC or alkalinity across the boundary was noted. Highest Fe^{2+} (and Mn^{2+}) concentrations were also observed just below the redoxcline in a UU intertill sand (EI-4). However, soluble SO^{2-} was not present at elevated concentrations near the redoxcline as predicted by the equation, but rather quite the opposite since concentrations were lowest in this zone (Table 4). Where did the sulfate go? An increase in soluble sulfur with depth, particularly noted in well EI-6 (120 mg/l), suggests that SO4 may have migrated downward into the till. It is possible that re-precipitation of soluble S into pyretic S may also occur during downward transport into reduced glacial till.

Pre-Illinoian Till as a Source of Contamination

Background Water Quality

Many municipal landfills in eastern Iowa, including Linn County landfill, have excavated into pre-Illinoian till for disposal of municipal solid waste. Operators have installed monitoring wells around the perimeter of the landfills and are required by Iowa Code to monitor groundwater for select indicator parameters (temperature, pH, SC, Cl^-, SO_4^{2-1}, NH_4^-, Fe^{2+}) and certain heavy metals. One method used for determination of landfill leachate migration away from the landfill is to reference water quality conditions in downgradient wells to upgradient background wells. Concentrations of indicator parameters or metals in excess of background conditions denote an impact to the groundwater resource. Although landfills are required to measure background water quality, groundwater mounding in the landfill often results in collection of questionable background concentration data. With no contaminant sources in the vicinity, it is reasonable to assume that conditions at the eastern Iowa till hydrology site represent typical background.

Results from this study suggest that concentrations of several parameters indicative of landfill leachate are found at detectable concentrations in background pre-Illinoian till water. While temperature, pH, SC, and Cl^- were clustered within relatively narrow ranges, NH_4^-, Fe^{2+} and SO_4^{2-} concentrations showed variability in till water. NH_4 was common in UU till water at concentrations averaging 0.18 mg/l (s.d. = 0.1). In other Quaternary aquitards, NH_4^- has been detected at concentrations higher than 5 mg/l, but these detections were commonly associated with recent Wisconsin till and loess materials (Schilling, 2002). Assuming that non-detected concentrations were one-half the detection limit, background concentrations of Fe^{2+} (mean = 0.7; sd = 2.4) and SO_4^{2-} (mean = 32.9; sd = 33.2), as well as NH_4^-, in pre-Illinoian till showed sufficient concentration and variability to caution against generalizations about using elevated NH_4, Fe^{2+} and SO_4 as indicators for landfill leachate migration.

In terms of heavy metals, with exception of barium and arsenic, concentrations were below laboratory method detection limits (Table 6). The detection of barium in all water samples suggests that this metal is rather ubiquitous in pre-Illinoian till water at a mean concentration of 0.19 mg/l (sd = 0.1). Arsenic was detected in several till water samples at a maximum concentration of 0.002 mg/l. Hence, detecting arsenic or barium in groundwater downgradient of a landfill may represent normal background conditions and not landfill leachate migration.

Pre-Illinoian Till as a Source of Nutrient Concentrations in Streams

As the major Quaternary aquitard beyond the extent of Wisconsin glaciation in central North America (Figure 1), streams have cut down into pre-Illinoian till and receive overland flow and baseflow derived from the till. Delivery of nutrients (N and P) to streams from pre-Illinoian till should be considered when loads from nonpoint sources are assessed. Delivery of N and P via surface runoff from a pre-Illinoian till landscape would primarily consist of organic nitrogen and phosphorus contained in eroded sediment in the range of 250-1900 mg/kg and 260-960 mg/kg, respectively. P concentrations are similar to the range of 364-550 mg/kg described by Hallberg (1980) for pre-Illinoian tills. Organic N and P inputs from eroded till would contribute to excessive total N and P loads in streams.

Baseflow from pre-Illinoian till delivers total nitrogen to streams in the form of nitrate and organic nitrogen from weathered till and ammonium and organic nitrogen from unweathered till. Total N (TN) contributions from pre-Illinoian baseflow would average approximately 1.8 mg/l from weathered till and 0.72 mg/l from unweathered till. Little variation in ortho-P or total P (TP) was observed in OU or UU till, but when detected, ortho-P was found at concentrations of 0.02 to 0.03 mg/l and TP concentrations varied from 0.03 to 0.08 mg/l. Concentrations of P from eastern Iowa pre-Illinoian till are similar to other Iowa Quaternary aquitards where P concentrations in fractured till had a median value of 0.04 mg/l (Burkart et al., 2004). Nutrient standards for streams are subject to debate, but one criterion recommends TN and TP standards set at 0.9 and 0.04 mg/l (Dodds and Welch, 2000). It can be seen that background concentrations from pre-Illinoian till water approach or exceed the recommended limit.

