ARSENIC IN UPPER MIDWEST GROUND WATER: OCCURRENCE AND GEOCHEMICAL MOBILIZATION MECHANISMS

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Abstract

In the upper Midwest, USA, elevated arsenic concentrations in ground water are related to the presence of northwest provenance Late Wisconsinan drift. Within the footprint of this sediment, 1,690 of 7,101 (23.8%) sample locations exceed 10 µg/l arsenic compared to only 186 of 4,333 (4.3%) outside the footprint. Wells screened in glacial drift and shallow bedrock wells overlain by this glacial sediment are most impacted by arsenic contamination. Elevated arsenic concentrations are spatially related to one another over significant distances – more than 150 kilometers. Elevated arsenic concentrations are not randomly distributed. Evidence suggests that the distinct physical characteristics of the northwest provenance Late Wisconsinan drift cause the geochemical conditions necessary to mobilize arsenic. This fine-grained, comparatively organic-rich, biologically-active sediment creates a geochemical environment that is favorable to a regional-scale mobilization of arsenic in ground water via reductive mobilization mechanisms such as reductive dissolution and reductive desorption.

Arsenic concentrations are positively correlated to analytes like iron and manganese, and it is negatively correlated to analytes like chloride and bromide. In this study, there is no correlation between arsenic and carbonate, sulfate, total organic carbon, or ammonium. There is a weak negative correlation between phosphorous and arsenic. Arsenic present in ground water is aqueous, and most of the arsenic present in Minnesota ground water is As(III). No extremely low pH waters were encountered.

Sediment and ground water arsenic concentrations from the same sample location are not correlated. In this study, measured total sediment arsenic concentrations are not particularly high, 0.6 mg/kg to 10.6 mg/kg. A small but significant concentration of sediment arsenic is adsorbed onto or coprecipitated with iron hydroxides; this arsenic is labile arsenic. This study highlights an important and often unrecognized phenomenon: high-arsenic sediment is not necessary to cause arsenic-impacted ground water – when 'impacted' is now defined as greater than 10 µg/l.

Arsenic contamination is more common in domestic wells and in monitoring wells than in public water system wells. Additionally, arsenic contamination is more prevalent in domestic wells with a short screen set in proximity to an upper confining unit, such as till. The geochemical environment at the interface between the confining unit and the aquifer is conducive to arsenic mobilization.

Public water system wells have distinctly different well construction practices and well characteristics when compared to domestic and monitoring wells. Public water system well construction practices such as seeking a thick, coarse aquifer and installing a long well screen, yield good water quantity. These well construction practices also, coincidentally, often yield low arsenic. Changes in routine domestic well construction practices to exploit deeper parts of an aquifer and use a longer screen could reduce the number of domestic wells that are affected by arsenic contamination in the upper Midwest.

Arsenic concentrations do not change systematically in newly-constructed, glacial sediment domestic wells in Minnesota. Over the course of nine months, there was no discernible pattern of arsenic concentration variability in three public water system wells. Arsenic concentration standard deviations ranged from 0.5 µg/l to 3.5 µg/l for the three public water system wells. Understanding and quantifying arsenic concentration variability may be of critical importance to public water systems with an average arsenic concentration just over 10 µg/l.

There is a pattern to arsenic concentration variability in some public water system wells because of reductive arsenic mobilization mechanisms. Four of eleven sampled public water system wells in Minnesota had notable arsenic concentration variability over a short period of time. In these wells, the arsenic concentration was less than 10 µg/l shortly after pumping started, but the arsenic concentration increased over time to a level exceeding 10 µg/l. In these wells, the arsenic concentration decreased to below 10 µg/l again four hours after pumping stopped. The arsenic concentration variability can be explained by reductive arsenic mobilization mechanisms.

The pe in three of these four wells had initial pe readings that were positive or only slightly negative, and the pe moved through the crucial positive-to-negative range, where the speciation of arsenic changes from being dominated by As(V) species to being dominated by As(III) species. Six of the seven wells that did not exhibit short-term temporal changes in arsenic concentration did not have pe measurements that traveled through the positive-to-negative pe range. Three of the four wells with arsenic concentration variability used turbine pumps. All of the remaining wells used submersible pumps.

Results of this research indicate that arsenic mobilization mechanisms such as adsorption/desorption to iron hydroxides, reductive dissolution of iron hydroxides, and microbially-mediated release of arsenic are likely to play an important role in upper Midwestern ground water.

Several arsenic mobilization mechanisms were either refuted or not supported based on the results of this research. These mechanisms include anthropogenic sources, anion competition for adsorption/desorption sites to various metal hydroxides, aging of iron hydroxides, resulting in a decreased number of adsorption sites, competition with or complexation with various organic species, and release from or coprecipitation with sulfide minerals (e.g. pyrite).

Most of the data used in this analysis were collected for other purposes; therefore, the cost of conducting this analysis was relatively low. In spite of the low cost, the results have considerable consequence. A regional-scale environmental problem was identified, and significant knowledge gaps that inhibit planning, such as the lack of information tying sampling results to a specific well, were exposed. An important result of this analysis is demonstration of the value of finding and using existing sampling results to cost-effectively observe and characterize regional-scale environmental problems. Regional-scale problems cannot be observed with only local-scale data analysis.

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1.0 Introduction

Arsenic exposure from contaminated drinking water at 50 μg/l is a significant environmental cancer risk, on par with environmental tobacco smoke and home radon exposure (Smith *et al.*, 1992). In response to reports by the National Research Council (1999; 2001) and others about risks from arsenic in drinking water at 50 μg/l, in 2001 the U.S. federal drinking water standard, or Maximum Contaminant Level (MCL), was tightened from 50 μg/l to 10 μg/l. Public water systems must comply with the new MCL by January 2006. In Minnesota, USA, over 100,000 people are estimated to use a public drinking water supply with arsenic concentrations over 10 μg/l (Peterson, 2003).

Welch, et al. (2000) made the association between glaciated areas in the upper Midwest and high arsenic in ground water. Statewide arsenic sampling in Minnesota indicates that a significant area of the state has detectable concentrations of arsenic in ground water (Centers for Disease Control, 1994; Minnesota Pollution Control Agency, 1995), with approximately 14% of sampled wells exceeding 10 μg/l. In Minnesota, 150,000 to 250,000 people are estimated to obtain their drinking water from domestic wells with arsenic concentrations exceeding 10 μg/l (Soule, 2004). A study of arsenic occurrence and exposure in western Minnesota found that over 50% of the 900 sampled domestic drinking water wells had arsenic concentrations over 10 μg/l (Minnesota Department of Health, 2001). However, even in this high-arsenic area, arsenic concentrations in water had significant variability.

1.1 Problem Motivation

State and local governmental agencies are evaluating potential low-cost ways for public water systems to meet the new MCL (Erickson and Barnes, 2004b). Low-cost options include drilling a different well or changing well operation practices. However, very little is known about the mechanisms that cause the observed high-arsenic concentrations and the significant spatial and temporal variations in arsenic concentrations. Without an understanding of the mechanisms that cause arsenic release from solids and into ground water, a public water supplier cannot implement a low-cost option with any assurance that it will be a long-term solution. Overall, lack of mechanistic understanding prohibits prediction of ground water arsenic concentrations, interferes with the formulation of sound public policy, and inhibits the development of effective regulations.

The overall objective of this research project was to better understand arsenic concentrations in upper Midwestern glacial aquifers. Two keys to meeting this objective are understanding the geochemical mechanisms governing arsenic in ground water, and understanding the relationship between the geology/hydrogeology and arsenic concentration in ground water. Joint evaluation of geochemical mechanisms and potential geologic/hydrogeologic controls is a new approach to the upper Midwest's arsenic problem. The results of this approach are permitting better characterization of spatial variability of arsenic in ground water, as well as modeling and prediction of temporal variability of arsenic in ground water. Results are also providing information to governmental units for the development of sound regulations and guidance regarding drilling and using drinking water wells in high-arsenic areas. The results may be applicable to other areas throughout the world that have similar geologic/hydrogeologic conditions (e.g. Inner Mongolia, Vietnam, Romania, and Hungary (Smedley and Kinniburgh, 2002)).

1.2 A Guide to this Dissertation

Chapter 2 presents a review of the state of scientific knowledge about arsenic occurrence and geochemistry. Topics covered in the literature review include a synopsis of the worldwide occurrence of arsenic in drinking water; a discussion of arsenic geochemistry, including mechanisms that mobilize arsenic from sediment to ground water; a summary of the history behind the recent drinking water rule change in the USA; a description of the physical characteristics of sediment and wells that influence arsenic mobilization, a summary of existing Minnesota arsenic sampling results, and an outline of available and developing arsenic treatment technologies.

The methods used to gather data, collect and analyze samples, and analyze data are presented in Chapter 3. As described in Section 3.1, existing data were gathered from many sources in order to cost-effectively draw a regional picture of arsenic occurrence and geochemistry. To fill specific and important data gaps in the existing data, sampling plans for sediment and ground water were developed to answer specific questions. Sections 3.2 – 3.4 describe sample collection methods. Water and sediment samples were analyzed as described in Section 3.5 – 3.7. Section 3.8 describes data analysis methods.

Chapter 4 presents results for Minnesota specifically. Arsenic sampling results from both statewide and local studies are presented. Results for samples collected during other studies and this study are included in this section. The results of sampling conducted during this study specifically fill defined data gaps.

The results and discussion of the regional-scale data compilation effort are presented in Chapter 5. Some of the background information provided in Chapter 2 is repeated in this chapter to aid the reader in following the discussion. Probable arsenic mobilization mechanisms causing the observed regional-scale arsenic contamination problem are presented and supported. Proposed mechanisms not supported and therefore eliminated are also discussed.

Chapter 6 presents results and discussion of regional- and county-scale analyses comparing the likelihood that differing well types would have elevated arsenic concentrations. Again, some of the information provided in Chapter 2 is repeated to aid the reader in following the discussion. In this chapter, observed differences in arsenic concentration based on well type, and the probable and unlikely arsenic mobilization mechanisms involved, are presented and discussed.

The results and discussion of the temporal variability sampling are presented in Chapter 7. Long- and short-term temporal variability of arsenic concentrations were measured in selected Minnesota public water system wells.

Significant immediate practical applications and regulatory influence resulted from this research effort. The practical applications relate to screening the appropriateness of low-cost arsenic compliance options, such as drilling a different well or changing well operations. The regulatory influence relates to potential changes to domestic well regulations. The practical applications and regulatory influences are presented in Chapter 8.

Chapter 9 presents a general summary of results and conclusions, an outline of regulatory implications for the research, and a list of suggested future work.

Tables and figures are presented in Chapters 10 and 11, respectively. Complete citations for cited references are provided in Chapter 12.

2.0 Literature Review

2.1 Arsenic Occurrence

Arsenic is present in a wide variety of geological materials. It is the twentieth most common element (Sullivan and Aller, 1996), and its crustal average concentration is 1.8 mg/kg (Hem, 1985). Only a few of the hundreds of existing arsenic minerals are common in hydrogeochemical environments (Hering and Kneebone, 2002; Kanivetsky, 2000). For example, in reducing environments, arsenic is present in iron sulfide minerals such as arsenopyrite (FeAsS), realgar (AsS) and orpiment (A_2S_3); it is also present in pyrite (FeS) as a contaminant. In oxidizing environments, arsenic is found in arsenolite (As_2O_3) and claudetite (As_2O_3).

