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Report on the Preliminary Investigation of Arsenic in Groundwater near Lake Geneva, Wisconsin

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Groundwater Section
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Project Summary

The purpose of this preliminary investigation is to characterize the hydrogeologic and groundwater quality conditions prevalent in the vicinity of the Wood School, between the towns of Lake Geneva and Williams Bay, Wisconsin (Figure 1). Results of groundwater sampling conducted by Wisconsin Department of Natural Resources (WDNR) personnel in 1998 showed total arsenic concentrations ranging from 15 to 120 µg/L in wells completed in the Silurian aquifer. Some of these data suggested a correlation between well chlorination and an increase in arsenic concentration. The main objective of this project was to evaluate the nature and extent of arsenic in well water in this limited area. Additional objectives were to determine 1) if well chlorination was the cause of the apparent increase in arsenic levels, and if so, the duration of the effect and 2) if oxidation or reduction of arsenic-bearing sulfides is a primary cause of arsenic contamination of groundwater.

Based on the results of this study, groundwaters in all three of the aquifers (unlithified sands and gravel, shallow bedrock (Silurian), and Cambrian-Ordovician sandstones) in the study area are, to some extent, impacted by arsenic. Levels exceeding the current federal maximum contaminant limit (M.C.L.) of 50 µg/L were found only in wells that are open to the shallow bedrock aquifer. Each of the eight wells completed in shallow bedrock that were tested during this study contain arsenic. Concentrations in excess of the proposed M.C.L. of 5 µg/L were found in the unconfined sand and gravel aquifer that overlies the Silurian bedrock, and in the deep Cambrian sandstone aquifer. However, concentrations exceeding 5 µg/L do not appear to be widespread within either the sand and gravel or the deep sandstone aquifers.

Hydrogeologic conditions in the study area suggest that arsenic in groundwater in the sand and gravel and shallow bedrock aquifers do not have the same geologic source as the arsenic that occurs in the confined, deep sandstone aquifer. Examination and limited analytical testing of drill cuttings from the study area did not reveal evidence of pyrite mineralization in sediments from any of the three aquifers. Extensive mineralization has been observed within the deep sandstone aquifer in a well in Lyons, Wisconsin, located about seven miles northeast of the study area.

The water quality conditions in the study area are significantly different than those documented in the arsenic-impacted areas of the Fox River Valley. The *maximum* arsenic concentration found in the Lake Geneva area (on the order of 100 µg/L) is significantly less than the *maximum* levels present in the Fox River Valley (on the order of 1000s µg/L). In the Fox River Valley, sulfide oxidation is believed to be the cause of high (>100 µg/L) arsenic concentrations in wells, while a mechanism causing the more prevalent, lower arsenic concentrations has not yet been identified. In this study area, data show generally reducing conditions, pH range between 7 and 8, and very low sulfate, iron, and trace metal concentrations. Static and pumping water levels in wells do not cause exposure of the aquifer matrix to the air-water interface. These conditions do not support sulfide oxidation or reduction of iron-oxyhydroxides as a mechanism for arsenic release to groundwater. Transport of dissolved or colloid-associated arsenic could occur under these conditions.

The well chlorination experiment carried out in this study showed that batch chlorination causes oxidizing conditions within the borehole, but it did not trigger a subsequent increase in arsenic concentration. The experiment provides further evidence that in the Lake Geneva area, oxidation of arsenic-bearing minerals *exposed at the borehole* is not a mechanism of arsenic release to groundwater. However, the result of this chlorination experiment should not be generalized to wells in the Fox River Valley, where wells with high (>100 µg/L) arsenic concentrations are likely open to sulfide-rich horizons.

Based on the results of this study, a public education effort in the Lake Geneva area is necessary to alert residents, well drillers, and real estate developers to the need to test for arsenic in well water. New wells drilled in the vicinity of the Wood School should be completed above, or cased through, the Silurian dolomite aquifer. This preliminary study could be followed by additional investigation to determine the source of arsenic and mechanism for its release to groundwater in the study area. Methods of investigation should include the collection of continuous samples through the sand and gravel deposits and the Silurian dolomite, subsequent characterization of the aquifer mineralogy, and leaching tests with geochemistry similar to the water quality of the study area. A well chlorination experiment should be conducted at an arsenic-impacted well in the Fox River Valley where the borehole is known to intersect the sulfide-cement horizon.

Introduction and Background

This project was designed to meet the need for information about arsenic in well water in southeastern Wisconsin. In 1998, in response to elevated arsenic levels in the Wood School well (located approximately 2 miles west of Lake Geneva, see Figure 1), the WDNR analyzed water from selected private and public water supply wells located near the school. Of the fifteen wells sampled, only four wells did not contain arsenic above the laboratory detection limit. Of these four wells, two are located within 0.5 miles of the Wood School and are completed above the bedrock, with screens open to sand and gravel deposits. The other two wells with non-detectable levels are completed in bedrock but are located approximately 2.5 miles northwest of the school. The Wood School well is completed in shallow bedrock.

The 11 wells that contained detectable levels of arsenic are located within 1.5 miles of the Wood School. One of these wells is completed in sand and gravel; the other ten are open to bedrock. Of the 10 bedrock wells, the highest arsenic concentrations occurred in wells completed in the uppermost bedrock, the Silurian dolomite. On the basis of these sampling results, it appeared that the Silurian formation provides a source of naturally occurring arsenic to water in this area.

The WDNR has supported significant efforts to document and investigate the causes of naturally occurring arsenic impacts to wells in the Fox River Valley (Burkel and Stoll, 1995; Simo et al, 1997; Schreiber et al, 2000). In the Fox River Valley, the source of arsenic is believed to be a sulfide-rich horizon at the base of the Platteville Formation. A well-supported hypothesis for the release of arsenic from the sulfide horizon is oxidation via exposure of the sulfides to air where the air-water interface in wells intersects the sulfide-rich rock. There is data supporting this mechanism from wells that are highly impacted (As concentrations greater than 100 µg/L), however a mechanism for release in low- to moderately impacted wells (As concentrations between 5 and 100 µg/L) has not been identified. Possible causes of the lower concentrations include oxidation of sulfides with lower arsenic concentrations, reduction of iron hydroxides, aquifer transport of dissolved-phase arsenic, or aquifer transport of colloid-associated arsenic. This preliminary study in the area of the Wood School was designed in part to compare the water quality conditions in the area to those in the Fox River Valley.

WDNR personnel have hypothesized that batch chlorination of the Wood School well, performed after a positive test for coliform bacteria, might have caused the dissolution of additional arsenic from rock into solution. The Wood School well had repeated detections of arsenic since it was sampled in 1995. However, the arsenic concentration generally increased (from about 40 to about 70 µg/L) following the 1987 well chlorination. However, the well was not sampled for arsenic immediately prior to or following the chlorination.

In order to obtain arsenic-free water, the Wood School drilled a new well in the upper, unconsolidated sand and gravel aquifer. When this well did not yield a sufficient water supply, the School considered drilling a well into the Cambrian sandstone aquifer, to a total depth of about 1000 feet. (The drilling was postponed after sample results from this project showed significant levels of arsenic, 39 µg/L, in the deep aquifer.)

In response to this situation, the WDNR provided financial support for this preliminary investigation into the nature and extent of elevated levels of arsenic in groundwater wells in the vicinity of the Wood School. The study was formulated to evaluate potential sources of arsenic to groundwater, and to determine if sulfide oxidation via introduction of oxygen at the borehole, which appears to be a primary cause of arsenic-impacts to groundwater in the Fox River Valley, plays a significant role in groundwater geochemistry in the Lake Geneva area. I also conducted an experiment to evaluate the potential for well chlorination to trigger an increase in arsenic levels.

Methods used in this study include evaluation of geologic and hydrogeologic conditions using water well construction reports, geologic logs, and available rock samples from drill cuttings. Water quality samples were collected and analyzed to evaluate groundwater geochemistry of the area. More extensive testing, such as mineralogical characterization of the aquifer units and determination of groundwater flow directions at the borehole scale, was not proposed in this preliminary study. Rather, I proposed to use the results of this project to determine if more detailed investigation is warranted.

Procedures and Methods

Maps and Cross Section

Maps and a stratigraphic cross-section of the study area (Figures 2 and 3) were constructed using residential and high capacity well logs. The data consisted of well construction reports (WCRs) and geologic logs maintained at the WGNHS. On the basis of the formation interpretations provided on the geologic logs, I assigned formation names to the geologic material descriptions on the WCRs. A critical evaluation of the formation interpretations on the geologic logs was not performed.