Pre-Illinoian Till as a Source of Contamination to Underlying Aquifers

Although unweathered pre-Illinoian till was found to be an effective geochemical barrier to nitrate migration to underlying aquifers, other constituents observed in UU till water may contribute to water quality impacts of underlying aquifers. As the oldest glacial deposits in North America, pre-Illinoian tills are often found draped on the bedrock surface or in buried bedrock channels in close proximity to aquifers. Hence, migration of naturally-occurring contaminants from pre-Illinoian till may potentially affect water quality of underlying aquifers. At our study site, several constituents were detected in both unweathered till and the underlying bedrock (well EI-1) at concentrations that approach or exceed water quality standards. Although concentrations of two metals, Ba and As did not exceed their respective maximum contaminant level (MCL) (2 mg/l and 0.01 mg/l), both were found in till and bedrock groundwater. Concentrations of Fe and Mn exceeded their secondary drinking water standards of 0.3 and 0.05 mg/l, respectively, in either till or bedrock groundwater. $NH4^-$ concentrations were found higher than levels that may interfere with drinking water chlorination (0.3 mg/l; Skadsen, 1993). Fluoride was detected in many till water samples at 0.7 mg/l, but not in underlying bedrock at the site. Excessive F has been a concern in other regional aquifer studies (Gosselin et al., 1999) and has a secondary drinking water standard of 2 mg/l.

To assess the potential for regional impact, the contaminant mass loading of pre-Illinoian till water to an underlying bedrock aquifer was evaluated. In the vicinity of the study site, 60-120 m of Devonian and Silurian carbonate rocks form the primary bedrock aquifer in Linn County (Wahl and Bunker, 1986). Within Linn County (1.88 x 10^9 m^2), unweathered pre-Illinoian till overlies approximately 1.19 x 10^9 m^2 (Figure 14). Considering a flow velocity of 0.4 cm/yr for the unweathered till, approximately 4.77 x 10^9 L of water is discharged from the till to the aquifer every year. Assuming pre-Illinoian water concentrations of Ba (0.1 mg/l), As (0.02 mg/l), NH_4 (0.3 mg/l), Fe (0.07 mg/l), Mn (0.2 mg/l) and F (0.7 mg/l), approximately 4.8 x 10^8, 9.5 x 10^7, 1.4 x 10^8, 3.3 x 10^8, 9.5 x 10^8, and 3.3 x 10^9 mg of these contaminants are discharged to the underlying aquifer each year. Estimating the volume of water in the Devonian-Silurian bedrock aquifer to be 5.43 x 10^{12} L (estimated aquifer thickness of 91 m with a porosity of 5%; Witzke, 1992), discharge of Ba, As, NH_4, Fe, Mn and F from pre-Illinoian till to the aquifer would produce aquifer concentrations of 0.09, 0.02, 0.3, 0.06, 0.2 and 0.6 ug/l, respectively. These estimated concentrations are considerably less than measured in bedrock well EI-1 at the site and suggest that pre-Illinoian till contributes little contamination to the regionally extensive Devonian-Silurian carbonate aquifer.

CONCLUSIONS

Conclusions from this study include the following:

- Wells EI-16 and EI-3 at the south well nest appear to be compromised and should not be considered in future monitoring efforts. High specific conductance indicative of grout migration was detected in EI-16, and modern recharge was measured in unoxidized till well EI-3.
- Groundwater sampling of slowly recovering aquitard wells should consider the use of a downhole probe to identify the line of dissolved oxygen and redox stratification developed in the well. Groundwater sampling should be conducted below this zone to ensure collection of water samples representative of formation water. Purging the entire water column and sampling slowly recovering water in the well casing results in samples biased from interaction with the atmosphere during water level recovery.
- Water quality samples from wells that require a long time for recovery present a challenge because the long time needed to achieve static water level recovery will likely allow in-well geochemical changes to occur. A balance must be achieved between collecting water quality samples that are truly representative of aquitard groundwater and measuring a hydraulic head in an aquitard well that accurately reflects site conditions. Depending upon which objective is deemed most important for a project, specific water level measurement or sampling procedures can be established.
- The groundwater velocity through pre-Illinoian till is orders of magnitude higher in oxidized versus unoxidized till. Hydraulic conductivity ranged from 10^{-7} m/s in oxidized till to 10^{-10} m/s in unoxidized till. Vertical groundwater velocity through the unoxidized till was estimated to range from 0.4 to 5.7 cm/yr.