Under a wide range of geochemical conditions, arsenic has also been associated with minerals such as iron oxides (Fe_2O_3), iron hydroxides (FeOOH), other metal oxides and hydroxides (e.g. Al), and magnetite $(Fe,Mg)Fe_2O_4$ (Hem, 1985; Holm and Curtiss, 1988; Hounslow, 1980; Kinniburgh and Smedley, 2001b; Korte, 1991; Ryker, 2003; Sullivan and Aller, 1996; Yan *et al.*, 2000).

In natural fresh waters, arsenic, if present, is generally an inorganic species. In reduced environments, the form of arsenite (As(III) as H_3AsO_3 and its dissociation constituents) is predominant; arsenate (As(V) as H_3AsO_4 and its dissociation constituents) predominates in oxic environments (Francesconi and Kuehnelt, 2002). Arsenite is most prevalent as a neutral species in the circumneutral pH range, while arsenate is present in one of two negatively charged species. See Table 1. Discussions regarding arsenic occurrences observed throughout the world are presented in Sections 2.5, 2.6, and 2.10.

2.2 Arsenic Contamination Mechanisms

Worldwide, both in the field and in the laboratory, numerous mechanisms have been shown or postulated to cause arsenic contamination in ground water. Some examples of arsenic release mechanisms discussed in the literature are summarized in Table 2. Table 2 does not present an exhaustive list of all references that cite the given mechanisms, nor do the references necessarily attribute the observed arsenic concentrations to only one mechanism. Many authors acknowledge that more than one mechanism is likely contributing to high arsenic concentrations in ground water.

Some arsenic mobilization mechanisms, such as anthropogenic contamination or mining-related contamination, are important only at a relatively local scale. Arsenic mobilization mechanisms such as evaporative concentration and high pH (i.e., pH > 8) desorption, are not known to occur in upper Midwest ground water are not relevant to this research. The geochemical mechanisms of focus for this regional-scale research are the following:

- Adsorption/desorption to iron hydroxides
- Anion competition for adsorption/desorption sites to various metal hydroxides
- Iron hydroxides aging, resulting in a decreased number of adsorption sites
- Reductive dissolution of iron hydroxides
- Competition with or complexation with various organic species
- Release from or coprecipitation with sulfide minerals (e.g. pyrite)
- Microbially-mediated release of arsenic

2.3 Arsenic Geochemistry

The oxidation state and mobility of arsenic are sensitive to the redox state of the solution (Plant *et al.*, 2001). Processes within an aquifer influence the redox state not only of arsenic, but also of iron and sulfur, which influence distributions of arsenic (Langner and Inskeep, 2000; Rochette *et al.*, 2000; Sracek *et al.*, 2004; Zheng *et al.*, 2004). Processes such as carbonate dissolution and biological activity, which control pH and the redox state of fluids infiltrating through tills or clay, have been well documented for numerous localities (Hounslow, 1980; Keller, 1991; Keller *et al.*, 1991b; Lawrence *et al.*, 2000; Simpkins and Parkin, 1993; Yan *et al.*, 2000). The reduction of As(V) to As(III) in the presence of iron has been shown to occur relatively quickly in the laboratory, as have adsorption processes for As(V). As(III) was shown to have less affinity for adsorption to iron oxides and to adsorb more slowly than As(V) (Bose and Sharma, 2002; Kim and Nriagu, 2000).

At present, a complete thermodynamic model for predicting arsenic species distributions in ground water does not exist (Inskeep *et al.*, 2002). A lack of understanding about arsenic speciation prohibits quantitative modeling of arsenic mobilization from sediment to ground water at this time (O'Day *et al.*, 2004). However, parameters such as pH and redox state are known to be important. Although it is an important parameter governing arsenic partitioning between the solid and aqueous phase, the *in situ* redox conditions of an aquifer is difficult – bordering on impossible – to measure accurately (Hering and Kneebone, 2002; Lindberg and Runnells, 1972). Measured redox states often do not agree with those calculated from measured redox couples (Holm and Curtiss, 1989; Lindberg and Runnells, 1984; Runnells and Lindberg, 1990). Measured redox states using oxidation reduction potential (ORP) probes often do not give accurate and precise measurements due to geochemical disequilibrium, but the readings can be used to obtain approximate values and categorize regimes (Holm and Curtiss, 1989; Kölling, 2000; vanLoon and Duffy, 2000). Measuring arsenic species can provide additional information about the redox state of the aquifer (Rude and Wohnlich, 2000). In the laboratory, equilibrium between arsenate and arsenite is reached in a timer period on the order of days in the presence of iron (Bose and Sharma, 2002).

Arsenic adsorption occurs when the ionic complexes of As(V) ($HAsO_4^{-2}$ and $H_2AsO_4^{-1}$) are adsorbed to iron and other metal hydroxide solid surfaces; As(III) (H_3AsO_3) sorbs to iron oxides (De Vitre *et al.*, 1991; Pierce and Moore, 1982; Sracek *et al.*, 2004; Tyrrel and Howsam, 1997; Welch *et al.*, 2000). Metal hydroxides are ubiquitous in most ground water aquifers (Zachara *et al.*, 2001). The species of arsenic present in an aquifer can have an important impact on the fate and transport of the arsenic. Stollenwerk (2003) summarizes numerous laboratory studies that present arsenic adsorption characteristics. Work by Pierce and Moore (1982), Zobrist (2000), and Garrido *et al*. (2003) all note that As(III) sorbs less strongly than As(V) . As As(V) is reduced to As(III), arsenic concentrations increase in water. Kanivetsky (2000) modeled arsenite adsorption equilibrium in Minnesota. Modeled arsenic was consistently and significantly lower than measured arsenic concentrations, indicating that geochemical processes are missing from the simple model.

Arsenic is often present in iron sulfide minerals such as pyrite (Goldhaber *et al.*, 2001). However, its presence in pyrite can make pyrite either a source or a sink for arsenic, depending upon the redox state of the water (Schreiber *et al.*, 2000; Welch *et al.*, 2000). Mineral formation/dissolution has been identified as an important arsenic-trapping and releasing

mechanism in a number of environments (Kirk *et al.*, 2004; Schreiber *et al.*, 2000; Smedley and Kinniburgh, 2002; Thorton, 1996).

One factor that can govern the presence of arsenic in ground water is its general presence in other environmental media. In the upper Midwest, the Pierre and similar Cretaceous shale in North Dakota and Canada were entrained and later deposited as a fraction of the Quaternary glacial sediments that overlay a large portion of the region (Hobbs and Goebel, 1972; Schultz *et al.*, 1980; Wright, 1972). The arsenic concentration in the Upper Cretaceous Pierre Shale has a measured range of 1 to almost 50 mg/kg (Rader and Grimaldi, 1961), primarily as arsenic in iron sulfides (US Geological Survey, 1962).

Kanivetsky (2000) summarized the arsenic concentrations measured in Minnesota Quaternary sediments. Mean arsenic concentrations range from <0.1 mg/kg to 26 mg/kg in the western part of the state, which is higher than concentrations measured in sediments in the eastern part of the state, where they range up to 11 mg/kg. Although categorized as 'eastern' and 'western,' all of the sample locations are within the footprint of Late Wisconsinan glacial sediments of northwestern source provenance. These glacial sediments are discussed in greater detail later in Section 2.8.

Arsenic and other trace metals are bound to iron oxide surfaces in one of several ways, including surface complexation with hydroxyl groups, coprecipitation with the iron oxide mineral, and complexation with humic substances that are, in turn, adsorbed to the iron oxide mineral. These processes can be complicated by the presence of other anions commonly present in natural waters.

Geochemical modeling suggests that carbonate and phosphate interfere with arsenic adsorption onto iron oxides (Appelo *et al.*, 2002; Hiemstra and Van Riemsdijk, 1999; Holm, 2002). The bicarbonate anion has been shown to mobilize arsenic in laboratory studies using sediments from Bangladesh (Anawar *et al.*, 2004). Kim *et al*. (2000) show that bicarbonate mobilizes arsenic from the Marshall Sandstone, in southeast Michigan, USA. In a field study in Bangladesh, high arsenic concentrations in ground water were accompanied by high bicarbonate concentrations (Zheng *et al.*, 2004). In laboratory studies, natural organic matter, dissolved organic carbon, and silicic acid interfere with arsenic sorption to iron oxides (Grafe *et al.*, 2001; Redman *et al.*, 2002; Waltham and Eick, 2002). Laboratory and modeling studies indicate that phosphate and silicate inhibit arsenic adsorption to iron oxides (Holm, 2002; Meng *et al.*, 2000; Sracek *et al.*, 2004; Su and Puls, 2003).

Authors working on buried glacial aquifers and other aquifer environments throughout the world document high arsenic concentrations in ground water and significant arsenic concentration variability (Erickson and Barnes, 2003; Holm and Curtiss, 1988; Kim *et al.*, 2002; Kinniburgh and Smedley, 2001b; Kirk *et al.*, 2004; Korte, 1991; Schreiber *et al.*, 2000; Sukop, 2000; Warner, 2001). Correlations between arsenic concentration in water and redox are noted, as is a correlation between elevated arsenic concentration and the general presence of organic material in the sediment.

The solid phase of the arsenic in sediment plays an important role in its potential for release from solid to water (Akai *et al.*, 2004). Procedures for quantifying the arsenic phase by performing sequential extractions have been presented in the literature (Gleyzes *et al.*, 2001; Keon *et al.*, 2001; Van Herreweghe *et al.*, 2003). Kinniburgh and Smedley (2001b) suggest that the labile arsenic is adsorbed onto metal oxides or coprecipitated with metal oxides; arsenic minerals and

arsenic coprecipitated with minerals other than metal oxides are strongly held and are not as available for release under normal ground water conditions. Microbial processes play an important role in mobilizing arsenic from sediment to water in reducing environments (Akai *et al.*, 2004) and in sequestering arsenic (Kirk *et al.*, 2004).

2.4 Iron Cycling in Reduced Aquifers

Iron(III) oxides and other iron minerals are ubiquitous in aquifer sediments throughout the world (Zachara *et al.*, 2001). Iron oxides can be present as discrete grains or as a coating on other sediment grains. Iron minerals, iron oxides in particular, have a high surface area and are reactive (Schwertmann and Cornell, 2000). The adsorptive capacity of iron hydroxides has an influence on dissolved ground water concentrations of many metals, such as phosphorus, arsenic, cobalt, and nickel (Houben, 2003a; Pierce and Moore, 1982; Schwertmann and Cornell, 2000). Iron oxide aging and dissolution mechanisms have been discussed extensively in the literature as potential mechanisms for mobilization of trace metals in aquifer systems (Bose and Sharma, 2002; Farquhar *et al.*, 2002; Lovley *et al.*, 1998). Natural trace metal mobilization has led to areas of both local and widespread contamination of ground water, particularly by arsenic (Mandal and Suzuki, 2002).

Although iron species distributions can be well-defined under ideal conditions, measured iron concentrations in natural ground water are often at odds with theoretical predictions based on pH and redox measurements. Therefore, other factors, such as other species present in the water, microbial activity, and/or other processes, must also play a role in iron species distributions in natural ground water systems (Bose and Sharma, 2002; Houben, 2003a; Houben, 2003b; Lovley *et al.*, 1998).

At circumneutral pH and under reducing conditions, iron oxides are present, but Fe(II) is the dominant iron species. However, other factors besides equilibrium partitioning of iron species affect the iron species distribution. One mechanism for creating Fe(III) oxides in a theoretically unfavorable reducing aquifer environment is microbial mediation. Specialized microbial species such as *Gallionella* and *Lapthorhrix*, which are commonly found in ground water, catalyze oxidation processes to form iron oxides. The bacteria gain energy from 'breathing' iron (Houben, 2003a). The iron oxide formed through this type of process is often ferrihydrite, a mineral phase that has little crystalline order and high surface area, and it is often the first iron oxide mineral to form. Ferrihydrite is also referred to as an 'amorphous iron oxide,' or HFO.