Rock Analysis

Whole rock chemical analysis was performed on 26 samples of well cuttings to determine the concentration of arsenic. The samples are from four locations in the study area (Figure 4). Samples from two of the locations (650538 and 650070) had been archived at the WGNHS and have accompanying geologic logs. The other two sample locations (650999 and 651347) were "samples of opportunity", collected recently by water well drillers who were aware of this study.

All samples available from each location were visually inspected for traces of mineralization, although none was apparent. Traces of pyrite noted on the geologic logs accompanying samples 650538 and 650070 were not readily apparent in the samples. Because no sample looked particularly suspect, samples from a variety of depths and lithologies (Table 1) were sent to Bondar-Clegg, Inc., where they were prepared and analyzed for arsenic by neutron activation.

Groundwater Chemistry

Samples from fourteen drinking water wells in the study area were collected in May and June 2000 to assess spatial and temporal trends in groundwater quality (Figure 2, Tables 2 and 3). Wells were purged by opening spigots for five to ten minutes prior to sample collection. Samples were collected from basement or outdoor spigots located before water treatment systems. Direct sampling of the wells was not feasible because each is used for drinking water supply and contains a submersible, dedicated pump.

Field measurements of specific conductance, pH, temperature, redox and dissolved oxygen were collected at all sampling locations, with the exception of those where reliable measurements of redox and DO could not be made due to the spigot configuration. Redox and DO measurements were collected by discharging a continuous stream of water into the bottom of a bucket and submerging the probes until readings stabilized. These sampling conditions are not ideal, and the dissolved oxygen and redox measurements should be regarded as general indicators of oxygenation and redox state.

Samples for total dissolved solids, cation, anion and trace metal analysis were filtered to 0.45 µm; samples for cation and trace metals analysis were then acidified with nitric acid to $pH < 2$. Samples were placed on ice until delivered to the Wisconsin State Laboratory of Hygiene for analysis. Groundwater chemistry data from wells in the study area that were sampled by Kevin Schurilla and others of the WDNR, and historical results from these and other wells in the DNR Groundwater Retrieval Network database, are also presented in this report (Tables 2 and 3).

Well Chlorination Experiment

The Wood School well was chlorinated consistent with the method used by school personnel in 1997. Osmonics Autotrol™ chlorine pellets were added to the well to achieve a borehole concentration of about 400 mg/L chlorine, as recommended by the manufacturer. One cup of chlorine pellets was dropped into the standing column of water and one cup was dissolved with warm water and poured into the well. This method is commonly used by homeowners and pump installers to ensure that some of the pellets dissolve in the borehole below the level of the pump (C. Fitzgerald, WDNR, verbal communication, 2000). Well water was then re-circulated until a strong chlorine odor developed. The chlorinated water column was left standing in the well for twenty-four hours, after which three borehole volumes of water were purged from the well.

Field measurements of specific conductance, pH, redox, dissolved oxygen and temperature were collected during borehole purging. Water quality samples and field measurements were collected prior to the well chlorination and subsequent to purging at intervals of 0 hrs, 2 days, 5 days, 10 days and 20 days (Table 4). Samples were collected from a basement spigot prior to water treatment system. The well was purged by opening spigots for a minimum of ten minutes prior to sample collection. Water quality samples were analyzed at the State Laboratory of Hygiene for cations, anions, total dissolved solids and arsenic levels. In order to replicate the sampling method used in 1997, samples collected for arsenic analysis were not filtered.

Results and Discussion

Geologic Setting

The study area is located on a topographic rise between Lakes Geneva and Como (Figure 1). Ground surface elevation is about 1050 feet M.S.L. near the Wood School and slopes steeply to the south towards Lake Geneva, at an elevation of 864 feet M.S.L., and to Lake Como to the north, at an elevation of 849 feet M.S.L. Figure 3 shows a simplified geologic section through the area. Interbedded and unlithified sand, gravel and clays are present at thicknesses ranging from about 225 to 360 feet. These deposits are believed to be of glacial origin (N. Hamm, St. Norbert's College, verbal communication, 2000). Along the topographic rise, these unconsolidated deposits are underlain by up to 45 feet of Silurian (Kankakee Formation) dolomite (Massie-Ferch, 2000). The Silurian dolomite pinches out to the north and south, where the uppermost bedrock unit consists of about 130 feet of interbedded shale and dolomite of the Maquoketa Formation. Sinnipee Group dolomite (about 300 feet thick) underlies the Maquoketa Formation. Cambrian-Ordovician sedimentary units, estimated to be about 600 feet thick in this area, underlie the Sinnipee dolomite (Eaton, et al, 1999).

Hydrogeologic Setting and Well Water Use

The hydrostratigraphy of Walworth County has been evaluated as a part of a larger study of groundwater resources of southeastern Wisconsin (Eaton, et al, 1999). A simplified hydrostratigraphic framework is illustrated in Figure 5. On a regional basis, the upper, unconsolidated deposits and the Silurian Group dolomites are considered to be an unconfined aquifer. The upper portion of the Silurian aquifer is highly fractured; wells completed in this unit are fed predominantly by water moving through horizontal fracture networks within the Silurian (verbal communication, K. Bradbury, WGNHS, 2000). The Maquoketa confining unit consists of the Maquoketa and Sinnipee shale and dolomites. The Cambrian-Ordovician confined aquifer system consists of a series of highly conductive sandstone formations (e.g. St. Peter, Wonewoc and Mt Simon) interbedded with lower permeability aquitards (the Tunnel City and Eau Claire units). The recharge area for the deep sandstone aquifer is to the west in Waukesha and Jefferson counties, where the Maquoketa confining unit is not present.

Well water use in the study area is consistent with this regional characterization. Water yield from shallow geologic materials is often sufficient for domestic use and to supply small public water systems. Accordingly, many wells are screened in the thick sequence of sand, gravel and clay, or are cased through these deposits and open to shallow bedrock (the Silurian dolomite). A small number of domestic wells are open to the Maquoketa Formation and Sinnipee Group dolomites, which provide sufficient water yield on a local basis. Larger public systems (such as those that serve local resorts and hospitals) are cased through the Maquoketa, and occasionally through the Sinnipee Group, and are open to the Cambrian-Ordovician (deep sandstone) aquifer system. Table 5 lists the aquifer that wells sampled for this study are open to.

Static water levels in wells (recorded on WCRs) and the physiographic setting indicate that the study area is an area of groundwater recharge to the upper, unconfined aquifer (Table 5). Water levels are highest in wells located on the topographic high just east of the Wood School (about 880 feet M.S.L. at the Hartshorne and Brunk residences), and decrease towards the lakes (about 860 ft M.S.L. at the Johnson residence). There is a significant downward vertical gradient across the Maquoketa confining unit, as demonstrated by water levels in near-by wells completed in the Silurian dolomite and the deep sandstone aquifer: the Wood School well, open to shallow bedrock, has a static water level of about 860 ft MSL, while the Sunset Hills Association well, completed in the deep sandstone aquifer, has a static elevation of about 786 ft M.S.L.

Water levels in wells under pumping conditions were evaluated using information on the WCRs (Table 5). On the basis of these data, it is highly unlikely that water levels in wells drop below the base of the well casings under pumping conditions. This is significant because in the Fox River Valley, at wells with high (greater than 100 μg/L) As concentrations, exposure of the aquifer formation to air within well boreholes is thought to be the source of oxygen acting on sulfide minerals in the Fox River Valley.

Occurrence of Arsenic in Well Water

Some of the sampled wells within each of the aquifers in the study area contained detectable levels of arsenic, but only wells completed in the Silurian dolomite have concentrations that exceed the current MCL of 50 µg/L (Table 6). Within the subgroup of eight Silurian dolomite wells, each contain arsenic with an average concentration of 33 µg/L. Three of the eight exceed 50 µg/L (Table 3).

Within the group of four wells completed in sand and gravel deposits, two contain arsenic at levels greater than the proposed MCL of 5 µg/L. These are the two deepest sand and gravel wells, Interlacken #2 at 273 feet below ground surface and the Connelly residence at 435 feet below ground surface, with concentrations of 13 and 8.9 µg/L, respectively. This finding suggests that a geologic source of arsenic to well water could be in the deep, unlithified sediments. If these sediments do contain arsenic, they could also be the source of arsenic to the wells completed in shallow bedrock-- dissolved- or colloidal-phase arsenic could migrate vertically downward from the unlithified sediments to wells completed in shallow bedrock.

Arsenic was detected in the deep sandstone aquifer at 39 µg/L in the Sunset Hills Association well and at 5.7 µg/L in the Interlacken Well #1. Both samples exceed the proposed MCL of 5 µg/L. The Mercy Center Hospital and the Geneva National #1 wells, open to the deep aquifer but located approximately two miles northwest of the Wood School, have arsenic at levels less than 1 µg/L. Although this is a very small sample size, the results indicate that water in the deep sandstone aquifer contains arsenic within the immediate vicinity of the Wood School.