- The oxidized and weathered portion of the till profile is a zone of recent groundwater circulation and much of the groundwater protection provided by pre-Illinoian till is associated with the unoxidized portion of the till weathering profile. Active groundwater circulation (less than 50 years old) through the oxidized profile at the study site was suggested by detectable tritium and nitrate concentrations in till water and a negative shift in stable isotope values in recent recharge. In contrast, the groundwater age at the base of the unoxidized till section ranged from 300 to more than 3000 years old
- Proposed siting criteria for waste disposal (landfills, CAFOs etc.) should consider identification of thick unoxidized pre-Illinoian till sections, and not total till thickness less than 15 m (~50 feet). Thicknesses less than 15 m would be most likely oxidized and not prevent vertical migration to aquifers within 50 years.
- Bedrock aquifers overlain by pre-Illinoian till less than 15 m thick should be considered vulnerable to contamination.
- Pre-Illinoian tills in eastern Iowa contain abundant nutrients (N, P and C) in soil and generally low concentrations in groundwater. Sediment delivery of N and P from a pre-Illinoian till landscape would primarily consist of organic nitrogen and phosphorus in the range of 250-1900 mg/kg and 260-960 mg/kg, respectively.
- Baseflow from pre-Illinoian till delivers total nitrogen to streams in the form of nitrate and organic nitrogen from weathered till and ammonium and organic nitrogen from unweathered till. Total N (TN) contributions from pre-Illinoian baseflow averaged approximately 1.8 mg/l from weathered till and 0.72 mg/l from unweathered till. When detected, ortho-P was found at concentrations of 0.02 to 0.03 mg/l and total P concentrations varied from 0.03 to 0.08 mg/l.
- Concentrations of several parameters indicative of landfill leachate are found at detectable concentrations in background pre-Illinoian till water. Background concentrations of NH_4 (mean = 0.18 mg/l; s.d. = 0.1), Fe^{2+} (mean = 0.7 mg/l; sd = 2.4) and SO_4^{2-} (mean = 32.9 mg/; sd = 33.2) in pre-Illinoian till showed sufficient concentration and variability to caution against generalizations about using elevated NH_4^-, Fe^{2+} and SO_4^{2-} as indicators for landfill leachate migration.
- Several constituents were detected in both unweathered till and the underlying bedrock (well EI-1) at concentrations that approach or exceed water quality standards. Although concentrations of two metals, Ba and As did not exceed their respective MCL's (2 mg/l and 0.01 mg/l), both were found in till and bedrock groundwater. Concentrations of Fe and Mn exceeded their secondary drinking water standards of 0.3 and 0.05 mg/l, respectively, in either till or bedrock groundwater. Fluoride was detected in many till water samples at 0.7 mg/l, but not in underlying bedrock at the site.
- Low concentrations of arsenic were detected in soils and reduced groundwater. Arsenic was detected in pre-Illinoian till at concentrations ranging between 3.2 to 7.4 mg/kg and in unoxidized pore water at 0.001 to 0.002 mg/l.
- Evidence suggests that denitrification is occurring at the redoxcline in pre-Illinoian till despite little apparent labile organic carbon. It is hypothesized that reduced sulfur in the till sediment may support autotrophic denitrification reactions, which is consistent with an abrupt increase in sedimentary sulfur at the redoxcline and relatively little change in TOC or alkalinity across the boundary. Unweathered pre-Illinoian till may be considered a geochemical barrier to nitrate migration to aquifers.

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APPENDIX A.

Lithologic Log for Soil Core at the I-380 Rest Stop Site

Sitename: 52STMAP-01

Location: T-82 N R-07 W section 33 NW1/4 SE1/4 SW1/4
Landscape position: till plain
Parent Material: diamicton
Soil Series: Kenyon
Vegetation: prairie
Slope: 1%
Elevation: 830 ft.
Quadrangle: Swisher
Date Drilled: 3/28/2002
Described by: Stephanie Tassier-Surine
Landowner: I-380 Northbound Rest Area
Remarks: 2.7 inch diameter core.
GPS Location:

Depth (ft)	Horizon /W. Zone	Description
		DeForest Formation-- Undiff.
0-0.4	Ap	Dark brown (10YR 3/2) loam; weak fine subangular blocky structure; friable; noneffervescent; clear smooth boundary
0.4-0.6	B	Yellowish brown (10YR 5/4) loam, gravel and pebbles common (till-like?); moderate fine subangular blocky structure; firm; few very thin dark brown (10YR 3/2) root traces; strongly effervescent; abrupt smooth boundary
0.6-1.0	2A (BA)	Very dark grayish brown (10YR 3/2) and dark brown (10YR 3/3) loam (more silt than above); moderate fine subangular blocky structure; friable; common fine roots; noneffervescent; clear smooth boundary
1.0-1.8	2A2	Very dark gray (7.5YR 3/1) loam; strong medium subangular blocky structure; friable; few fine roots; common dark brown (7.5YR 3/3) coatings on ped faces; noneffervescent;
1.8-2.1	2B	Very dark gray (10YR 3/1) and brown (10YR 4/3) clay loam; strong coarse subangular blocky structure; firm; few fine root traces; common dark brown (7.5YR 3/3) coatings on ped faces; noneffervescent; gradual smooth boundary
		Pre-Illinoian Formation-- diamicton
2.1-3.5	OL	Dark yellowish brown (10YR 4/4) grading to yellowish brown (10YR 5/4) at base, common yellowish brown (10YR 5/6) areas, clay loam with few gravel and pebbles up to 0.5" throughout; weak fine subangular blocky structure; firm; few fine very dark grayish brown (10YR 3/2) Mn accumulations; few clay coatings; few fine root traces; noneffervescent;

Depth (ft)	Horizon /W. Zone	Description
3.5-4.8	OL	Yellowish brown (10YR 5/6) clay loam (silty clay loam?) with trace pebbles typically <1" diameter but may be up to 1.5"; few medium discontinous gray (5Y 6/1) depletion areas throughout; weak fine subangular blocky structure; friable; few medium very dark gray (10YR 3/1) Mn accumulations throughout; few fine dark yellowish brown (10YR 4/6) Fe accumulations on ped faces; noneffervescent; few fine dark grayish brown (10YR 4/2) root traces
4.8-8.5	OU	Yellowish brown (10YR 5/6) clay loam (silty clay loam?) with trace pebbles typically <1" diameter but up to 1.5"; weak fine subangular blocky structure; friable; few medium discontinous gray (5Y 6/1) depletion areas throughout and at 6-6.5'; few medium very dark gray (10YR 3/1) Mn accumulations throughout; moderately effervescent; Fe and Mn accumulations increase slightly below 5.5'
8.5-9.5	OU	Yellowish brown (10YR 5/6) sandy clay loam with few pebbles up to 0.5" (igneous, quartz, granite); weak fine subangular blocky structure; firm; few dark yellowish brown (10YR 3/6) Fe accumulations on ped faces throughout and common from 8.9-9.1'; moderately effervescent
9.5-13.5	OU	Olive brown (2.5Y 5/4) clay loam (sandy clay loam?) with few pebbles up to 1" diameter, siltier to base; light brownish gray (2.5Y 6/2) depletion areas common at 9.6', few to 10.8', along joints below; weak fine subangular blocky structure; firm; dark yellowish brown (10YR 4/6) and yellowish brown (10YR 5/6) along joints up to 1" wide; strongly effervescent
13.5-15.5	OU	Yellowish brown (10YR 5/6) loam with common gravel and pebbles up to 0.5" diameter; fine subangular blocky structure; firm; strongly effervescent; very uniform color and texture
15.5-18.5	OJU	Yellowish brown (10YR 5/6) loam (slightly lighter and more clay than above) with pebbles up to 1" (quartz, igneous, carbonate, biotite flake); firm (more than above); joints less than 0.5" wide with depleted light brownish gray (2.5Y 6/2) centers; strongly effervescent; very few fine Mn accumulations
18.5-22.5	OJU	Yellowish brown (10YR 5/6) loam, common gravel and pebbles up to 0.5" diameter (quartz, carbonate, igneous, granite, biotite, sandstone); firm; few fine dark yellowish brown (10YR 4/6) Fe accumulations on joint faces; common light brownish gray (2.5Y 6/2) joints; strongly effervescent
		Pre-Illinoian Formation-- Undiff. SAND
22.5-23.2	OU	Yellowish brown (10YR 5/6) to dark yellowish brown (10YR 4/6) fine to medium sand, coarsening with depth; single grain structure; loose; moderately effervescent; clear smooth boundary; moderately well sorted