Other iron oxides that are also commonly present in aquifer systems are goethite and magnetite. Two physical characteristics of each of these iron oxides, specific surface area and crystallinity, directly affect the mineral adsorption capacity and, thus, trace metal mobility (Dixit and Hering, 2003; Houben, 2003a; Jones *et al.*, 2000). Iron oxides can be differentiated from one another using a number of different techniques, including x-ray diffraction (XRD) and scanning electron microscopy (SEM). HFO can also be differentiated from more crystalline minerals using acid oxalate extraction carried out in the dark (Schwertmann and Cornell, 2000).

Although it is the first iron oxide mineral to form, HFO is not the most thermodynamically stable form of iron oxide solid. Over time periods ranging from months to years, HFO will recrystallize to the more stable form, goethite (Houben, 2003a; Schwertmann and Cornell, 2000). Although the sorptive strength of the two minerals is similar, an important ramification of this iron oxide recrystallization, or 'aging' process, is the loss of surface area. As shown in Table 3, HFO has ten times more surface area than the same mass of goethite (Dixit and Hering, 2003;

Houben, 2003a). Trace metals that are adsorbed to oxide surfaces are affected by this loss of surface area because there are fewer sorption sites available per mass of iron oxide if there is less surface area. Therefore, mineral aging can lead to mobilization of trace metals simply because there are fewer sorption sites for binding the same number of competing trace metal ions.

Iron oxides can be reduced to $Fe(II)_{(aq)}$ through two primary mechanisms: microbial and abiotic reduction. Both mechanisms have the effect of changing the surface layer of the iron oxide from a solid to an aqueous state. The effect of this mobilization of the iron phase can have the effect of coincidentally mobilizing adsorbed or coprecipitated trace metals.

2.4.1 Microbial Iron Reduction

Bacteria such as *Shewanella putrefacians* CN32 have been identified as 'iron-reducing bacteria.' These iron reducers change Fe(III) oxide solids to $Fe(II)_{(aq)}$. Although they can act upon many iron minerals, the iron-reducing bacteria are most effective at reducing HFO, which has a low degree of crystalline structure and extensive surface area. Unlike other mechanisms, the crystallinity and the amount of surface area in the mineral, not its thermodynamic properties, are the rate-controlling factors for biological iron reduction (Roden, 2003). Iron oxides act as terminal electron acceptors for iron-reducing bacteria respiration. The presence of PO_4^{3-} can enhance the rate of Fe(II) production from Fe(III) oxides via bacterial reduction (Zachara *et al.*, 2001).

Formation of $Fe(II)_{(aq)}$ does not invariably lead to a sustained increased concentration of $Fe(II)_{(aq)}$. Rather, $Fe(II)_{(aq)}$ can participate in other reactions that will keep it out of solution. These other reactions include adsorption of Fe(II) itself onto the Fe(III) oxide surface or formation of Fe(II) solid phases, such as green rust or siderite. However, the presence of PO_4^{3-} can inhibit the formation of siderite. The presence of ligands that either promote precipitation of Fe(II) minerals or increase Fe(II) solubility enhance bacterial Fe(III) oxide reduction by maintaining a lower background concentration of $Fe(II)_{(aq)}$ (Zachara *et al.*, 2001).

2.4.2 Abiotic Iron Reduction

A primary abiotic mechanism for reduction of Fe(III) oxide solids to $Fe(II)_{(aq)}$ is electron transfer via humic substances. Humic substances are complex organic acids, and they are present in aquifer sediment as the result of natural organic matter decomposition processes (Deutsch, 1997). Humic substances shuttle electrons; iron acts as the terminal electron acceptor. Even in the presence of small amounts of humic substances, this mechanism can be an effective oxide-reducing mechanism because the humic substances can be oxidized and reduced repeatedly (Lovley *et al.*, 1998; Zachara *et al.*, 2001).

The abiotic humic substance electron-shuttling iron-reduction mechanism can also be enhanced by bacteria. In this case, bacteria reduce humic substances that, in turn, interact with iron oxides and become oxidized while the iron oxides become reduced. The simultaneous presence of humic substances and the proper bacteria significantly increases both the rate at which and degree to which iron oxides are reduced (Lovley *et al.*, 1998).

The presence or absence of iron-reducing bacteria and/or humic substances determines which mechanism is the primary iron-reducing mechanism at work in the system.

2.5 Arsenic in Ground Water in Bangladesh and West Bengal, India

Since the late 1980s, arsenic contamination in ground water has been an urgent public health concern in Bangladesh and West Bengal, India. Up to 77 million people are estimated to use drinking water with arsenic concentrations over 50 μg/l, the drinking water standard in these areas (Anawar *et al.*, 2002).

In the 1970s and 1980s, the international community assisted in funding a change in the primary drinking water sources for many people in the Bengal basin region. Tube wells were drilled to provide ground water for domestic use because surface water posed health risks from bacterial and other contamination. Unfortunately, the ground water geochemistry was not comprehensively tested at the time of well drilling. By the mid-1980s, the significant health problems caused by arsenic exposure were becoming apparent, spurring extensive research efforts to determine the cause of the problem (A.Mushtaque R.Chowdhury, 2004; Kinniburgh and Smedley, 2001b; Nickson *et al.*, 2000). Hundreds of articles related to arsenic and arsenic exposures in the Bengal basin have been published in various referred journals (Arsenic Crisis Information Centre, 2004).

There has been vigorous, sometimes even hostile, debate in the literature and in electronic discussion groups regarding the identification of the primary arsenic mobilization mechanisms responsible for the arsenic contamination observed in the Bengal basin (Various Authors, 2004). The two broad categories of arsenic mobilization mechanisms being considered are oxidation mechanisms, such as oxidation of arsenic-rich sulfide minerals (i.e., pyrite), and reductive mechanisms such as reductive desorption or reductive dissolution of metal oxides (Anawar *et al.*, 2003; Kinniburgh and Smedley, 2001a; Kinniburgh and Smedley, 2001b; Pal *et al.*, 2002). The hostile tone of portions of the debate comes, seemingly, from a desire of some authors to assign a blame for the region's arsenic contamination problem. Oxidation mechanisms, which could be caused by over-pumping aquifers for irrigation and other uses, are amenable to an assignment of blame, if it is shown to be the cause of arsenic contamination. Reductive mechanisms, however, are 'natural,' and it appears more difficult to cast blame.

In spite of the tone of some authors, significant scientific understanding about arsenic mobilization mechanisms, described in various sections of this dissertation, has been gained from the research conducted in the Bengal basin. The understanding gained is, in many cases, applicable to other types of geologic regimes.

2.6 Arsenic Occurrence in Ground Water in Other Parts of the World

Although probably the most well-known area of arsenic contamination in the world, the Bengal Basin region is not the only area with significant arsenic contamination. In Asia, natural and anthropogenic arsenic contamination has been noted in countries such as China, Taiwan, Korea, Cambodia, and Japan (Kinniburgh and Smedley, 2001b; Kondo *et al.*, 1999; Liu *et al.*, 2003; Liu *et al.*, 2004; Polya *et al.*, 2004; Saxena *et al.*, 2004; Smith *et al.*, 1992). Arsenic contamination is also widely reported in Europe, from Great Britain to Italy. Arsenic contamination in Europe is also caused by natural mobilization mechanisms and human contamination (Daniele, 2004; Fytianos and Christophoridis, 2004; Hernaandez-Garcia and Custodio, 2004; Kinniburgh and Smedley, 2001b; Pfeifer *et al.*, 2004; Tamasi and Cini, 2004).

In Australia, arsenic contamination near Perth has been attributed to aquifer draw-down and acidification of aquifers (Appleyard *et al.*, 2004). In Africa, somewhat localized arsenic

contamination due to mining activities is reported in Ghana, Zimbabwe, and South Africa (Kinniburgh and Smedley, 2001b; Williams, 2001).

Both North and South America – from Alaska to Chile – have local-scale to regional-scale geographic areas with reported arsenic contamination. Arsenic contamination sources are both naturally occurring and anthropogenic in the Americas, as in other parts of the world. The USA has widespread, naturally occurring arsenic contamination in the northern continental USA as well as in the Southwest (Ayotte *et al.*, 2003; Chadima, 1996; Erickson and Barnes, 2005a; Erickson and Barnes, 2005b; Gotkowitz *et al.*, 2004; Holm and Curtiss, 1988; Kim *et al.*, 2002; Kim *et al.*, 2003b; Kirk *et al.*, 2004; Roberts *et al.*, 1986; Schreiber *et al.*, 2000; Warner, 2001). Mexico, Chile, and Argentina have well-documented arsenic contamination problems (Bexfield and Plummer, 2003; Bundschuh *et al.*, 2004; Kinniburgh and Smedley, 2001b; Mahlknecht *et al.*, 2004; Romero *et al.*, 2004).

2.7 The American Debate about the Arsenic Drinking Water Standard

Prior to 2001, the federal drinking water standard for arsenic in the United States was 50 µg/l. In 2001, 15 years after Congress directed the United States Environmental Protection Agency (USEPA) to do so, and 12 years after the 1989 deadline set by Congress in 1986, USEPA announced a new, stricter arsenic standard of 10 µg/l. The World Health Organization arsenic standard has been 10 µg/l for decades. In fact, the US Public Health Service recommended a 10 µg/l standard for the US as early as 1962 (Smith *et al.*, 2002).

During the 1980s and 1990s, a growing body of epidemiological evidence showed that the lifetime cancer risk from drinking water at 50 µg/l arsenic is unacceptably high. The cancer risk routinely applied by USEPA to set drinking water standards is one excess cancer per ten thousand exposed people (1:10,000). The lifetime cancer risk from drinking water at 50 µg/l arsenic has been calculated to be 21:1,000 (approximately 2:100), which is more than 100 times less protective than USEPA's own guidelines. There are only two known environmental cancer risks that are of similar concern: environmental tobacco smoke and radon (Smith *et al.*, 1992).

The Science Advisory Committee's Drinking Water Advisory Board of USEPA prepared a report in 1995 (Drinking Water Committee of the Science Advisory Board, 1995). The 1995 report primarily focused on potential technical obstacles to implementing a lower arsenic standard, such as a sufficiently low laboratory practical quantitation limit and the efficacy of arsenic-removal technologies. The National Research Council issued two reports urging USEPA's adoption of a more protective drinking water standard for arsenic (National Research Council, 1999; National Research Council, 2001).

There were (and continue to be) significant political obstacles to implementing a lower arsenic drinking water standard in the United States. The obstacles were and are primarily related to the cost of implementing a more stringent arsenic standard due to the widespread presence of arsenic in ground water in the United States (Frey *et al.*, 1998; Welch *et al.*, 1999), disagreement within the scientific community with regard to determination of the 'right' standard (Chappell *et al.*, 1997; Thornton, 1996), disagreement about the cancer risk from relatively low concentrations of arsenic (Lamm *et al.*, 2004), and disagreement about the appropriate cost/benefit analysis of a more stringent arsenic standard (Burnett and Hahn, 2001; Frost *et al.*, 2002; Sunstein, 2001). In fact, on June 25, 2004, HR 4717 was introduced in the U.S. House of Representatives by Representative C.L. Otter (R-ID). For contaminants such as arsenic, HR 4717 would "allow small public water systems to request an exemption from the requirements of any national

primary drinking water regulation for a naturally occurring contaminant, and for other purposes" (American Water Works Association, 2004).