Several factors make it unlikely that the source of arsenic to the deep sandstone aquifer is the same as the source of arsenic impacting wells open to the Silurian aquifer. The thickness (180 feet at the Sunset Hills well) and low vertical hydraulic conductivity (on the order of 10^{-7} m/d, D. Feinstein, U.S.G.S, verbal communication, 2000) of the Maquoketa make it unlikely that a significant volume of water recharges the deep aquifer through the confining unit. The two aquifers have distinct recharge regimes; the shallow, unconfined bedrock aquifer is recharged locally by precipitation through the unlithified deposits, while the deep, confined aquifer recharges to the west in Waukesha and Jefferson Counties.

Potential Sources of Arsenic to Well Water

Because lead arsenate was historically used as a pesticide on orchards, a visual survey of orchard and agricultural fields in the study area was undertaken to evaluate the potential for an anthropogenic source of arsenic to groundwater. On the basis of this survey, there is no obvious anthropogenic source of arsenic within the study area. There are no orchards or extensive fields located directly adjacent to the more highly impacted water wells. Additionally, the highest arsenic concentrations are not found in the shallowest of wells, which would likely be the case if the source were at the ground surface.

Visual inspection of drill cuttings available from the study area (Figure 4) and whole rock analysis for arsenic of some of these samples, did not suggest an obvious geologic source of arsenic to well water. No appreciable amount of pyrite was visible in any of the samples examined. The subset of these samples laboratory analyzed for arsenic have relatively low levels of arsenic, ranging from 1.4 to 18 mg/kg (Table 1). These levels are considered low on the basis of comparison to the levels in rock samples collected from the sulfide cement horizon found in Winnebago County, which range from 6 to up to 674 mg/kg (Simo et al, 1997).

The Schamm residence and the Sunset Hills Association wells are the two locations in the study at which both rock and groundwater samples were available for analysis. The Schamm well is completed in shallow Silurian dolomite and has an arsenic concentration of 57 µg/L. Samples of the Silurian dolomite analyzed from this well were from the open interval of the well and had arsenic concentrations under 3 mg/kg. The Sunset Hills well, with an arsenic concentration of 38 µg/L, is completed in the deep sandstone aquifer. A sample of the unlithified materials from this borehole, collected from a depth of 125 to 135 feet, had an arsenic concentration of 2.8 mg/kg. Samples from the open interval of this well did not appear to contain any pyritic material.

The only rock sample with any appreciable amount of arsenic (18 mg/kg) was collected from location 650070, which is near the Wood School (Figure 4). This sample is from the archived drill cuttings collection maintained at the WGNHS, and is a composite of unlithified materials from a depth of 70 to 115 feet. The results from this sample are not particularly useful because they are representative of a long interval of geologic materials. (A water sample was not collected from the well; the well was drilled in 1905 and its current status is unknown.)

Pyrite minerals were encountered while drilling Country Estates Well #5, approximately 7 miles northeast of the study area, in the Town of Lyons. A significant mineralized zone is present at the top of the Prairie du Chien, at a depth of 805 feet below ground surface. Whole rock arsenic concentration in this rock is 20 mg/kg and a water sample collected during drilling contained arsenic at of 3 µg/L (verbal communication, D. Johnson WDNR, 2000). Similar mineralized zones in the vicinity of the Wood School may account for the arsenic concentration detected at the Sunset Hills Association well.

Groundwater Chemistry

Figure 6 shows a trilinear diagram with the percentage composition of the major cations and anions in groundwater in the study area. The diagram shows that groundwater from each of the three aquifers in the study area can be classified as Ca-Mg-HCO3 type water. The diagram illustrates that water from the Silurian bedrock is slightly higher in sodium and lower in sulfate than the other water.

The geochemical data does not strongly support a particular hypothesis for the source of arsenic in groundwater. If the source were sulfide oxidation, one would expect elevated levels of dissolved sulfate and iron, and elevated levels of other metals present in the sulfides, such as nickel, chromium, cobalt, copper and zinc. While this is the case at highly-impacted wells in the Fox River Valley (Schreiber, 2000), this is not apparent with the data collected in this study. As shown in Figure 7 and Tables 2 and 3, there are very low levels of sulfate, iron and trace metals in all wells sampled. Additionally, there is no apparent oxidant present in the aquifers tested: dissolved oxygen levels in the sampled wells are less than 1 mg/L, nitrate and iron levels are very low, and water levels in wells during pumping do not expose the formations to air.

The low iron concentrations found in the study area also indicate that the reduction of iron oxyhydroxides is not a predominant mechanism for arsenic release. While arsenic concentrations are higher in wells with lower redox values (Figure 7), there is no correlation between arsenic and iron concentrations.

The magnitude of arsenic detected in this study, at a maximum of 62 µg/L in a filtered sample, is not as high as concentrations detected in the Fox River Valley area, where arsenic is present at levels ranging from 100's to 1000's µg/L. In the Fox River Valley, sulfide oxidation via oxygen introduced in the borehole appears to cause high arsenic concentrations. It is unclear what causes lower-level impacts in the Fox River area. Possibilities include sulfide oxidation of host rock with lower arsenic content, reduction of arsenic-iron oxyhydroxides, or colloidal transport of arsenic from highly impacted areas (Schreiber, 2000).

Arsenic release to groundwater may also be caused by carbonation of arsenic-bearing sulfide minerals under anaerobic conditions (Kim et al, 2000). This has been proposed as a mechanism in the Marshall sandstone aquifer of southeastern Michigan, and has been tested under laboratory conditions. Although it appears that arsenic concentrations *decrease* with increasing alkalinity in the study area (Figure 7), there may be sufficient carbonate ion present in the groundwater to cause dissolution of arsenic where the arsenic is present in aquifer materials.

Well Chlorination

The batch chlorination of the Wood School well carried out during this study did not cause a subsequent increase in arsenic concentration. Figure 8 shows historic sampling results and the concentrations measured after well chlorination. Arsenic concentrations *decreased* after chlorination, although not by a significant amount. Redox measurements (Table 4) collected during the experiment confirm that the oxidizing conditions caused by chlorination are transient (on the order of days), and do not appear to induce long-term changes in well water quality.

The finding that the batch chlorination caused oxidizing conditions in the borehole for a period of about five days without causing an increase in the arsenic concentration suggests that arsenic-bearing minerals are not present in the aquifer matrix exposed at the borehole. Therefore, the results of this experiment may not hold in wells in the Fox River Valley, where affected wells intersect the sulfide-bearing horizon.

Conclusions and Recommendations

Results of this study indicate that arsenic concentrations in the Lake Geneva area are at moderate levels in the shallow bedrock aquifer and occur at lower levels in overlying, unlithified sand and gravel deposits and in the deep sandstone aquifer. Of the 22 wells sampled in the study area, three wells exceed the current arsenic M.C.L. of 50 μg/L and 11 wells exceed the proposed MCL of 5 μg/L. Eight of the 22 sampled wells are open to the shallow bedrock aquifer. All of these had detectable levels of arsenic; arsenic concentrations exceed 5 μg/L in seven of these wells and exceed 50 μg/L in three of the wells.

There is not an obvious anthropogenic source of arsenic, nor has a geologic source been identified. Hydrogeologic conditions, including the presence of the Maquoketa Formation and very separate and distinct recharge areas, indicate that the source of arsenic to the upper aquifers is unlikely to be the same as that affecting the deep sandstone aquifer. Extensive sulfide mineralization has been observed in the deep aquifer within the Prairie du Chien group, at a site seven miles northeast of the study area.

Groundwater chemistry data show generally reducing conditions, pH range between 7 and 8, and very low sulfate, iron, and trace metal concentrations. Static and pumping water levels in wells do not cause exposure of the aquifer matrix to the air-water interface. These conditions do not support sulfide oxidation or reduction of iron-oxyhydroxides as a mechanism for arsenic release to groundwater. Transport of dissolved or colloid-associated arsenic could occur under these conditions. Carbonate ion dissolution of arsenic sulfide minerals has been proposed in the literature as a mechanism of arsenic release under the reducing conditions in the study area. However, wells sampled for this study show *decreasing* arsenic concentrations with increasing alkalinity.

Although a source and mechanism of arsenic release have not been identified, based on the water quality results presented here, a public education effort should be launched to alert residents of the area to the need to test for arsenic in well water. Well drillers and real estate developers should also be made aware of the need to test new wells drilled in the area. Although there is no depth at which a well would *necessarily* encounter arsenic-free water, the shallow bedrock aquifer should be avoided in the vicinity of the Wood School.