Depth (ft)	Horizon /W. Zone	Description
		SAND and GRAVEL
23.2-23.5	OU	Light olive brown (2.5Y 5/4) to olive brown (2.5Y 4/4) fine sand to coarse gravel with some silt and clay (colluvium?); friable; moderately effervescent clear smooth boundary; poorly sorted
		SAND
23.5-29.5	OU	Fine to coarse sand, some gravel; poorly sorted; No Sample (mud rotary through sands)- end of gravel 29.5' as per driller
		Pre-Illinoian Formation-- diamicton
29.5-33.5	OJU	Olive brown (2.5Y 4/3) and dark grayish brown (2.5Y 4/2) loam with trace pebbles less than 0.5" (quartz, igneous, carbonate); very dark grayish brown (2.5Y 3/2) from 30.5-31' and 31.3-31.4'; clear to gradual color changes; firm; common black (2.5Y 2.5/1) joints grading outward to yellowish brown (10YR 5/6) and then to reduced colors, less than 0.5inch diameter and greater than 3inch spacing; strongly effervescent
33.5-34.3	UJU	Very dark gray (5Y 3/1) clay loam (loam?) with trace gravel and pebbles up to 0.5" diameter; massive; firm; fine olive brown (2.5Y 4/3) areas (possibly joints); strongly effervescent; clear boundary
34.3-38.2	OJU	Olive brown (2.5Y 4/3) loam (clay loam?- more silt and sand than above) with trace gravel and pebbles up to 1" diameter; massive; firm; olive brown (2.5Y 4/4) patches from 35.7-35.9' and 37.3-37.8' with gradual color change to surrounding matrix; gray (2.5Y 5/1) joints less than 1 inch width; strongly effervescent
38.5-39.3	RU and UU	Olive brown (2.5Y 4/3) very dark gray (5Y 3/1) loam to clay loam with few gravel and pebbles up to 0.5" diameter; firm; 1" pod of light olive brown (2.5Y 5/4) sandy clay near base in RU strongly effervescent; alternates RU-UU-RU-UU
39.3-41.8	RJU	Dark olive brown (2.5Y 3/3) grading downward to olive brown (2.5Y 4/4) and dark olive brown (5Y 3/2) loam to clay loam with localized sandier areas; medium subangular blocky structure; firm; clay coatings common dark gray (2.5Y 4/1) and light olive brown (2.5Y 5/4) joints less than 0.5" diameter; strongly effervescent; clear angled (45 degrees) boundary, reduced very dark grayish brown (2.5Y 3/2) along 0.5" boundary
41.8-43.5	UU	Very dark gray (5Y 3/1) clay loam to loam? with few gravel and pebbles up to 0.5" diameter; massive; very firm; strongly effervescent;
43.5-46.0		SAND- as per driller, no sample

Depth (ft)	Horizon /W. Zone	Description
46.0-47.0	UU	Very dark gray (5Y 3/1) clay loam (sandier than above?), common gravel, few pebbles up to 0.5" diameter; massive; very firm; strongly effervescent; sand pocket at 46.7' (saprolite); moderately effervescent very dark gray (7.5YR 3/1) zone from 46.3 to 46.5'
47.0-48.0		Granite Boulder
		SAND and GRAVEL
48.0-52.0		Coarse sand and gravel, poorly sorted; no sample
		Pre-Illinoian Formation-- diamicton
52.0-57.0	UU	Very dark gray (5Y 3/1) silt loam (sandier to top), trace gravel and pebbles up to 0.5"; massive; very firm; strongly effervescent
57.0-57.5		GRANITE- drilling cuttings
57.5-58.0		SAND- No sample
		Pre-Illinoian Formation-- diamicton
58.0-58.6	UU	Very dark gray (5Y 3/1) silt loam with common gravel and pebbles up to 0.5" diameter; massive; very firm; strongly effervescent
		SILT
58.6-59.0	UU	Dark gray (5Y 4/1) silt with some very fine sand; massive; strongly effervescent; abrupt smooth boundary
		Pre-Illinoian Formation-- diamicton
59.0-63.8	UU	Very dark gray (5Y 3/1) silt loam with common gravel and pebbles to 0.5" diameter; massive; very firm; strongly effervescent
		SAND
63.8-63.9	RU	Dark grayish brown (2.5Y 4/2) medium to coarse sand; moderately well sorted; moderately well rounded; single grain structure; loose; abrupt smooth boundary
		Pre-Illinoian Formation-- diamicton
63.9-64.0	UU	Very dark gray (5Y 3/1) silt loam (possibly more sand than above), common gravel (igneous, quartz); very firm; strongly effervescent; smooth boundary
64.0-68.0		No Sample