The current debate notwithstanding, USEPA did adopt a more stringent arsenic standard in 2001. Barring a change in the current law, all US public water systems have until January 2006 to comply with the new arsenic standard. Adoption of the new rule has spurred industry research to develop cost-effective and creative treatment alternatives for affected communities, especially small communities (Gurian and Small, 2002; Han *et al.*, 2003; Kim *et al.*, 2003a; Vaishya and Gupta, 2003). Research on basic and applied science related to arsenic mobilization mechanisms, such as the research presented in this dissertation, has also been stimulated.

The results of a recent USEPA study (Lytle *et al.*, 2004) may initiate a new phase of the arsenic public health debate. The study shows that a significant amount of arsenic accumulates in drinking water distribution system infrastructure (i.e., distribution system pipes). Total arsenic concentrations were measured from 107 μg/g to 9,936 μg/g in hydrant flush solids, and from 3 μg/g to 13,650 μg/g arsenic in pipe sections. These arsenic concentrations dwarf arsenic concentrations measured in natural sediment associated with elevated arsenic in water. Even systems with very low arsenic concentrations in water discharged to the distribution system had significant pipe or flush solids arsenic concentrations. These results illustrate how effectively iron minerals precipitate on pipe surfaces and adsorb arsenic (Lytle *et al.*, 2004). The study also illustrates that there is a risk that arsenic concentrations in water entering the distribution system may not represent the arsenic concentrations in water at an individual user's tap at any given moment.

2.8 Upper Midwest Late Wisconsinan Geology

The upper Midwest states of North Dakota, South Dakota, Minnesota, and Iowas comprise the study area. The geologic setting of the study area is composed of heterogeneous glacial sediments overlying bedrock in most locations. The exceptions are the southwestern part of North Dakota, the western part of South Dakota, and the southeastern part of Minnesota, which were either never glaciated or have no preserved glacial sediment (Soller, 1997). The recent geologic history of the upper Midwest is complex. The area has been subject to numerous glacial advances and retreats. Based on the conjectures of a previous study (Minnesota Department of Health, 2001), the glacial advances of most relevance to this study are the multiple Late Wisconsinan period glacial advances (16,000 to 12,000 years ago) from the Keewatin ice center in central Canada, north-northwest of the study area. From west to east, the ice advances of interest and their associated glacial sediments include the Souris lobe, the James lobe, the Red River Lobe, and the Des Moines lobe (Clayton *et al.*, 1980; Fullerton *et al.*, 1995; Lusardi, 1997; Meyer, 1997). Figure 1 (Knaeble and Meyer, 2004) illustrates the ice flow directions and source provenances in Minnesota sediment. In this dissertation, the source material of Riding Mountain and Winnipeg provenance, as described in Meyer (1997), is described as 'northwest provenance.' Clayton (1980), Fullerton *et. al*. (1995), Lusardi (1997), Meyer (1997), and Soller (1997) are all in general agreement regarding the approximate footprint of the northwest provenance Late Wisconsinan sediment. This drift (the till and the associated meltwater features (Bates and Jackson, 1984)) is the glacial drift of particular interest to this study.

Superior lobe sediments, also Late Wisconsinan, were deposited over northeastern and north-central Minnesota and areas north and east of the study area by ice traveling from the northeast,

the Labrador ice center. The Superior lobe matrix composition is distinctly different in both texture, pebble composition, and color; it has a larger fraction of sand, and it is red (Boerboom, 2002; Lusardi, 1997; Wright, 1972). Other glacial sediments also exist in the upper Midwest, either underlying the Late Wisconsinan sediments or as the uppermost glacial unit. Older sediments are not of specific interest to this study. A generalized map of the glacial sediment in the study area is presented in Figure 2.

Northwest provenance Late Wisconsinan till, which is the uppermost till in much of the study area, has several distinct features important to this study. This sediment has significant fractions of both carbonate and shale, it is generally gray, and it has a large fraction of fine-grained material (Fullerton *et al.*, 1995; Harris *et al.*, 1995; Harris, 1999; Matsch, 1972; Patterson, 1999).

Simpkins and Parkin (1993) noted that the Des Moines lobe till near Ames, Iowa, has organic entrainment, active anaerobic biological activity documented by the presence of methane in ground water samples, and pyrite disseminated within the till matrix. The presence of methane in ground water and similarly, pyrite within the till, is indicative of reducing conditions in the aquifer. Arsenic was not measured in the study.

In North America, regional-scale Quaternary aquitards, which include the northwest provenance Late Wisconsinan sediment of interest to this study, have elevated levels of solid and aqueous organics when compared to coarser materials (Rodvang and Simpkins, 2001). The organics entrained in the aquitard sediment derive from Quaternary forests, soils, and lakebeds. Simpkins and Parkin (1993) discuss the existence of a periglacial, coniferous forest that was incorporated into the Des Moines lobe sediment. Patterson (1999) remarks on the presence of wood in Des Moines lobe sediments. Soller (1997) comments that patchy, organic-rich sediments in Minnesota are primarily associated with poorly-drained, Late Wisconsinan sediments.

An internal Minnesota Department of Health report indicates that organic matter such as wood, peat, lignite, and coal are often mentioned in well logs in locations that are consistent with the mapped extent of northwest provenance Late Wisconsinan till in Minnesota (Soule, 2003). Correlations between ground water arsenic concentration and redox are noted in the literature, as is a correlation between elevated ground water arsenic concentration and the general presence of organic material in the sediment (Holm and Curtiss, 1988; Kim *et al.*, 2002; Kinniburgh and Smedley, 2001b; Korte, 1991; Schreiber *et al.*, 2000; Sukop, 2000; Warner, 2001). Soule (2003) also notes a relationship between the thickness of a clay layer in a well log, as described by a driller, and the probability of having elevated arsenic in the well.

2.9 Well Characteristics and Arsenic

A well can introduce air, and thus oxygen, into the aquifer around the well. Even more significantly, pumping can lower the water table such that an unsaturated zone is created around a well (Gotkowitz *et al.*, 2004). The introduction of oxygen into the aquifer changes the water chemistry and, thus, the concentration of dissolved arsenic in water. The arsenic concentration in the aquifer can significantly increase if arsenic-rich sulfide minerals are oxidized (Schreiber *et al.*, 2000). In contrast, oxygenation of the aquifer immediately surrounding a well may be effective in lowering arsenic concentrations by providing oxidized iron to which arsenic can adsorb (Tyrrel and Howsam, 1997). Changing the ground water flow regime can also change the aquifer geochemistry. Moving organic matter or carbonate-rich water through the aquifer can change the water chemistry in such a way as to release arsenic into the water (Harvey *et al.*, 2002; Kinniburgh and Smedley, 2001b).

Using vertical flow-profiling and specific-depth ground water sampling, Sukop (2000) shows that there can be significant variability in flow and arsenic concentration over the thickness of an aquifer. Arsenic concentrations are lower in public water supply wells than in domestic wells in the same geographic area in Michigan (Kim *et al.*, 2002). Warner (Warner, 2001) notes without elaboration that well construction characteristics may affect arsenic concentrations in ground water. McMahon (2001) details crucial biogeochemical reactions, including Fe(III) reduction, which occur at the interface between aquitards and aquifers to create a unique geochemical environment. The geochemical environment at the interface is different from the environment in either the aquitard or the aquifer. The interface environment may be particularly conducive to arsenic mobilization via reductive mechanisms.

2.10 Arsenic in Minnesota Groundwater

Two statewide ground water quality assessments that measured arsenic were conducted in Minnesota during the 1990s (Centers for Disease Control, 1994; Minnesota Pollution Control Agency, 1995). Results of these studies indicated that arsenic concentrations in Minnesota ground water are elevated in the western part of the state. Additional research was recommended to determine the cause of high arsenic concentrations in buried drift aquifer in western Minnesota with the goal of reducing the risk of installing high-arsenic wells (Minnesota Pollution Control Agency, 1998). The Minnesota Arsenic Study (MARS), a study of arsenic occurrence and health effect biomarkers in western Minnesota (Minnesota Department of Health, 2001), was conducted in 1998-1999. The MARS summary report hypothesized that elevated arsenic concentrations in ground water are likely due to pyrite oxidation and an arsenic 'sweeping' mechanism involving pyrite cycling. Kanivetsky (2000) hypothesized that high-arsenic source material and arsenic adsorption/desorption mechanisms control arsenic concentrations in Minnesota ground water.

2.11 Arsenic Removal Technologies

Numerous technologies have been shown to be effective for arsenic removal, either on a large scale for public water system treatment or small scale for home use. Many of the treatment technologies involve ion exchange or adsorbing arsenic onto a metal oxide media (Amy *et al.*, 2000; Badruzzaman *et al.*, 2004; Chwirka *et al.*, 2000; Daus *et al.*, 2004; Goel *et al.*, 2004; Ladeira and Ciminelli, 2004; Wickramasinghe *et al.*, 2004). These treatment technologies often target As(V), so these technologies often require a pre-process to oxidize As(III) to As(V) (Kim and Nriagu, 2000; Thirunavukkarasu *et al.*, 2005; Zhang *et al.*, 2003b; Zhang *et al.*, 2003a). Interference by site-specific geochemical conditions, such as elevated silicate, is being explored (Holm, 2002; Kundu *et al.*, 2004).

Infrastructure costs can be over $1 million, even for small communities. New, innovative, and potentially less expensive technologies are in the process of being developed and tested (Ghimire *et al.*, 2003; Han *et al.*, 2003; Kim *et al.*, 2003a; Kumar *et al.*, 2004; Loukidou *et al.*, 2003; Smith and Edwards, 2002; Vaishya and Gupta, 2003).

3.0 Materials and Methods

3.1 Database Creation

As part of this research, a regional database of measured ground water arsenic concentrations in the upper Midwest was created for large-scale analysis. Data were obtained for North Dakota, South Dakota, Minnesota, and Iowa from a variety of sources, as described in the following sections. This is the first compilation of a comprehensive database of ground water arsenic measurements in the upper Midwest.

This compilation was undertaken, in part, to address significant data gaps in the often-referenced literature pertaining to arsenic occurrence in the United States. Publications such as Welch *et al*. (2000) and the arsenic occurrence maps and links published on the USGS website (Ryker, 2001; US Geological Survey, 2005) are often cited in the literature as representing arsenic occurrence in the United States. Although tens of thousands of samples were included in these studies, only limited data sources were compiled. Significant portions of the United States, including North and South Dakota and Iowa, are shown in these publications as having no available data. See Figure 3. In fact, many water chemistry data were available from public water system monitoring and other state-managed programs.

Most of the data used in this analysis were collected for other purposes; therefore, the cost of conducting this analysis was relatively low. The results, however, have enormous value and consequences: identifying a regional-scale environmental problem and exposing significant knowledge gaps that inhibit planning, such as the lack of information tying sampling results to a specific well. This analysis demonstrates the value of finding and using existing analytical results to cost-effectively observe and characterize regional-scale environmental problems, a significant result in itself.

3.1.1 Public Water System Databases

Public water systems (PWS) in the United States (US Environmental Protection Agency, 2004), are required to test for arsenic and other regulated parameters. As such, each state has data available for measured arsenic concentrations in its public water systems. The agencies responsible for regulating drinking water in Iowa, Minnesota, North Dakota, and South Dakota provided the public water system water quality databases and the approximate locations of the public water systems (Iowa Environmental Protection Division, 2003; Minnesota Department of Health, 2002; North Dakota Department of Health, 2003; South Dakota Drinking Water Program, 2003). Surface water samples were excluded from the database.