The well chlorination experiment conducted at the Wood School well showed that, in this setting, well chlorination does not appear to cause an increase in arsenic concentration. However, the batch chlorination did result in an oxidizing environment in the borehole for a period of five days. The experiment should be repeated in a well where sulfide minerals are exposed in the borehole.

This preliminary study could be followed by additional investigation to determine the source of arsenic and mechanism for its release to groundwater. Methods of investigation might include the collection of continuous samples through the sand and gravel deposits and the Silurian dolomite, subsequent characterization of the aquifer mineralogy, and leaching tests on the samples under conditions similar to the water quality of the study area. A similar well chlorination experiment should be conducted at a arsenic-impacted well in the Fox River Valley where the borehole is known to intersect the sulfide-cement horizon.

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Table 1. Arsenic content of geologic samples

Well Id	As (ppm)	Sample Interval (ft below grd srfc)	Stratigraphic Unit	Sample Lithology
650070	4.1	335-343	Maquoketa	Dolomite
650070	3.2	320-335	Maquoketa	Shale
650070	3.5	160-240	Unlithified deposits	Sand and Gravel
650070	18	70-115	Unlithified deposits	Sand, Gravel and Clay
650070	6.9	244-285	Silurian	Dolomite
650070	2.1	285-315	Silurian	Dolomite
650538	2.8	125-135	Unlithified deposits	Clay
650999	2.3	305	Silurian	Clay
650999	1.6	301	Silurian	Dolomite
650999	2.1	303	Silurian	Dolomite
650999	1.8	304	Silurian	Dolomite
651347	2.5	185	Unlithified deposits	Sand and Gravel
651347	2.4	190	Unlithified deposits	Sand and Gravel
651347	2.4	195	Unlithified deposits	Sand and Gravel
651347	2.3	200	Unlithified deposits	Sand and Gravel
651347	2.9	205	Unlithified deposits	Sand and Gravel
651347	4.0	210	Unlithified deposits	Sand and Gravel
651347	3.1	215	Unlithified deposits	Sand and Gravel
651347	3.2	220	Unlithified deposits	Sand and Gravel
651347	5.4	225	Unlithified deposits	Sand and Gravel
651347	2.7	230	Unlithified deposits	Sand and Gravel
651347	1.9	235	Unlithified deposits	Sand and Gravel
651347	1.7	239-240	Silurian	Dolomite
651347	2.3	241-244	Silurian	Dolomite
651347	1.5	245-247	Silurian	Dolomite
651347	1.4	248-250	Silurian	Dolomite

notes:

Location 650538 is the Sunset Hills Assoc well.

Location 650999 is the Schamm well.

Water samples were not collected at locations 650538 and 651347

Table 2. Water Quality Results

		Cations and Anions (mg/L)										
Well Name	Date	Cl	Ca	Mn	Fe	Mg	NO3	Na	SO4	K	CaCO3	TDS
Wells open to Unlithified Deposits												
Interlacken 2	11/17/94							30.3				
Interlacken 2	5/30/00	1.5	50		0.9	30	<.01	28	<4.5	2.3	323	
Cook	3/17/98	83.80	100	24	.8	50		32	13.0		413	558
Schmidt	6/17/00	1.5	69		2	25		39	<4.5	1.3	342	362
Connelly	6/17/00	1.7	66		8.5	38		14	<4.5	1.3	350	346
Crane	6/17/00	21.8	90		2.6	47		14	35.9	1.4	384	466
Johnson	6/17/00	4.5	76		0.78	40		13	28.9	1.2	334	380
Hartshorne	3/17/98	2.5	81	59	5.4	51		12	46		412	462
Wells open to Silurian dolomite												
Brunk	5/8/98	2.4	43	10	1.7	32	.07	30			315	306
Brunk	5/30/00	2.9	44		0.06	32	<.01	28	<4.5	2.1	307	
Wood School	10/30/95						.29					
Wood School	5/30/00	1.8	31		0.97	24	<.01	39	<4.5	2.4	276	270
Devlin/Honkesh	5/8/98	1.9	26	4.0	2.9	27	.07	35	7.2		269	256
Devlin/Honkesh	5/30/00	3.1	27		0.75	28	<.01		<4.5	2.3	272	
Foleys	5/8/98	2.5	29	2	.36	30		37	8.6		284	284
Foleys	5/30/00	2.8	30		0.2	30	<.01	38	<4.5	1.2	278	282
Paxson	6/6/00	2	37		1.4	28	<.01	38	<4.5	4.4	300	302
Schamm	6/6/00	2.1	34		1.7	28	<.01	41	<4.5	1.3	289	298
Wells open to Maquoketa and Sinnipee Confining Unit												
Chochola	5/8/98	7.2	75	96	4.8	44		11	13.6		384	412
Wells open to Cambrian/Ordovician sandstones												
Mercy Center Hosp.	3/28/95						.70					
Sunset Hills Assoc.	5/30/00	7.8	40		0.88	31	<0.01	34	<4.5	2.0	300	318
Interlacken 1	11/17/94							16.6				
Interlacken 1	5/30/00	1.2	53		.40	33	.025	18	<4.5	2.6	317	

Note: Sample dates in 2000 indicate sample collected by WGNHS.
Collection dates prior to 2000 indicate sample collected by WDNR personnel

Table 3. Trace metals and field measurements

Well Name	Date	Metals (ug/L) As	Cr	Co	Mo	Ni	Cd	Zn	Field Tests Diss. Oxygen (mg/L)	Specific Con. (umhos/cm)	Redox (mV)	pH	T (deg.C)
Wells open to Unlithified Deposits													
Interlacken 2	11/17/94	12*											
Interlacken 2	5/30/00	13	<.5	<3	7	< 6	0.03	76		.53		7.7	14.2
Cook	3/17/98	<.06*											
Geneva Nat'l 2	11/17/94	0*	0										
Schmidt	6/17/00	0.7							0.2	.665	-72	7.3	12.8
Connelly	6/17/00	9											
Crane	6/17/00	0.9							0.3	0.789	256	7.2	13.6
Johnson	6/17/00	1.2							0.2	0.726	178	7.3	13
Hartshorne	3/17/98	<.06*											
Wells open to Silurian dolomite													
Brunk	5/8/98	16*											
Brunk	5/30/00	4.0	<.5	<3	<4	9	0.04	<8	0.3	.561	179	7.5	14.4
Wood School	10/30/95	85*											
Wood School	4/10/96	34*											
Wood School	2/10/98	61*											
Wood School	5/30/00	62	<.5	<3	6	7	0.15	74	0.1	.517	-109	7.9	13.0
Devlin / Honkesh	5/8/98	120*											
Devlin / Honkesh	5/30/00	54	<.5	3	5	14	<0.02	11	0.3	.497	-70	7.9	14.2
Foleys	5/8/98	23*											
Foleys	5/30/00	25	<.5	<3	10	13	0.02	110	0.6	.470	40	7.8	13.5
Einbeck	7/29/98	24*											
Spitz	7/2/98	20*											
Paxson	7/2/98	15*											
Paxson	6/6/00	15							0.4	.545	-157	7.8	13.8
Schamm	6/6/00	57	<.5	<3	9	< 6	0.04	51	1.0	.553	-130	7.6	13
Wells open to Maquoketa and Sinnipee Confining Unit													
Chochola	5/8/98	0.9*											
Wellhausen	8/11/98	5.9*											
Wellhausen	5/30/00	3.7							0.2	.512	-106	7.6	13
Wells open to Cambrian/Ordovician Sandstones													
Mercy Center Hosp.	3/28/95	0.8*	2.9										
Geneva Nat'l 1	11/17/94	0*	0										
Sunset Hills Assoc.	5/30/00	39	<0.5	<3	5	10	0.03	19		0.58	6	7.6	14.5
Sunset Hills Assoc.	6/17/00	38											
Interlacken 1	11/17/94	6*											
Interlacken 1	5/30/00	5.7										7.7	15.9

notes:

* indicates sample not filtered; result is total metal concentration

Sample dates in 2000 indicate sample collected by WGNHS.