68.0-69.0	UU	Very dark gray (5Y 3/1) loam (more clay and fine sand than above), common coarse sand and gravel, more coarse fragments than above, pebbles up to 1" diameter; massive; very firm; strongly effervescent; Recovery = 12"
69.0-73.0		No Sample
73.0-74.0	UU	Very dark gray (5Y 3/1) loam with pebbles up to 1" diameter (Baraboo Quartzite?, igneous, quartz); massive; very firm; strongly effervescent; Recovery = 11"
74.0-78.0		No Sample
78.0-79.0	UU	Very dark gray (5Y 3/1) loam, common coarse sand and gravel (dominantly quartz and igneous), pebbles up to 0.5" diameter; massive; very firm; strongly effervescent; Recovery = 14"
79.0-83.0		No Sample
83.0-84.0	UU	Very dark gray (5Y 3/1) loam (easier to texture than above- less dense or more fine sand?), pebbles up to 0.5" diameter; massive; very firm; strongly effervescent; Recovery = 17"
84.0-88.0		No Sample
88.0-89.0	UU	Very dark gray (5Y 3/1) loam (more fine sand as above); massive; very firm; strongly effervescent; Recovery = 18"
89.0-93.0		No Sample
93.0-94.0	UU	Very dark gray (5Y 3/1) loam with pebbles >1" diameter (granite, brown chert, igneous, quartz); massive; very firm; strongly effervescent; bottom few mm of core limestone; Recovery = 15.5"

APPENDIX B.

Summary of Hydrolab Measurements

Summary of Hydrolab Measurements, October 30, 2002

Well No.	TOC Elev	Sample Elev	Depth (ft)	Depth (m)	Temp C	pH	SC (umohs/m)	DO (mg/l)	ORP (mv)
EI-1	841.4	758.4	83	25.23	10.45	8.99	604	0.12	-10
		746.4	95	28.88	10.47	9	603	0.06	-25
		738.4	103	31.31	10.48	9.02	603	0.05	-33
EI-2	843.77	833.77	10	3.04	14.05	9.2	281	4.24	187
		828.77	15	4.56	13.8	9.1	283	4.17	188
		823.77	20	6.08	12.86	9.03	282	4.11	190
		813.77	30	9.12	11.18	9.04	282	3.92	192
		803.77	40	12.16	10.53	9.06	282	3.54	194
		793.77	50	15.20	10.42	8.79	337	1.37	199
		783.77	60	18.24	10.44	8.49	435	0.1	199
		773.77	70	21.28	10.47	8.79	445	0.07	-25
		763.77	80	24.32	10.47	8.82	444	0.058	-44
		751.77	92	27.97	10.46	8.62	447	0.05	-27
EI-3	844.24	834.24	10	3.04	13.97	8.02	269	3.38	214
		829.24	15	4.56	13.76	8.1	264	2.53	203
		824.24	20	6.08	12.81	8.08	264	2.46	199
		814.24	30	9.12	11.16	8.05	263	2.58	198
		804.24	40	12.16	10.52	8.07	263	2.52	198
		794.24	50	15.20	10.39	8.11	263	2.23	198
		786.24	58	17.63	10.42	8.13	263	2.37	199
EI-4	844.35	834.35	10	3.04	13.54	8.69	94	4.38	192
		829.35	15	4.56	13.5	8.44	266	0.76	197
		824.35	20	6.08	12.79	8.65	269	2.05	188
		814.35	30	9.12	11.21	8.56	269	1.68	187
		804.35	40	12.16	10.54	8.64	269	2.18	189
		794.35	50	15.20	10.41	8.63	292	1.35	189
EI-17	844.59	834.59	10	3.04	13.56	8.39	348	0.67	186
		829.59	15	4.56	13.38	8.37	352	0.68	176
		824.59	20	6.08	12.47	8.36	350	0.98	173
		814.59	30	9.12	10.92	8.31	349	0.7	170
		804.59	40	12.16	10.41	8.26	349	0.08	161
EI-18	845.47	835.47	10	3.04	13.65	8.38	339	1.91	184
		830.47	15	4.56	13.36	8.22	340	0.85	176
		825.47	20	6.08	12.67	8.31	338	0.56	169
		820.47	25	7.60	11.53	8.28	337	0.34	163
		814.47	31	9.42	10.87	8.3	336	0.18	158
EI-19	845.78	835.78	10	3.04	13.53	8.71	85	4.02	206
		830.78	15	4.56	13.57	8.47	95	0.67	190
		825.78	20	6.08	12.72	8.52	189	0.15	181
		819.78	26	7.90	11.49	8.24	269	0.13	175
EI-20	846.52	836.02	10.5	3.19	13.4	8.18	493	4.38	178
		832.52	14	4.26	13.93	7.9	532	3.29	176