Although different analytical methods were used in different states to measure arsenic concentrations in drinking water, each method had a detection limit of 10 μg/l or lower, which conveniently coincides with the MCL for arsenic. Many measurements were reported as 'not detected' at a detection limit of 10 μg/l, so the regional analysis presented in this paper is presented as an indicator analysis (Barabas *et al.*, 2001; Juang and Lee, 1998; Oh and Lindquist, 1999; Saito and Goovaerts, 2000). The indicator variable was created based on measured arsenic concentration: a '1' was assigned to each measurement that was 10 μg/l or more, and a '0' was assigned to each measurement of less than 10 μg/l, including measurements that were not detected at a reporting limit of 10 μg/l (Berry and Lindgren, 1990).

The public water supply wells are screened in or open to a multitude of different aquifers, and all data were included in this analysis. Well depth and aquifer information were available for

approximately 50% of the reported sample locations. The wells for which there was depth information were, in most cases, the same wells for which the aquifer at the open interval of the well had been characterized. Well depth was used as an indicator of the depth of the open interval. The final data set is based upon approximately 4,000 public water system sample locations. The study area and PWS sampling points are shown in Figure 4.

Because of increased security concerns related to public water supply locations, the locations released by North Dakota and Iowa were not exact latitude and longitude locations. The locations are, instead, the centroid of the zip code in which the public water supply is located. The analysis using these data examines the potential influence of a geologic feature that is of a scale of hundreds of square kilometers and zip code areas are on the order of kilometers to tens of square kilometers. This level of location accuracy is acceptable for a regional-scale analysis.

3.1.2 Other Minnesota Water Quality Databases

Three additional Minnesota water quality databases were obtained for use in this research: MARS (Minnesota Department of Health, 2001), Centers for Disease Control/Minnesota Department of Health (CDC) (Centers for Disease Control, 1994), and Ground Water Monitoring and Assessment Program (GWMAP) (Minnesota Pollution Control Agency, 1995). The MARS and CDC databases were obtained from the Minnesota Department of Health, and the GWMAP database was obtained from the Minnesota Pollution Control Agency. Figure 4 illustrates the sample locations for these data sets.

MARS was an arsenic exposure study conducted in nine west-central Minnesota counties by the Minnesota Department of Health during 1998 and 1999. The MARS database contains trace element and field parameter results for approximately 875 locations. Because MARS was an exposure study, the collected water sample at each location was representative of the drinking water used by a family. All arsenic measurements are used in spatial analyses because arsenic concentration is not affected by water softening. Only untreated samples were used in correlation analyses.

Approximately half of the MARS samples underwent some form of water treatment, such as softening or iron removal. The present study is interested in ambient ground water quality and potential relationships between constituents in natural ground water. All treated samples were, therefore, eliminated from the analysis examining potential relationships between arsenic concentrations and other trace element concentrations. Water treatments are known to effectively remove elements such as iron and manganese, which are related to arsenic geochemistry. Each MARS well was located using a handheld global positioning system unit. Each sampled well was identified by a unique well number, so some well construction and geologic information is available about each well from Minnesota's County Well Index, as described at the end of this section.

The CDC database contains statewide ambient ground water quality samples collected jointly by the Centers for Disease Control and the Minnesota Department of Health in 1994 and 1995. Approximately 850 sample locations were chosen on an approximate 11-mile grid across the state. No effort was made to exclusively sample wells that have a unique number, so no well construction information is available for the wells sampled in the CDC study. Arsenic was the only parameter of interest measured in this study.

The GWMAPS database contains statewide ambient ground water quality samples collected by the Minnesota Pollution Control Agency from 1992 to 1996. Water samples were analyzed for major anions and cations, trace elements, and field parameters. Approximately 950 sample locations were chosen on an approximate 11-mile grid across the state. Only wells with unique well numbers were sampled, so well construction and geologic information is available for wells in the GWMAPS database.

Minnesota maintains a public database of wells, which is known as the County Well Index (CWI) (Minnesota Department of Health and Minnesota Geological Survey, 2005). The CWI is a database of water well information, cataloged by a unique well number, for approximately 340,000 water wells; geologic information is available for about 285,000 of the wells. Well construction information is available for most of the wells, and location information, ranging from as general as Township-Range-Section to as specific as a global positioning system point, is also available for most of the wells. The CWI database was started in 1974 when state regulations began requiring well drillers to submit well logs to the Minnesota Department of Health. Therefore, virtually all wells drilled since 1974 are included in the database, but many older wells are also included because well records were available from drillers and local governments.

3.1.3 Other North Dakota Database

The North Dakota Water Commission maintains a public, web-based database of statewide ground water monitoring data, as well as other monitoring information (North Dakota Water Commission, 2004). Monitoring wells and domestic wells are routinely sampled by the North Dakota Department of Health and the North Dakota Water Commission. Ground water quality, well construction, location, and geologic information were downloaded and compiled into a database of measured arsenic concentrations. Approximately 2,000 sample locations throughout the state have been measured for arsenic at least once. Most of these sampled wells have well construction and geologic information. Figure 4 shows the sample locations for this data set.

3.1.4 Other South Dakota Database

The South Dakota Geological Survey maintains and routinely samples a statewide network of monitoring wells (South Dakota Geologic Survey, 2003). Water quality, well construction, and well location information were obtained. Approximately 600 sample locations throughout the state have been measured for arsenic at least once. Most of these sampled wells have well construction and geologic information. Figure 4 shows the sample locations for this data set.

3.1.5 United States Geological Survey Database

The United States Geological Survey (USGS) has conducted ground water quality monitoring for decades. Water quality and well construction databases were obtained from the USGS web-based data repository: the National Water Information System (NWIS) (US Geological Survey, 2004). Many of the 2,200 ground water sample locations in the NWIS database and located in the upper Midwestern states have well construction and some geologic information available. Figure 4 shows the sample locations for this data set.

3.1.6 Regional Arsenic Database Summary

Although statewide domestic well sampling has been conducted in Iowa, arsenic was not one of the measured parameters. Well depth and aquifer information were available for approximately 50% of the reported public water system sample locations and for approximately 85% of the

non-public water system wells. Figure 5 illustrates the complete regional arsenic database sample locations and whether or not the well depth is known at the sample location. For the regional-scale analysis, myriad aquifer names and missing information were lumped into one of three aquifer type categories: glacial sediment, bedrock, or unknown. Figure 5 also shows the well types for the wells in the regional arsenic database.

3.1.7 Quaternary Geology GIS Databases

Each of the states has mapped important geologic features, such as various tills. Therefore, maps representing the extent of northwest provenance Late Wisconsinan till in each state were obtained electronically for use with ArcView, a geographic information system software package.

3.2 Well Water Sampling Protocol for 2002 and 2003

3.2.1 Drilling date sampling of new domestic wells

During 2002, water samples from new wells were collected at the end of the well development. At least two trace element samples – one unfiltered and one field-filtered with a 0.45 micron filter – were collected at each well. Water samples were collected in acid-washed 30-milliliter sample containers. Each trace element sample was preserved in the field with three drops of metal-free concentrated nitric acid. The nitric acid preserves the sample by lowering the sample pH to 2m which prevents the precipitation of iron. Iron precipitation would decrease measured aqueous arsenic concentrations because of arsenic adsorption onto precipitated iron oxides. An ongoing log of samples collected was maintained for each well. Each sample was assigned a unique sample ID. At selected locations, samples were also collected for major anions. Major anion samples were filtered and were not preserved.

During 2003, water samples from new wells were collected a variable amount of time after well installation. Hydrologists from the Minnesota Department of Health identified new domestic drinking water wells being installed in the high-arsenic areas of Minnesota. The hydrologists collected trace element samples from the new wells after the well had been put into service for the home. Each trace element sample was immediately preserved in the field with nitric acid.

3.2.2 Other sampling of domestic wells

Additional samples were collected at various time intervals after well installation. Some samples were collected by the author; some samples were collected by the well owner or Minnesota Department of Health staff. Each sample was assigned a number and recorded on the water sample log. Existing domestic wells (wells that were not new wells) were also sampled in the manner outlined in this section.

Samples that were collected by the author on any date other than the drilling date used the following procedure: A flow-through cell was used to monitor field water quality parameters (temperature, pH, conductivity, oxidation/reduction potential (ORP), and dissolved oxygen (DO)) for 20-30 minutes prior to sample collection. These measurements were recorded approximately every five minutes. Analytical samples were collected for trace elements. Some locations also were sampled for major anions, arsenic species, total alkalinity, total organic carbon, and ammonium.

Speciation samples were collected into a prepared 250 mL container containing 0.1M EDTA and 2M acetic acid (EDTA/HAc). As(III) was segregated by passing 60 ml of the ETDA/HAc-

preserved well water sample through a strong anion exchange column. The column adsorbed the negatively-charged arsenate complexes from the water. The uncharged arsenite complex passed through the column and into the sample container. The samples were analyzed for total arsenic. Samples were collected for total arsenic and As(III); As(V) was calculated by subtracting As(III) from total arsenic (Clifford *et al.*, 2003).

Samples for total alkalinity were collected into a 125 mL plastic container. The samples were not preserved. Samples for total organic carbon and ammonium were collected into a 250 mL plastic container and were preserved with sulfuric acid. The Minnesota Department of Health Environmental Laboratory analyzed samples for total organic carbon, ammonium, and total alkalinity.

3.2.3 Public Water Supply Sampling

Temporal variability sampling was conducted at 14 public water systems. The locations of the participating public water systems are presented in Figure 6. Two different types of temporal sampling were conducted at public water system wells: long-term variability sampling and short-term variability sampling. Table 4 indicates which type of sampling was conducted in each participating community.

Long-term arsenic variability sampling was conducted to examine potential hourly, daily, weekly, monthly, or seasonal arsenic concentration trends. Samples were collected at three wells at four different time scales: hourly, daily, weekly, and monthly. Nine months of sampling was conducted at one well in Climax and at two wells in Cosmos. Climax is located in Polk County, in northwestern Minnesota, in the valley of the Red River of the North. Cosmos is located in Meeker County in central Minnesota, about 75 miles west of the Twin Cities. Filtered (0.45 µm filter) and unfiltered samples for arsenic and other trace elements were collected hourly for approximately 12 hours. Unfiltered samples were then collected daily for one week, weekly for six weeks, and then monthly thereafter for the remainder of the sampling period.

Short-term arsenic variability sampling was conducted at 11 public water system wells to examine arsenic variability that may be related to the presence and operation of the well. The participating public water suppliers are geographically spread throughout Minnesota and have reported average arsenic concentrations in at least one well ranging from 11 µg/l to 35 µg/l. Each well that was sampled was 'rested' (not pumped) for a minimum of 12 hours prior to sampling. After the resting period, the well pump was turned on at a normal operational pumping rate. Samples were collected 5 minutes, 20 minutes, 40 minutes, and 60 minutes after the well pump started running continuously. A flow-through cell was used to monitor field water quality parameters during the sample collection period.

At most locations, field measurements of temperature, pH, conductivity, oxidation/reduction potential (ORP), and dissolved oxygen (DO) were collected during the one-hour sampling period. Field measurements were collected using pH, conductivity, ORP, and DO probes inserted into a flow-through cell. Probes were calibrated prior to usage at each site. ORP readings were corrected for temperature (YSI Incorporated, 2003). ORP readings often do not give accurate and precise measurements due to geochemical disequilibrium, but the readings can be used to obtain approximate values and categorize regimes (Holm and Curtiss, 1989; Kölling, 2000; vanLoon and Duffy, 2000). Although the study system is clearly not in equilibrium, the ORP readings are converted to pe (Benjamin, 2002) and plotted as pe for use in comparisons with equilibrium arsenic speciation fields presented in Chapter 7.

Analytical parameters sampled at each time interval included some or all of the following: arsenic and other trace elements, major anions, arsenic species, total alkalinity, total organic carbon, and ammonium. The well pump was then shut off. A final sample for trace elements was collected after a rest period of approximately four hours.