Collection dates prior to 2000 indicate sample collected by WDNR personnel

Table 4. Well Chlorination Experimental Results

Sample Date	Sample Time	As (ug/L)	Fe (mg/L)	Cl (mg/L)	$CaCO_3$ (mg/L)	Ca (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	SO_4 (mg/L)	TDS (mg/L)	Redox (mV)	Field pH (SU)	Diss. Ox. (mg/L)	Spec.Cond. (umhos/cm)
5/30/00	back-ground	62 (1)	0.97	1.8	276	31	39	2.4	24	<4.5	270	-109	7.9	0.1	520
6/16/00	pre-test	53													
6/17/00	time = 0 (2)	51	0.23	9.5	276	35	38	2.3	26	<4.5	288	176	7.7	0.1	540
6/19/00	2 days	5.2	0.06	77.5	253	59	45	2.3	29	<4.5	410	175	7.3	0.5	720
6/22/00	5 days	40										-120	7.6	0.5	340
6/27/00	10 days	37	2.0			37	38	2.1	25			-290	7.8	0.7	530
7/6/00	19 days	51	2.3	2.7	275	32	38	2.2	25	<4.5	266	-138	7.8	1.0	530

notes:

(1) Samples for arsenic analysis were unfiltered with the exception of that collected on 5/30/00, which was field filtered to 0.45 microns.

(2) Sample at time = 0 was collected immediately following purging about 3 well volumes from the well, about 24 hours after addition of chlorine pellets

Table 5. Well construction and water levels

Map ID	Well Name	Aquifer	Note	Total Well Depth (ft)	Ground Surface Elevation (ft, M.S.L.)	Static Water Level (ft, M.S.L.)	Pumping Water Level (ft, M.S.L.)	Elevation of Bottom of Casing (ft, M.S.L.)
8	Interlacken 2	Unlithified sands and gravels	5	273	860	796	771	602
11	Cook	Unlithified sands and gravels		105	1005	957	952	904
19	Geneva National 2	Unlithified sands and gravels		237	1035	960	935	945
20	Schmidt	Unlithified sands and gravels		210	1025	865	865	815
22	Crane	Unlithified sands and gravels		110	945	890	850	835
23	Johnson	Unlithified sands and gravels		161	990	859	856	833
21	Connelly	Unlithified sands and gravels	4	435	1045	855	760	610
2	Hartshorne	Unlithified sands and gravels		229	1035	876	850	809
1	Brunk	Silurian dolomite		305	1065	885	820	783
3	Wood School	Silurian dolomite		321	1045	860	855	742
4	Devlin/Honkesh	Silurian dolomite	1	380	1055			
6	Foleys	Silurian dolomite	2	unknown	1035			
7	Einbeck	Silurian dolomite	3	380	990			
12	Spitz	Silurian dolomite		370	1025	810	775	655
13	Paxson	Silurian dolomite		363	1040	840	820	678
17	Schamm	Silurian dolomite		305	1035	795	790	734
14	Wellhausen	Maquoketa and Sinnipee confining unit		690	1025	760	665	616
15	Chochola	Maquoketa and Sinnipee confining unit		448	1010	795	780	636
10	Mercy Center Hosp.	Cambrian-Ordovician sandstone		795	1025	845	775	625
5	Sunset Hills Assoc.	Cambrian-Ordovician sandstone		900	1040	786	767	503
9	Interlacken 1	Cambrian-Ordovician sandstone		1194	950	717	467	38
18	Geneva National 1	Cambrian-Ordovician sandstone		1112	1030	669	583	537

notes:

1 No log available. Well depth measured; aquifer is assumed based on well depth and nearby logs.
2 No log available. Aquifer assumed based on near-by wells.
3 No log available. Well depth reported by owner; aquifer is assumed based on well depth and nearby logs.
4 Driller reports gravel at 410 feet but nearby WCRs indicate bedrock at 360 feet
5 Well is constructed with two screens; recorded water level is not indicative of water table elevation
Ground surface elevations estimated from topographic map

Table 6. Summary statistics of arsenic concentrations in well water

Hydrostratigraphic Unit	Number of Wells Sampled	No. of samples below detection limit	Average As conc. (ug/L)	Range of As conc (ug/L)
Unlithified deposits	8	3	3.1	<0.06 to 13
Silurian dolomite	8	0	33	4 to 62
Maquoketa and Sinnipee confining unit	2	0	2.3	0.9 to 3.7
Cambrian-Ordivician sandstones	4	1	11	<0.06 to 38

Average As concentration is calculated using the most recent result from each location.

A value of one-half of the detection limit is used for censored data.