Summary of Hydrolab Measurements, October 30, 2002

Well No.	TOC Elev	Sample Elev	Depth (ft)	Depth (m)	Temp	pH	Cond	DO	ORP
EI-5	830.12	805.12	25	7.60	12.04	8.1	414	2.09	209
		800.12	30	9.12	11	8.38	444	3.65	209
		795.12	35	10.64	10.56	8.45	444	3.8	212
		785.12	45	13.68	10.38	8.46	444	3.06	216
		775.12	55	16.72	10.37	8.07	452	0.22	218
		765.12	65	19.76	10.39	8.09	452	0.15	214
		754.12	76	23.10	10.4	8.12	453	0.21	208
EI-6	831.48	820.48	11	3.34	13.28	8.75	378	3.8	214
		811.48	20	6.08	12.43	8.6	382	3.98	218
		801.48	30	9.12	10.95	8.58	382	4.12	222
		791.48	40	12.16	10.38	8.59	382	4.05	224
		781.48	50	15.20	10.32	8.1	434	0.28	227
		771.48	60	18.24	10.34	8.3	434	0.14	94
EI-7	831.59	828.59	3	0.91	9.41	8.51	297	0.48	216
		821.59	10	3.04	12.17	8.53	298	0.37	208
		811.59	20	6.08	12.12	8.31	325	0.14	151
		801.59	30	9.12	10.9	8.29	327	0.11	128
		791.59	40	12.16	10.35	8.32	327	0.06	117
EI-22	831.83	825.83	6	1.82	12.65	8.9	305	4.42	186
		816.83	15	4.56	13.1	8.5	316	2.19	196
		806.83	25	7.60	11.57	8.32	320	1.11	197
		796.83	35	10.64	10.54	8.2	330	0.16	195
EI-23	831.63	824.13	7.5	2.28	12.9	8.5	295	2.95	224
		816.63	15	4.56	13.1	8.26	312	1.33	220
		806.63	25	7.60	11.38	8.08	336	0.14	213
EI-24	831.93	823.43	8.5	2.58	13.03	8.17	112	2.58	215
		819.93	12	3.65	13.36	7.96	421	0.41	221

Summary of Hydrolab Measurements, December 2, 2003

Well No.	TOC Elev	Sample Elev	Depth (ft)	Depth (m)	Temp	pH	Cond	DO	ORP
EI-1	841.4	756.4	85	25.84	10.43	7.54	780	2.53	79
		749.4	92	27.97	10.51	7.89	785	3.09	-29
		739.4	102	31.01	10.53	7.91	785	3.33	-47
EI-2	843.77	828.77	15	4.56	11.32	7.38	584	5.44	340
		823.77	20	6.08	11.71	7.22	650	3.86	344
		813.77	30	9.12	10.96	7.21	649	3.94	346
		803.77	40	12.16	10.49	7.2	648	3.78	348
		793.77	50	15.20	10.42	7.2	648	3.46	350
		783.77	60	18.24	10.47	6.98	653	1.59	354
		773.77	70	21.28	10.51	6.98	653	1.4	352
		763.77	80	24.32	10.52	6.98	653	1.13	289
		752.77	91	27.66	10.52	6.99	675	0.99	223
EI-3	844.24	830.24	14	4.26	11.38	6.74	575	3.54	361
		824.24	20	6.08	11.66	6.79	592	2.09	359
		814.24	30	9.12	10.9	6.8	592	1.78	358
		804.24	40	12.16	10.45	6.81	593	1.39	357
		794.24	50	15.20	10.4	6.81	592	1.31	361
		786.24	58	17.63	10.45	6.84	596	0.75	354
EI-4	844.35	830.35	14	4.26	11.01	6.72	146	2.14	362
		824.35	20	6.08	11.54	7.25	273	0.61	348
		814.35	30	9.12	10.92	7.22	525	1.49	351
		804.35	40	12.16	10.46	7.22	524	1.56	350
		793.35	51	15.50	10.42	7.08	534	0.83	352
EI-17	844.59	831.59	13	3.95	10.79	7.33	565	3.61	361
		824.59	20	6.08	11.49	7.19	576	1.76	361
		814.59	30	9.12	10.78	7.15	574	1.28	360
		804.59	40	12.16	10.41	7.1	571	0.61	358
EI-18	845.47	831.47	14	4.26	10.81	7.17	456	3.4	366
		825.47	20	6.08	11.53	7.21	540	2.51	360
		820.47	25	7.60	11.23	7.19	540	1.87	357
		813.47	32	9.73	10.73	7.18	537	1.52	354
EI-19	845.78	830.78	15	4.56	10.74	6.99	127	4.56	354
		825.78	20	6.08	11.58	7.17	195	1.5	337
		819.78	26	7.90	11.25	7.25	535	1.4	334
EI-20	846.52	831.52	15	4.56	10.99	6.67	839	7.28	393