3.3 2002 Sediment Sampling Protocol

3.3.1 Site Selection

Sites were chosen for sampling if they met all of the following criteria:

- Geographic location was within a known area at high risk for arsenic in ground water
- Well driller expected to screen the well at a depth known or suspected to be at high risk for arsenic in ground water
- Well owner agreed to allow sampling
- Well was being drilled for use as a drinking water supply

3.3.2 Sediment Sample Collection

Once on the site, the driller and well owner selected the specific well location. Wells were drilled using the mud-rotary method. Sediment samples consisting of drill cuttings were collected by the driller using a shovel at the outlet from the drill stem. No samples were taken directly from the mud box. The driller placed samples on the ground in piles representing approximately 10-foot intervals. To the degree possible, composite samples representing the stratigraphy were collected. In clayey layers, an effort was made to select samples of intact mud balls. In sandy layers, an effort was made to collect representative layers of sand for different intervals. Samples were placed in labeled Ziploc bags, one interval per bag.

A generalized well log was maintained with respect to texture and color over 10-foot intervals, or as a change in texture or color was noted.

3.3.3 Sediment Sample Processing

Sediment samples were processed in the Civil Engineering Soil Laboratory in the following manner.

For fine-grained samples, a representative sample weighing approximately 150 grams was dried overnight or longer at approximately 50 degrees Celsius. The dried sample was placed on a nest of the following sieves: 2.0 mm, 1.0 mm, 0.075 mm (US #200), pan. The nest of sieves was then placed on a shaker for 10 minutes. The fraction passing through to the pan (i.e., <0.075 mm sieve) was weighed and the weight was recorded on a data table. When possible, this fraction was then divided into two envelopes, one for archive and one (weighing at least 4 grams) to go to the USGS for geochemical analysis.

The fractions ≥ 0.075 mm were recombined and placed in a labeled Ziploc bag for potential washing and sorting of the larger-grained fractions by lithology at a later time. For several samples, the 1 – 2 mm fraction, which is the coarse sand fraction, was then analyzed under a microscope to determine the stratum lithology. Each coarse sand grain was separated into one of three categories: crystalline, shale, or carbonate.

Selected samples were submitted to USGS for geochemical analysis. Each sample was assigned a unique sample ID number. Samples of fine-grained material were analyzed as-is by USGS. Samples of coarser-grained material were first crushed to a fine texture and then analyzed.

3.4 2003 Sediment Sampling Protocol

3.4.1 Site Selection

The site for monitoring well installation was chosen for the following reasons:

- The site was in a known high-arsenic area
- The site was publicly owned
- The site owner (Moorhead State University) gave permission for the wells to be installed
- The water table is located at a sufficiently shallow depth so that water sampling with a small, submersible pump was practical

3.4.2 Sediment Sampling

Once on the site, the driller and well owner selected the specific well location. Drilling was conducted using the rotasonic method. Four-inch diameter sediment cores were collected in 10-foot intervals. The sediment samples were removed from the core barrel and immediately placed in a plastic sleeve before being laid on the ground. Cores remained inside the plastic sleeve until sample collection to maintain an anaerobic environment in the sediment core. A generalized well log was maintained with respect to texture and color. Cores were divided into 4-foot sections and placed in labeled boxes for long-term archive at the Minnesota Geological Survey and at the Moorhead State University Regional Science Center.

Sediment samples were collected in two different ways for two different types of analysis.

Bulk composite samples were collected from selected intervals for geochemical analysis by the USGS. Each composite sample was placed in a Ziploc bag that was labeled with the well unique number, the composite sample interval, and the sample collection date.

Discrete samples were collected for laboratory sequential extraction of arsenic in an anaerobic environment. An effort was made to minimize air exposure of these sediment samples.

A field glove bag was erected onsite for collection of the laboratory samples. The glove bag was flooded with 99.9% pure nitrogen prior to sample collection to ensure that an anaerobic environment existed in the glove bag. Sample containers were allowed to rest, uncovered, in the glove bag prior to sample introduction. Samples were collected from the aquifer sand. The core bags were opened and then large core sections from discrete intervals were immediately placed intact into labeled Ziploc bags. Excess air was squeezed out of the Ziploc bags, and the bags were immediately sealed and placed into the glove bag, where they were reopened and allowed to equilibrate with the anaerobic environment.

Once inside the glove bag, each large core was sectioned, and the parts of the core likely exposed to air were discarded. Central portions of each core were placed in labeled jars, and then the jars were lidded. After all jars had been filled and lidded, the glove bag was opened and each jar lid was securely taped in place with electrical tape. The jars were placed inside of a Ziploc bag, sealed, and frozen until chemical extraction.

3.4.3 Sediment Sample Processing

Each sediment sample for analysis by USGS was processed in the Civil Engineering Soil Laboratory. Approximately 10 grams of each sample was placed on aluminum foil and dried overnight or longer at approximately 50 degrees Celsius. The dried sample was then placed in a labeled envelope and transmitted to USGS for analysis. USGS crushed and homogenized each sample prior to analysis.

Each sediment sample for sequential extraction was processed in a laboratory anaerobic glove bag. Approximately 20 grams of each sample was dried, crushed with a mortar and pestle, and then 3 replicate, homogenized samples of 4 grams of each were placed in centrifuge tubes for sequential extraction procedures. Four grams of each homogenized samples were also placed in small beakers for a water extraction. The remaining homogenized sediment was placed in a labeled envelope for analysis by USGS as a comparison of total arsenic concentration.

3.4.4 Sediment Sequential Extraction

Sediment sequential extraction was completed according to a portion of the methods of Keon *et al.* (2001), as outlined in Table 5.

All extractant solutions were prepared in the glove bag with Milli-Q water deoxygenated by sparging with nitrogen gas for two hours per liter. Ultra-pure HCl and reagent grade NaH_2PO_4, ammonium oxalate, and oxalic acid were used to prepare the extractants. Extractant pH was adjusted with HCl or NaOH to the value listed in Table 5. Blanks were prepared for each extractant solution both to verify that there was no arsenic contamination in the reagents and to prepared matrix spikes. All samples were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in the University of Minnesota Aqueous Geochemistry Laboratory as described in a later section.

For each step of the sequential extraction, 40 mL of the extractant was added, in the order presented in Table 5, to the centrifuge tubes containing 4 grams of homogenized sample. The suspensions were sealed and then tumble-shaken for the specified time outside of the glove bag. After the first step, the samples were centrifuged for 25 minutes at 11000g. Three of the nine centrifuge tubes broke at this force, so after the subsequent extractions, the samples were centrifuged for 60 minutes at 3650g.

The centrifuge tubes were transferred back to the glove bag where the supernatant was decanted using a syringe, filtered through a 0.45 μm filter, and acidified to pH 2 with HNO_3 for analysis using ICP-MS. The next extractant was added to the residue in the centrifuge tube, and the process was repeated.

After all extractions were completed, the sediment residue was placed on aluminum foil and dried overnight at approximately 50 degrees Celsius. The dried residue sediment sample was then placed in a labeled envelope and transmitted to USGS for analysis.

One 4-gram sample from each depth interval was also extracted with water. A 4-gram sample was placed in a small beaker with 40 ml of deoxygenated water in the glove bag. A clean stir bar was placed in each beaker. The beakers were covered and placed on a stir plate, stirring at approximately 200 rpm in the glove bag for seven days. At the end of seven days, the sediment was allowed to settle for one hour, and then a 50 ml sample was decanted off, filtered through a 0.45 μm filter, and acidified to pH 2 with HNO_3 for analysis using ICP-MS. The sediment residue was placed on aluminum foil and dried overnight at approximately 50 degrees Celsius.

The dried residue sediment sample was then placed in a labeled envelope and transmitted to USGS for analysis.

3.5 Water Analytical Methods

3.5.1 University of Minnesota Department of Geology and Geophysics Aqueous Analytical Laboratory

Arsenic and the other trace elements were analyzed on a ThermoElemental PQ ExCell inductively coupled plasma mass spectrometry system (ICP-MS). The other elements and compounds analyzed were chosen due to their potential usefulness as indicators of general water geochemistry or a known relationship/interaction with arsenic. The analytical isotopes for each element were chosen to minimize isobaric overlaps (i.e., two or more elements or compounds sharing the same mass). Because arsenic was measured at mass 75, a potential exists for interference with an ArCl polyatomic overlap. However, a separate investigation done on the instrument revealed that the magnitude of the overlap was small, approximately 4.6 µg/l equivalent As per 1,000 mg/l Cl. This overlap would have only minimal effect on the sample results in this study because most of the samples had measured Cl concentrations less than 50 mg/l. Additionally, all samples were acidified using nitric acid (HNO_3) rather than hydrochloric acid (HCl).

Calibration standards were prepared from National Institute of Standards (NIST) traceable single-element and multi-element stock solutions diluted in Fisher Scientific Optima grade nitric acid. The same standard stock solutions were used throughout the study, and the primary calibration standard was prepared each time at the same concentration levels for each element. A NIST check standard (NIST-1640: trace elements in a natural water) was run approximately every 30 samples to ensure that the instrument system was functioning properly. Calibration was achieved by using a 0.1 M HNO_3 solution as a blank and artificially prepared standards of known concentration. Standards and samples also were prepared as 0.1 M HNO_3 solutions.

Element concentrations in the standards were chosen to represent common levels in ground water. The instrument was recalibrated with standards and blanks between a maximum of every four samples to eliminate problems associated with instrument drift. The PQ ExCell ICP-MS has a dual analog and pulse counting detector, which was cross-calibrated before every sample set to ensure accurate µg/l to mg/l concentrations. A stabilization time of 30 seconds was used once the sample reached the plasma and before data were collected, and a wash time of 90 seconds in 0.1 M HNO_3 was used to minimize carryover between samples. Each data collection per sample included 5 replicate measurements on each mass, which were then averaged to determine the mean and standard deviation values. On occasion, the samples themselves were replicated in a data set to give an indication of the reproducibility of the data collection process.

Sediment extraction fluids were also analyzed by ICP-MS for the appropriate elements by calibrating the samples against blank and standard solutions that were prepared in matrices identical to the sample and spiked with the appropriate levels of the elements of interest. Extractions prepared with EDTA/acetic acid were run undiluted and were analyzed for As and Fe. Extraction samples prepared with dilute HCl, oxalic acid, and NaH_2PO_4 were first diluted to a total of 500X with 0.1 M HNO_3 before analysis. Calibration blanks and standards were made in an identically diluted matrix. Deionized water washes of the sediment between extractants were diluted to a total of 200X with 0.1 N HNO_3 before analysis.

Ammonium (NH_4+) was analyzed on a Dionex ICS-2000 ion chromatography system utilizing a reagent-free methanesulfonic acid eluent generation system, an AS40 autosampler, a CSRS suppressor, and a CS16 analytical column and guard column. Samples were run in duplicate and were calibrated against NIST traceable multi-element standards. Ions were detected by suppressed conductivity.

Anion samples were analyzed on a Dionex DX500 system and later on an ICS-2000 ion chromatography system. Both systems use a dilute carbonate/bi-carbonate eluent, an AS40 autosampler, an ASRS suppressor, and dual AS14A analytical columns. Ions were detected by suppressed conductivity.

Detection levels for the analyzed parameters are presented in Table 6.

3.5.2 Minnesota Department of Health Environmental Laboratory

Total arsenic was determined using method EPA 200.8. Total alkalinity was determined using method SM 2320B. Total organic carbon (TOC) was determined using method SM 5220 D (Minnesota Department of Health, 2004).