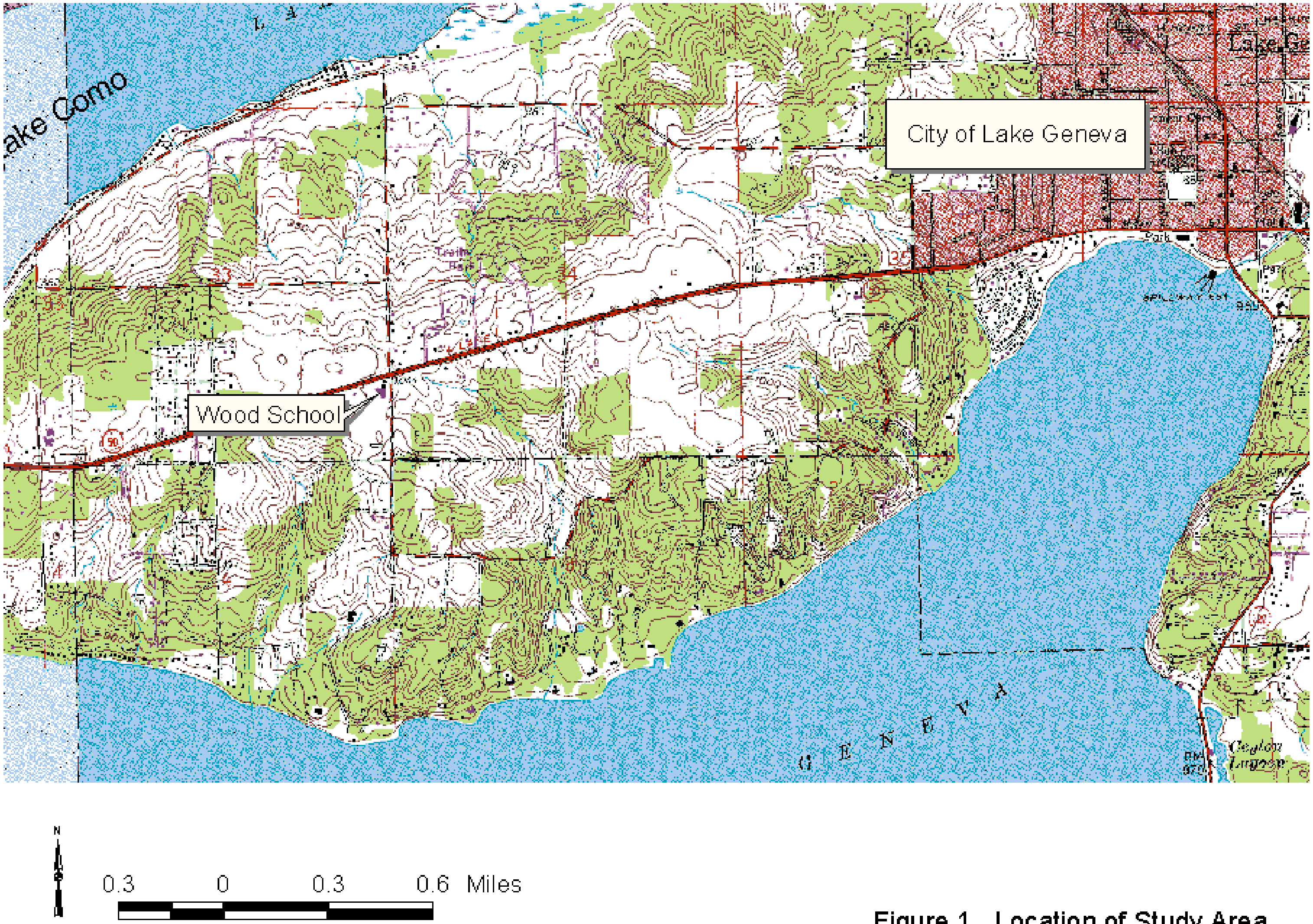


Figure 1. Location of Study Area

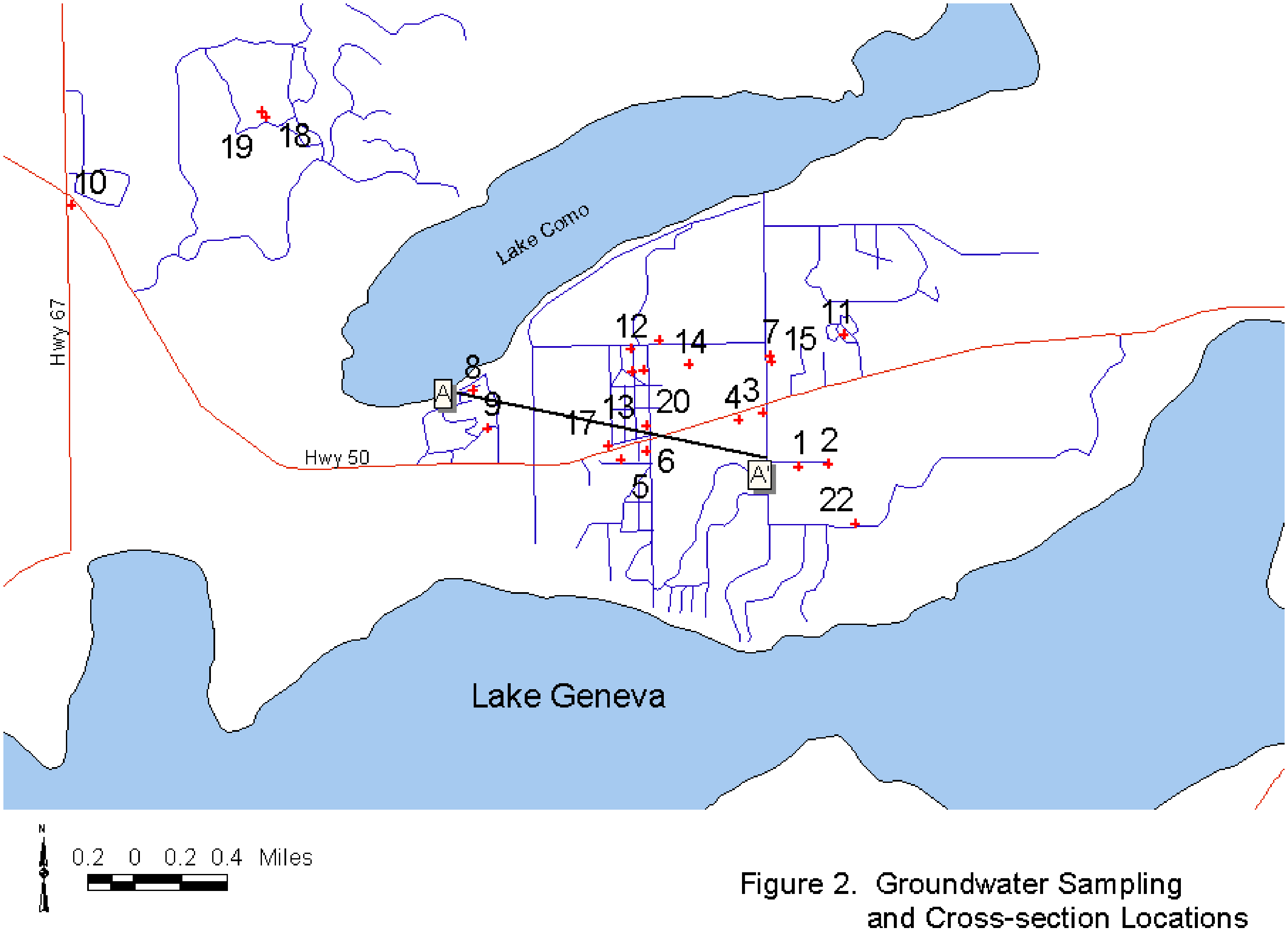


Figure 2. Groundwater Sampling and Cross-section Locations

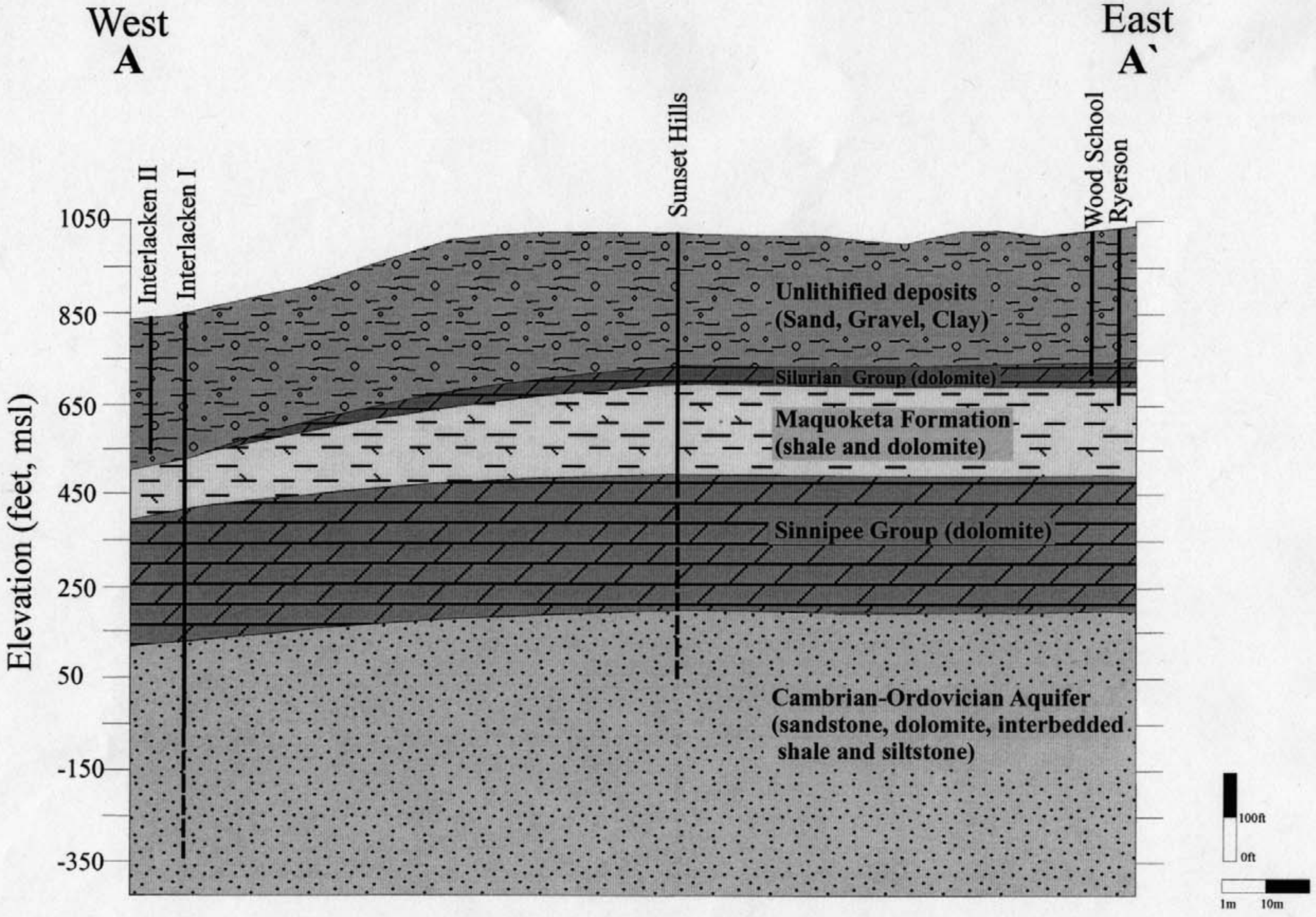


Figure 3. Geologic Cross Section

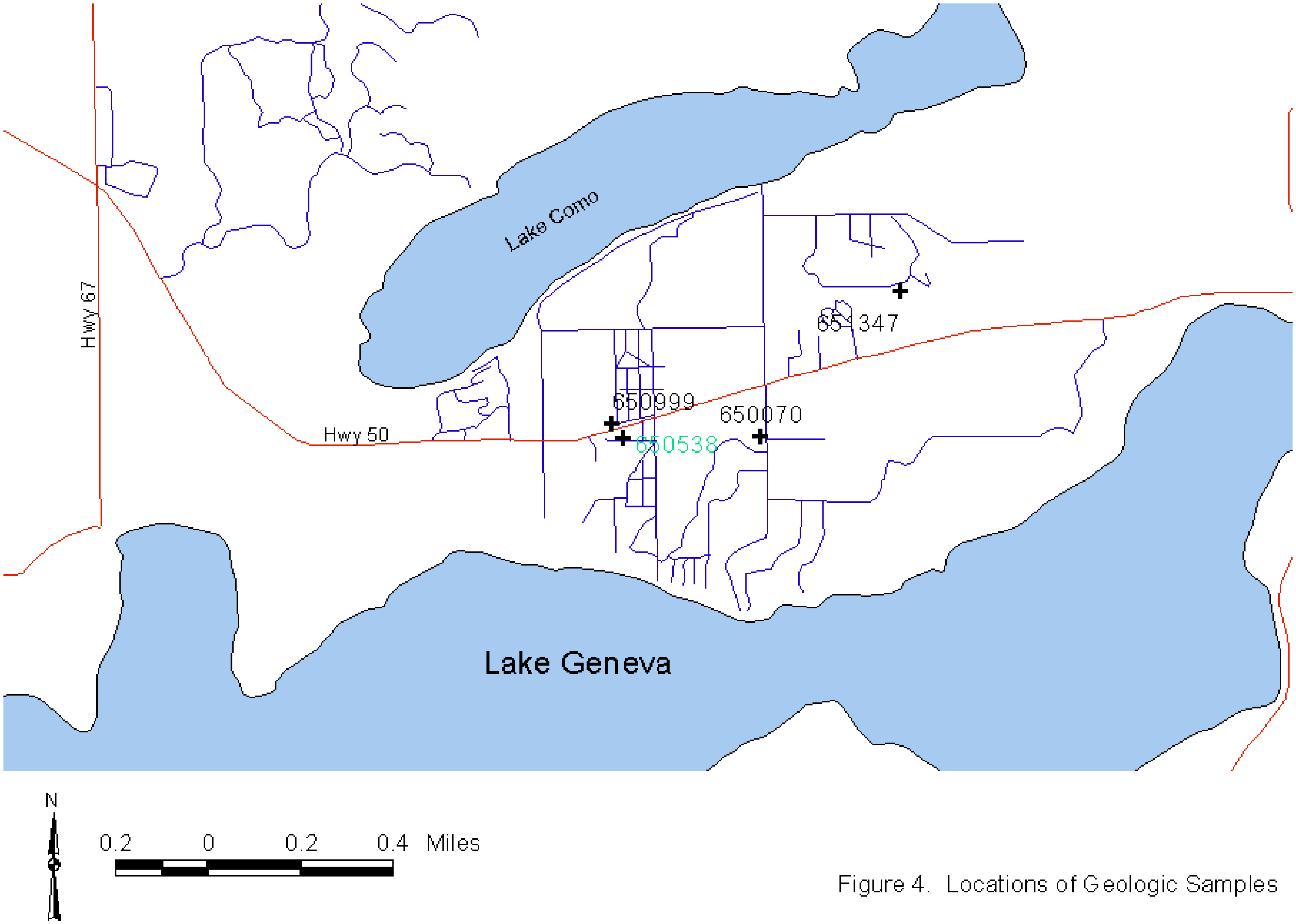
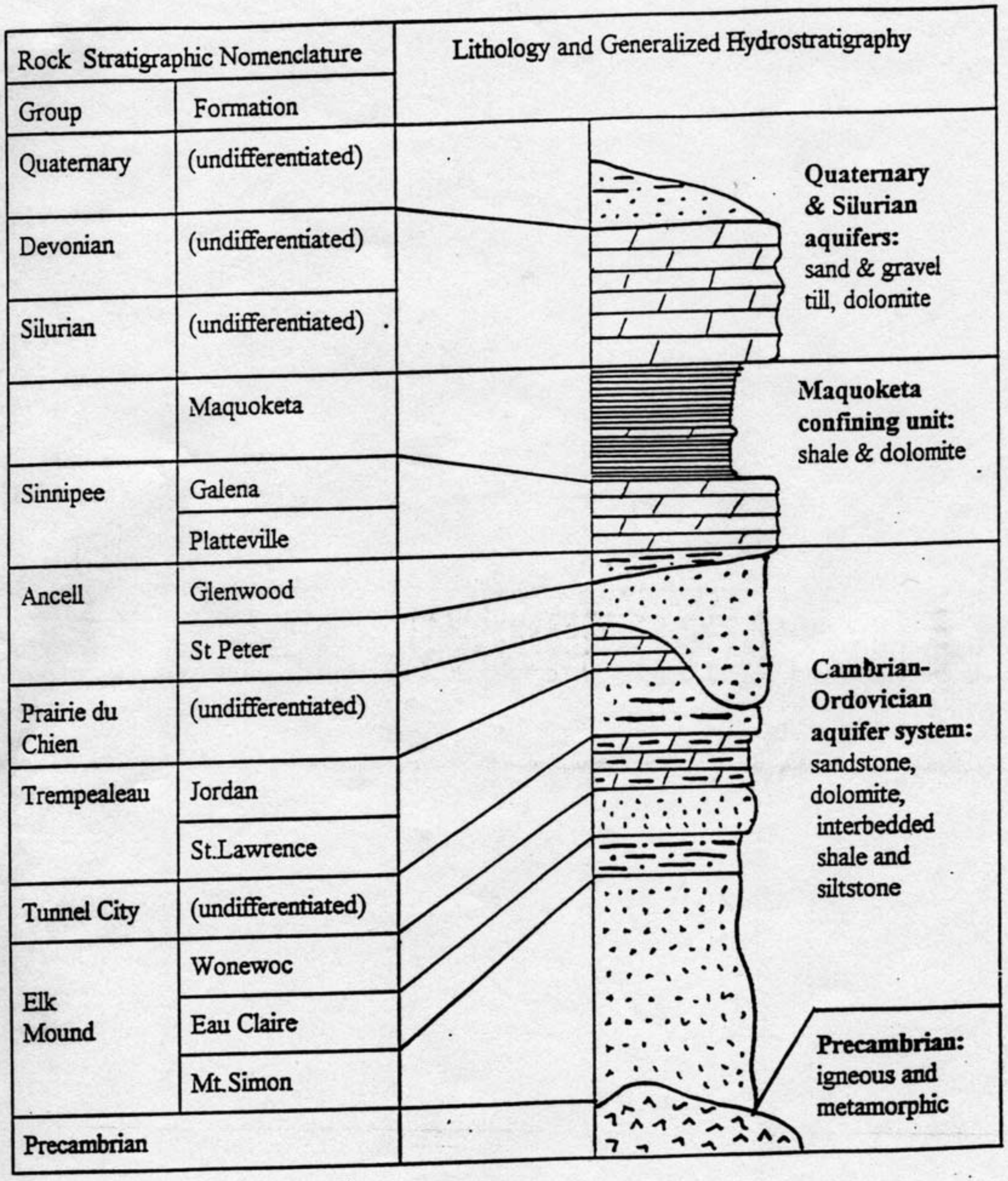


Figure 4. Locations of Geologic Samples



Rock Stratigraphic Nomenclature	
Group	Formation
Quaternary	(undifferentiated)
Devonian	(undifferentiated)
Silurian	(undifferentiated)
	Maquoketa
Sinnipee	Galena
	Platteville
Ancell	Glenwood
	St Peter
Prairie du Chien	(undifferentiated)
Trempealeau	Jordan
	St.Lawrence
Tunnel City	(undifferentiated)
Elk Mound	Wonewoc
	Eau Claire
	Mt.Simon
Precambrian	

Figure 5. Regional hydrostratigraphy, adapted from Eaton et al, 1999.