Summary of Hydrolab Measurements, December 2, 2003

Well No.	TOC Elev	Sample Elev	Depth (ft)	Depth (m)	Temp	pH	Cond	DO	ORP
EI-5	830.12	813.12	17	5.17	10.83	7.31	609	3.61	174
		800.12	30	9.12	10.65	7.14	664	2.09	180
		785.12	45	13.68	10.3	7.14	664	1.91	177
		775.12	55	16.72	10.33	7.14	664	1.8	178
		765.12	65	19.76	10.39	7.13	664	1.55	177
		755.12	75	22.80	10.43	7.12	664	1.48	175
EI-6	831.48	798.48	33	10.03	9.89	7.18	633	4.02	174
		791.48	40	12.16	10.19	7.01	665	0.92	174
		781.48	50	15.20	10.22	7.02	667	0.55	142
		771.48	60	18.24	10.31	7.02	667	0.46	121
EI-7	831.59	827.59	4	1.22	7.68	7.38	489	4.53	180
		821.59	10	3.04	9.68	7.33	492	4.41	180
		811.59	20	6.08	11.11	7.2	509	3.09	180
		801.59	30	9.12	10.64	7.06	526	0.61	116
		791.59	40	12.16	10.29	7.06	527	0.43	84
EI-22	831.83	825.83	6	1.82	9.28	7.37	516	4.01	163
		816.83	15	4.56	10.9	7.37	517	3.98	169
		806.83	25	7.60	11.07	7.07	529	0.87	166
		796.83	35	10.64	10.42	7.06	529	0.59	164
EI-23	831.63	822.63	9	2.74	10.04	7.07	264	1.57	183
		816.63	15	4.56	11.1	7.14	369	0.73	52
		806.63	25	7.60	11.05	7.03	543	0.53	95
EI-24	831.93	821.93	10	3.04	9.85	7	665	6.4	205

Summary of Hydrolab Measurements, December 8, 2003

Well No.	TOC Elev	Sample Elev	Depth (ft)	Depth (m)	Temp	pH	Cond	DO	ORP
EI-1	841.4	756.4	85	25.84	10.52	7.15	801	1.11	38
		749.4	92	27.968	10.54	7.19	803	0.71	20
		739.4	102	31.008	10.54	7.19	803	0.53	16
EI-2	843.77	763.77	80	24.32	10.48	6.97	663	3.42	194
		751.77	92	27.968	10.52	7	669	1.04	203
EI-3	844.24	791.24	53	16.112	10.38	6.88	611	2.95	238
		786.24	58	17.632	10.44	6.86	611	2.2	250
EI-4	844.35	831.35	13	3.952	10.89	6.94	350	1.05	240
		824.35	20	6.08	11.49	7.01	522	0.62	237
		814.35	30	9.12	10.94	7.02	531	0.53	237
		804.35	40	12.16	10.48	7.03	531	0.49	238
		793.35	51	15.504	10.41	7.03	531	0.45	238
EI-17	844.59	831.59	13	3.952	11.12	7.16	572	3	247
		824.59	20	6.08	11.47	7.11	575	2.27	250
		814.59	30	9.12	10.87	7.1	574	1.63	252
		804.59	40	12.16	10.47	7.09	583	1.41	253
EI-18	845.47	831.47	14	4.256	11.24	7.29	531	2.68	255
		825.47	20	6.08	11.54	7.23	533	1.69	254
		820.47	25	7.6	11.32	7.2	534	0.96	253
		813.47	32	9.728	10.8	7.19	534	0.65	251
EI-19	845.78	831.78	14	4.256	11.34	7.24	549	3.2	258
		825.78	20	6.08	11.65	7.22	558	2.7	259
		819.78	26	7.904	11.32	7.23	560	2.6	261
EI-20	846.52	831.52	15	4.56	11.43	6.7	840	6.54	289
EI-5	830.12	760.12	70	21.28	10.32	7.08	653	3.52	231
		755.12	75	22.8	10.41	6.99	677	0.65	235
EI-6	831.48	771.48	60	18.24	10.12	7.05	660	1.23	199
EI-7	831.59	827.59	4	1.216	7.97	7.09	519	1.59	268
		821.59	10	3.04	9.22	7.07	519	1.21	268
		811.59	20	6.08	10.85	7.08	524	1.14	267
		801.59	30	9.12	10.63	7.05	525	0.48	194
		791.59	40	12.16	10.31	7.07	526	0.45	107
EI-22	831.83	825.83	6	1.824	9.13	7.12	526	1.97	276
		816.83	15	4.56	10.63	7.1	526	1.37	274
		806.83	25	7.6	11.03	7.08	529	1.01	273
EI-23	831.63	822.63	9	2.736	10.34	7.05	540	1.94	273
		816.63	15	4.56	11.04	7.05	540	1.73	275
		806.63	25	7.6	11.08	7.01	544	1.14	274
EI-24	831.93	819.93	12	3.648	11.03	6.94	685	5.01	279
		831.93							

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