3.6 Sediment Analytical Methods

With the exception of six organic carbon analyses, sediment geochemical analyses were conducted by the USGS laboratory in Denver, Colorado. Detailed analytical methods are presented in Taggart (2002). Brief descriptions of the analytical methods, as provided in Taggart (2002), are included in the following paragraphs.

Chapter A1 discusses sample preparation prior to analysis. Samples are split, if necessary, and fed into a Braun vertical pulverizer equipped with ceramic plates. The sample is ground to approximately minus 100-mesh (<150 µm) and mixed to ensure homogeneity for subsequent analysis.

Chapters G and I present the analytical method used to determine the concentrations of major, minor, and trace elements. These elements are determined in geological materials by inductively coupled plasma atomic emission spectrometry (ICP-AES). The sample is decomposed using a mixture of hydrochloric, nitric, perchloric, and hydrofluoric acids at low temperature. The digested sample is aspirated into the ICP-AES discharge where the elemental emission signals are measured simultaneously for 40 or 42 elements, Chapters G and I, respectively. Calibration is performed with digested rock reference materials and a series of multi-element solution standards.

Chapter L presents the analytical method used to determine low-level concentrations of arsenic. Geologic samples are digested using a multi-acid procedure in an open Teflon vessel. At the end of the digestion period, arsenic is reduced As(III). Sodium borohydride is added to the solution resulting in rapid formation of a gaseous arsenic hydride. The gaseous hydride is stripped from the analytical stream and transported with inert gas to the atomizer of the atomic absorption spectrophotometer. The arsenic furnace is electrically heated to 900°C. Concentrations of arsenic are determined using calibration standards in solutions of similar matrix.

Chapter R presents the analytical method used to determine total carbon in sediment samples. Total carbon in geologic materials is determined using an automated carbon analyzer. A weighed sample (approximately 0.20 g) is combusted in an oxygen atmosphere at 1350°C to oxidize

carbon (C) to carbon dioxide (CO_2). Moisture and dust are removed and the carbon dioxide gas is measured by a solid state infrared detector.

Chapter S presents the analytical method used to determine carbonate carbon in sediment samples. Carbonate carbon in geologic material is determined as carbon dioxide, CO_2, by coulometric titration. The sample is treated with hot 2 *N* perchloric acid and the evolved CO_2 is passed into a cell containing a solution of monoethanolamine. The CO_2, quantitatively absorbed by the monoethanolamine, is coulometrically titrated using platinum and silver/potassium iodide electrodes.

Six sediment samples were analyzed by the University of Minnesota Limnological Research Center for total inorganic carbon and total carbon. Total inorganic carbon was determined as follows: Carbon dioxide gas evolved by dissolution in acid from carbonates in the sample was swept by the gas stream into a coulometer cell. The coulometer cell was filled with a partially aqueous medium containing ethanolamine and a colorimetric indicator. Carbon dioxide was quantitatively absorbed by the solution and reacts with the ethanolamine to form a strong, titratable acid which caused the indicator color to fade. The titration current automatically turned on and electrically generated base to return the solution to its original color (blue).

Total carbon was determined as follows: Carbon dioxide gas evolved by combustion of organic matter and carbonates in the sample was swept by an oxygen gas stream into a coulometer cell. The coulometer cell was filled with a partially aqueous medium containing ethanolamine and a colorimetric indicator. Carbon dioxide was quantitatively absorbed by the solution and reacted with the ethanolamine to form a strong, titratable acid which caused the indicator color to fade. The titration current automatically turned on and electrically generated base to return the solution to its original color (blue).

3.7 Geochemical Modeling

MINEQL+ (Schecher and McAvoy, 1998) was used to conduct geochemical modeling to explore the behavior of arsenic under differing geochemical regimes. MINEQL+ calculates equilibrium species concentrations for the given geochemical input; thus, information about reaction rates is not revealed. The reduction of As(V) species to As(III) species in the presence of iron has been shown to occur relatively rapidly in the laboratory, as have the rates of adsorption processes for As(V) species. As(III) species were shown to have less affinity for adsorption to iron oxides and to adsorb more slowly (Bose and Sharma, 2002).

Geochemical modeling was conducted to explore theoretical speciation differences for differing redox conditions and differences in arsenic adsorption partitioning given differing arsenic speciation. Input parameters were selected to represent measured arsenic concentrations, redox conditions, and pH levels observed in Minnesota. Input parameters for different model runs are provided in Table 7.

3.8 Statistical Analyses

A key component of the success of the analyses presented in this dissertation was the accessing and screening of existing results that were collected for other purposes. Appropriate statistical analyses of the data, as described next, were fundamental to examining large and imperfect data sets. The software packages SAS and Minitab were used to perform all statistical analyses with the exception of the geostatistical analyses. The software package Surfer was used for this purpose.

Proportions of sample locations with As ≥ 10 μg/l were compared to test null hypotheses of differences in proportions in specified groups of data. For example, the null hypothesis that the proportion of As ≥ 10 μg/l is the same both inside and outside of the footprint of the sediment of interest was tested: $p_{Inside} - p_{Outside} = 0$ (Berry and Lindgren, 1990). The null hypothesis was rejected if the proportions were sufficiently different ($z \geq 1.96$) at the 95% confidence level (P-value ≤ 0.05). The same criteria were used to evaluate whether the means of well depths for different groups of wells are different from one another.

Geostatistical analysis was performed using a directional indicator variogram. The directional indicator variogram reveals anisotropic spatial continuity by analyzing the variance of groups of sample points segregated by separation vectors (separation distance and direction). Spatial continuity was revealed when samples near one another were more alike. Anisotropy was revealed when samples lying along different directional vectors were more or less alike (Isaaks and Srivastava, 1989). The spatial distribution of elevated arsenic concentrations was tested for randomness using a nearest-neighbor analysis (Cressie, 1991) and a binomial distribution (Berry and Lindgren, 1990).

Both parametric and non-parametric analyses were used to look for correlations between arsenic and other water chemistry parameters. The commonly-used Pearson correlation coefficient was calculated. The data are not normally (or lognormally) distributed, however. Normal distribution is a requirement for Pearson correlations to be reliably useful in detecting correlations. The Spearman correlation coefficient, therefore, is also presented. Spearman correlations do not have a distributional requirement (StatSoft, 2004).

Factor analysis was performed to examine whether linear combinations of fewer variables could explain a significant portion of the data set variance (Kim and Mueller, 1978a; Kim and Mueller, 1978b; Malinowski, 2002).

4.0 Arsenic in Ground Water and Sediment in Minnesota

This section presents results of ground water and sediment sampling conducted in Minnesota. Statistical analysis of results and brief discussions of the implications of the results are also presented.

4.1 Existing Data

4.1.1 Statewide Descriptive Statistics

Three Minnesota ground water monitoring programs collected ground water arsenic measurements: PWS, CDC, and GWMAPS. Figure 7 presents locations and results for the 3,303 statewide arsenic measurements and the extent of the northwest provenance Late Wisconsinan drift in Minnesota. Table 8 presents a summary of indicator arsenic results by sample location: inside or outside of the northwest provenance Late Wisconsinan drift. As noted in the Literature Review presented in Chapter 2, elevated arsenic concentrations in Minnesota ground water are associated with the lateral extent of the northwest provenance Late Wisconsinan drift. A discussion of the three-dimensional distribution of elevated arsenic concentrations is presented in Chapter 6.

4.1.2 Correlations Between Arsenic and Other Analytes

Statewide, several analytes are weakly correlated to arsenic at a 95% confidence level. These analytes, along with the correlation coefficient and the P-value, are presented in Table 9. Figure 8 illustrates that the correlation between arsenic and iron, an analyte with one of the strongest correlations to arsenic in this and other data sets presented in the literature, is not readily discernible visually.

Geostatistical analysis indicates that elevated arsenic concentrations in Minnesota ground water are correlated over long distances, as is true regionally. Variograms of arsenic indicator data and arsenic data using the statewide Minnesota data are presented in Figures 9 and 10. In neither case does the variogram model reach its sill (flatten out) over the distance for which data are available for Minnesota. These results indicate that the correlation length for elevated arsenic concentration is longer than the state's data are able to demonstrate. Elevated arsenic concentrations in ground water are a regional phenomenon, as discussed in detail in Chapter 5. These results support the hypothesis that elevated arsenic concentrations are indeed a large-scale rather than a small-scale effect.

Elevated arsenic concentrations in Minnesota ground water are highly clustered. In the total data set, 319 of 3302 (9.7%) measurements exceeded 10 μg/l As. Of the locations that exceeded 10 μg/l, 96 of 319 (30.1%) locations had a nearest neighbor that also exceeded 10 μg/l. The null hypothesis that the elevated arsenic values are randomly distributed was tested using a binomial distribution. For 319 observations of elevated arsenic, 31 nearest neighbors were expected to have elevated arsenic (standard deviation of 5). The observed result, 96 nearest neighbors with elevated arsenic, was 12 standard deviations above the expected value. The null hypothesis is rejected. The data are highly clustered, which is consistent with the fact that the nugget effect in the variogram model accounts for less than 30% of the total model variance (Barnes, 1991).

4.1.3 Western Minnesota Descriptive Statistics

Figure 11 presents locations and results for the 823 MARS arsenic measurements for which there is well construction and geologic information in the CWI. All of the MARS wells are located

within the footprint of the northwest provenance Late Wisconsinan drift. Summary statistics for the raw water subset of the MARS data are presented in Table 10.

4.1.4 Correlations Between Arsenic and Other Analytes in Western Minnesota

As with the GWMAPS data set, several analytes from the raw water MARS data set are weakly correlated to arsenic at a 95% confidence level. These analytes, along with the correlation coefficient and the P-value (a measure of the likelihood of making a Type I error), are presented in Table 11.

Factor analysis (Table 12) indicates that two factors account for approximately 50% of the MARS data set variability. The magnitudes and signs (positive or negative) of Factor 2 illustrate that groups of analytes are geochemically related to one another. The analytes arsenic, iron, and manganese have relatively large positive values, while pH, boron, bromine, and chlorine are relatively large and negative. This result mirrors the correlation results presented in Table 11.

4.2 New Data

4.2.1 Descriptive Statistics for New Ground Water Sampling

Public water system, domestic, and monitoring wells were sampled during this project. Wells were selected by location and type to meet project goals, as described previously. Table 13 provides a summary of wells that were sampled during this project, the year(s) that samples were collected, and a summary of analytes measured in the wells.

Two different types of temporal sampling were conducted at public water system wells: long-term variability sampling (Long Temporal) and short-term variability sampling (Short Temporal). The locations of the participating public water systems were presented in Figure 6. Detailed temporal sampling results and discussion are presented in Chapter 7.

Four different types of sampling were conducted at domestic wells: new domestic wells (New), new monitoring wells (Monitoring), domestic wells near arsenic-affected public water system wells (Community), and domestic wells with known arsenic concentration from previous sampling (Known). Seventeen new domestic wells were sampled. Seven of those new domestic wells were sampled for sediment and water at the time of construction, and again for water approximately one year after well construction. The remaining ten new wells were sampled for water within approximately one month of construction and again six months later. Two monitoring wells were sampled for both sediment and water at the time of construction and, periodically, for water for approximately one year. Domestic wells were sampled in the vicinity of two arsenic-affected public water systems, Climax and Cosmos (see locations Figure 6), to examine spatial arsenic variability. Selected domestic wells with known arsenic concentrations and well construction characteristics were resampled for an expanded list of parameters. Summary statistics for selected parameters are presented in Table 14.

4.2.2 Correlations Between Arsenic and Other Analytes

As with the GWMAPS and MARS data sets, several analytes are weakly correlated to arsenic at a 95% confidence level. These analytes, along with the correlation coefficient and the P-value, are presented in Table 15.