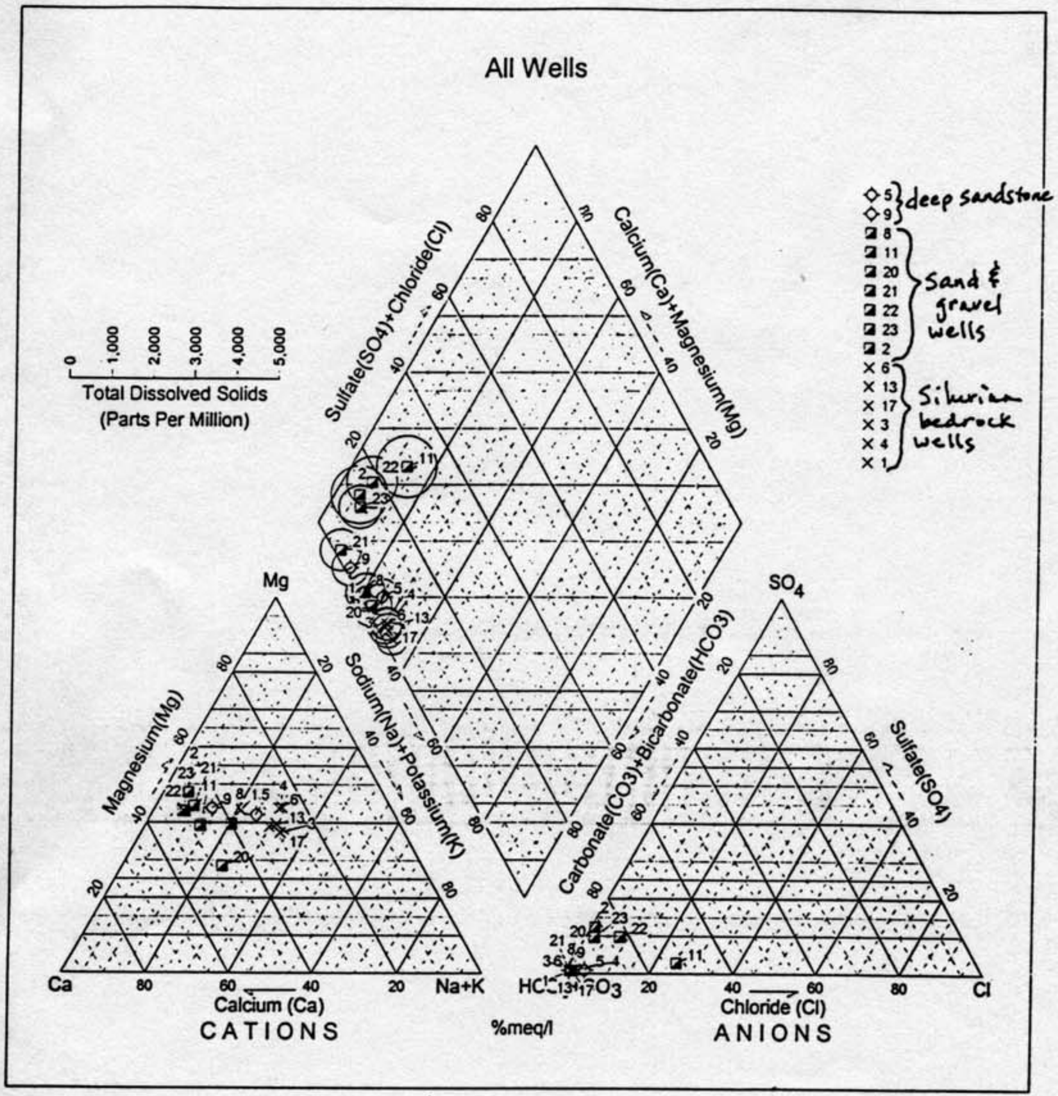


Figure 6. Trilinear diagram of groundwater quality.

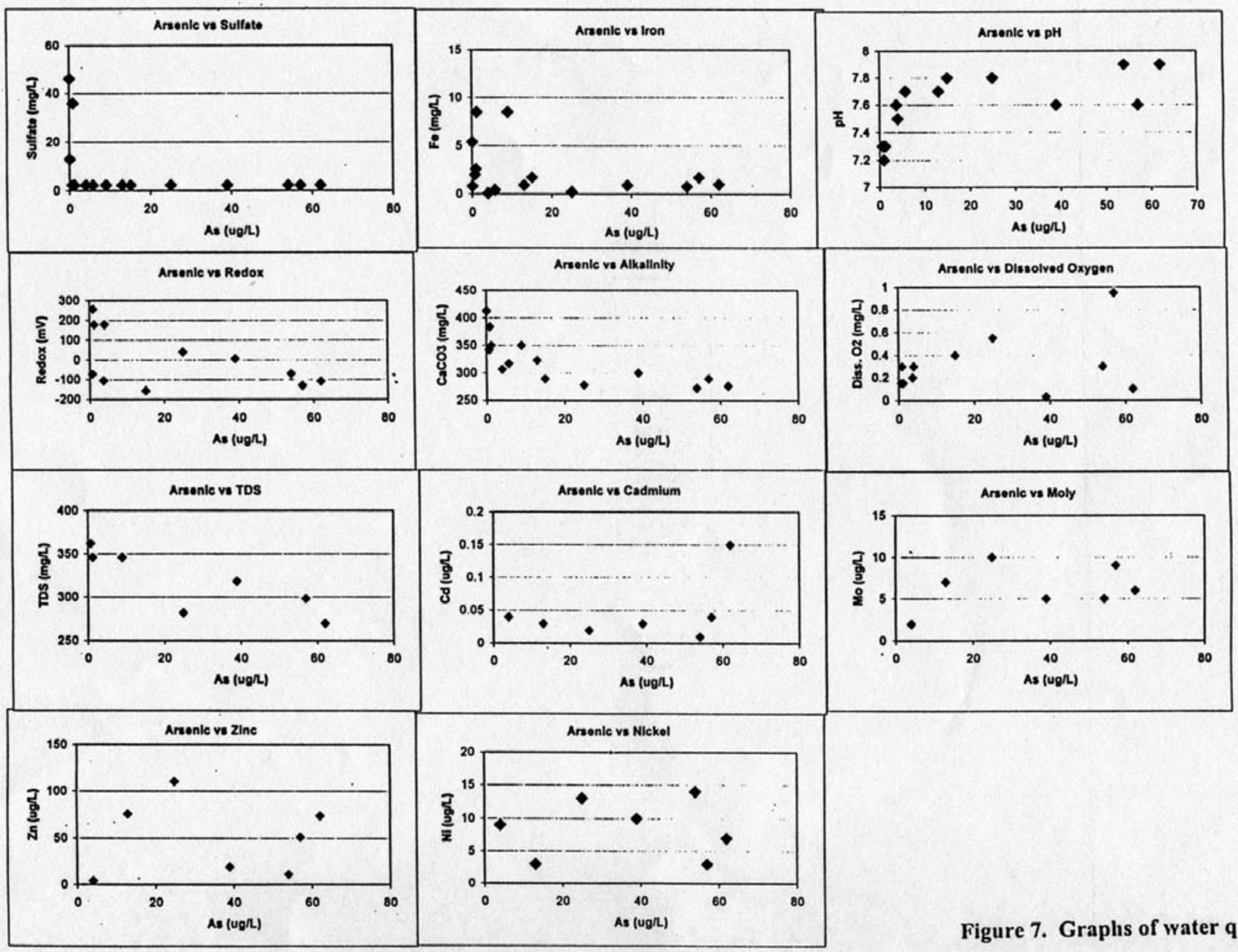


Figure 7. Graphs of water quality results.

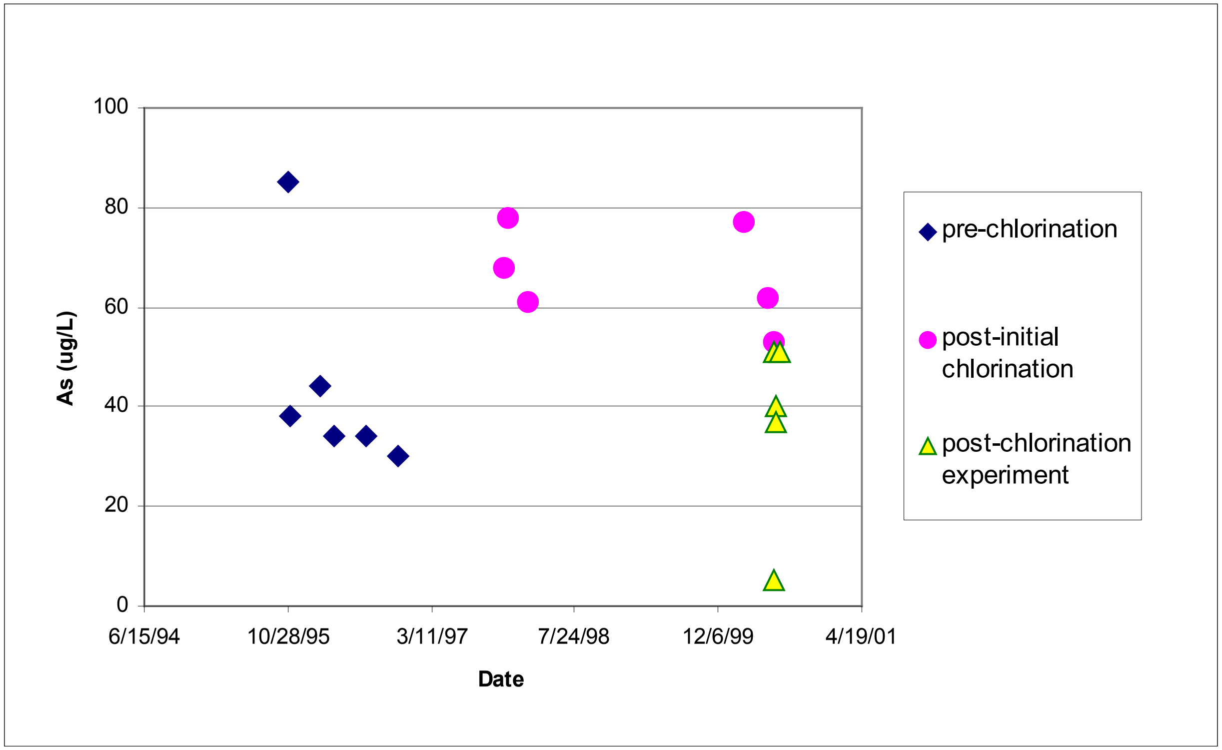


Figure 8. Historical and well chlorination data from Wood School Well