Although anion competition cannot be eliminated as an arsenic mobilization mechanism based on the data, anion competition is not strongly supported by the data either. The fact that phosphorous is weakly negatively correlated to arsenic concentration does not support a

competition mechanism. Sulfate is weakly positively correlated to arsenic concentration. Bicarbonate, total organic carbon, and ammonium are not correlated to arsenic concentration.

4.2.3 Sediment and Ground Water Arsenic Concentrations

This project provides the first reported Minnesota arsenic geochemical results for sediment and water samples collected from the same well.

Sediment and water samples were collected at nine new wells: seven domestic water supply wells and two monitoring wells. The well locations and arsenic concentrations measured in the ground water are presented in Figure 12. Sediment arsenic concentrations ranged from 0.6 to 10.6 mg/kg. Figure 13 summarizes the average sediment and water arsenic results for these wells. Results indicate that water arsenic concentrations are not correlated to either till arsenic concentrations ($R^2 = 0.147$, P-value = 0.309) or aquifer sediment arsenic concentrations ($R^2 = 0.0032$, P-value = 0.885).

4.2.4 Particulate and Dissolved Arsenic in Ground Water

An important unanswered question regarding arsenic occurrence in Minnesota ground water was whether the arsenic in ground water is adsorbed to particulates or is in the aqueous phase. To help answer this question, pairs of filtered and unfiltered samples of raw water were collected from public and domestic water supply wells. Numerous water samples were collected at three public water system wells, and average arsenic results are presented in this section. Detailed results from the public water system wells are presented in Chapter 7.

A summary comparison of filtered and unfiltered water results is presented in Figure 14. Raw water was collected and analyzed at all but one sample location. Samples of chlorinated water were inadvertently collected from one public water system well, and the average results from the chlorinated water are also presented in Figure 14.

As is clearly illustrated in Figure 14, all of the arsenic in the raw water samples is aqueous. In the chlorinated sample, however, approximately 1/3 of the total arsenic is associated with particulates. Figure 15 presents a summary of filtered and unfiltered iron results. As described next, the iron results help explain the smaller amount of aqueous arsenic in chlorinated water.

Aqueous iron is also significantly less than total iron in the chlorinated water sample. Chlorine is known to be a strong oxidizing agent. An explanation for the observed difference between total and aqueous iron and arsenic is as follows: in the raw water aqueous iron, Fe^{2+}, is virtually instantaneously oxidized to Fe(III) when it comes into contact with chlorine. Fe(III) quickly forms a solid Fe(III) iron hydroxide. Arsenic has a strong affinity for adsorbing to iron hydoxides, particularly the high surface area HFO that are formed first. A fraction of the aqueous arsenic in the raw water adsorbs to the newlyformed HFO. These observed results illustrate the rate at which arsenic can adsorb to HFO under strongly oxidizing conditions.

4.2.5 Arsenic Speciation in Ground Water

For the first time in Minnesota, arsenic speciation sampling was undertaken as part of this project. It was hypothesized that most of the arsenic present in Minnesota ground water would be As(III), the more reduced form of inorganic arsenic. Figure 16 provides a summary of arsenic speciation results for samples collected. Most of the measured arsenic is indeed As(III), but the percentage of As(III) is not correlated with measured Eh or pH. Three analytes are weakly correlated to arsenic at a 95% confidence level, as shown in Table 15. The percentage of As(III)

is positively correlated to measured phosphorous, and negatively correlated to measured nitrate and dissolved oxygen.

These results – the overwhelming presence of As(III) and the negative correlation between the percentage of As(III) and nitrate and dissolved oxygen – support the hypothesis that the widespread arsenic contamination in Minnesota ground water is more likely due to reductive mechanisms, not oxidative mechanisms. Figure 17 illustrates the percent As(III) on a pe-pH diagram. The distribution of high and low percentages of As(III) illustrates that the ground water is likely not in geochemical equilibrium.

4.2.6 Sediment Extraction Results

Although numerous sediment samples in Minnesota have reportedly been analyzed for total arsenic, this is the first study that has performed an analysis capable of differentiating between the different forms of arsenic in sediment. It was hypothesized that a portion of the total arsenic present in aquifer sediments would be labile arsenic, which is more easily mobilized by relatively small changes in geochemical conditions than arsenic that is present within a mineral structure. Selected sequential extraction steps were performed as described in Chapter 3 on selected sediment samples to differentiate between arsenic that is part of a mineral structure and arsenic adsorbed to sediment grains, which is the labile arsenic. Sequential extraction results for arsenic and iron are summarized in Table 16.

Most of the labile arsenic was extracted in the first step (PO_4), indicating that most of the labile arsenic is ionicly bounded to iron oxides. Sequential extraction results also show that at least a portion of the iron oxides present in the aquifer sediment are high surface area HFO, which are specifically extracted during the ammonium oxalate/oxalic acid step in the sequence, as described in Chapter 3.

In addition to chemical extractions, sediment samples were extracted with water as a comparison. As described in Chapter 3, sediment samples were extracted for seven days in an anaerobic environment. Water extraction results are also presented in Table 16. Water extraction resulted in less total arsenic extraction than the chemical extractions, and it extracted virtually no iron. Organic growth was observed on the surface of the water samples at the end of seven days. Samples were not collected of the organic growth.

No arsenic was present in the extractant blanks.

4.2.7 Scanning Electron Microscopy Results

Scanning electron microscopy (SEM) showed that two, possibly three, iron minerals of potential interest are present in the aquifer sediment collected from the western Minnesota monitoring well. The mineral phases of potential interest are the high surface area amorphous iron hydroxide HFO, lower surface area iron oxides of magnetite and goethite, and pyrite. Magnetite and pyrite were confirmed to be present by chemical scan. Neither goethite nor HFO was conclusively confirmed present with this technology; however, the sequential extraction results presented in the previous section show conclusively that HFO are present in the aquifer sediments. One mineral of potential interest, siderite, was not found to be present using SEM. SEM images of the three iron mineral phases are presented in Figures 18 through 20.

Geochemical modeling using MINEQL+ was conducted to explore the observation of these minerals. At circumneutral pH, and pe conditions ranging from 2.0 to -2.0, geochemical modeling indicates that HFO, magnetite, siderite, and pyrite do not exist together as solids at

equilibrium. The modeling results combined with the observation of magnetite, HFO, and pyrite indicate that the ground water and aquifer sediment are not in a state of geochemical and thermodynamic equilibrium.

None of the three observed mineral phases had arsenic at a concentration above 10 mg/kg, the detection limit of the SEM instrument. This result is consistent with analytical results, which showed that the total arsenic concentration in aquifer sediment was significantly less than 10 mg/kg. The labile arsenic in aquifer sediment, as measured using the sequential extraction procedure, ranged from 0.4 to 0.8 mg/kg.

4.2.8 Rotasonic Core

Physical examination of the rotasonic core collected from western Minnesota shows that there is a thin organic layer present at the interface between the upper confining till unit and the aquifer sediment. Sediment samples were collected from the 58-foot depth interval for organic carbon analysis to confirm that the layer did contain elevated organic carbon levels when compared to deeper aquifer sand samples. Analytical results are presented in Table 17. A photograph of the interface organic layer is presented in Figure 21.

The presence of this organic layer is important because it lends more support to the hypothesis that the interface zone has geochemical conditions conducive to arsenic mobilization via reductive mechanisms. Decomposition of organics present at the interface would create reducing conditions that would facilitate arsenic mobilization. The significance and influence of the interface zone is discussed in more detail in Chapter 6.

4.2.9 Community-Scale Spatial Variability of Arsenic

Plan view and section view results are presented in Figures 22 through 25 for domestic well sampling conducted in two communities with arsenic-affected public water system wells. Both plan and pseudo cross-section views are provided.

Domestic well sampling was conducted in Climax, located in Polk County in northwestern Minnesota. Climax is within the river valley of the Red River of the North. Sampling results show that there is clearly a relationship between the well depth and high arsenic in ground water in this community. The Minnesota Geological Survey has completed a detailed geologic and hydrogeologic interpretations of the river valley of the Red River of the North. Therefore, relatively good geologic information was available in Climax to combine with the ground water sampling results. Shallower wells are screened in the Quaternary sediment, which is known to have physical characteristics that are conducive to arsenic mobilization. The deeper wells, however, although also screened in Quaternary sediment, are very near to deep bedrock aquifers that are discharging to the Red River of the North. Therefore, the deeper wells are more affected by the water quality in the bedrock than they are by the geochemistry of the shallower Quaternary aquifers. Shallower wells have higher arsenic concentrations than deeper wells, as illustrated in Figure 23.

Domestic well sampling conducted in Cosmos, located in Meeker County in central Minnesota, shows no clear correlation between the well depths and high arsenic in ground water in this community. No detailed geological investigations have been conducted in this area. The area is overlain by northwest provenance Late Wisconsinan glacial drift, as well as outwash (Hobbs and Goebel, 1982). The area likely has complex stratigraphy because of numerous glacial advances and retreats.

4.3 Summary

Arsenic concentrations are positively correlated to analytes like iron and manganese, and negatively correlated to analytes like chloride and bromide. These relationships support the hypothesis that reductive processes are mobilizing metals from aquifer sediment. The negative correlation between arsenic and chloride and bromide, along with the sampling results for Climax, indicate that ground water that is influenced by deeper cretaceous aquifers is not geochemically favorable for arsenic mobilization. No extremely low pH waters were encountered.

Sediment and ground water arsenic concentrations from the same sample location are not correlated. Measured total sediment arsenic concentrations are not particularly high. Arsenic present in ground water is aqueous, not associated with particulates, and most of the arsenic present in Minnesota ground water is As(III). A small but significant concentration of sediment arsenic is adsorbed onto or coprecipitated with iron hydroxides; this arsenic is labile arsenic. There was no correlation between arsenic and carbonate, sulfate, TOC, or ammonium, and there was a weak negative correlation between phosphorous and arsenic.

Magnetite, HFO, and pyrite are all present in western Minnesota aquifer sediments, although geochemical modeling indicates that these species should not exist together at equilibrium. A thin layer of sediment with elevated organic content was present at the interface between the glacial drift and the aquifer in a monitoring well in western Minnesota.

Based on the results presented in this section, arsenic mobilization mechanisms due to anion competition, organic complexation, mineral aging, and pyrite oxidation are not supported. The other potential arsenic mobilization mechanisms presented in Chapter 2 cannot be eliminated. These results do, however, indicate that one or several reductive arsenic mobilization mechanisms are likely to be occurring.

5.0 Arsenic Concentrations in Upper Midwestern Ground Water

5.1 Introduction

As presented in Chapter 2, portions of the upper Midwest are overlain with glacial drift that was deposited by glacial ice that advanced from the north-northwest during the Late Wisconsinan. The northwest provenance Late Wisconsinan till has two distinct features important to this study: a large fraction of fine-grained sediment and organic matter that causes active anaerobic biological activity. Arsenic concentrations in northwest provenance Late Wisconsinan sediment are not particularly high, nor are arsenic concentrations in this sediment significantly different from arsenic concentrations in sediment of northeastern provenance.

Results presented in Chapter 4 indicate total arsenic concentrations in sediment are not related to arsenic concentration in ground water. Hering and Kneebone (2002) show that mobilization of just 0.09% of the average crustal arsenic concentration in sediment, 1.8 mg/kg, yields water arsenic concentrations exceeding 10 μg/l. They assume sediment specific gravity of 2.6 g/cm^3 and porosity of 30%, which is consistent with the characteristics of the sediment of interest to this study. Hering and Kneebone's example calculation illustrates that total arsenic concentration in sediment is less important than the availability of the arsenic to mobilization. Results presented in Chapter 4 show that adsorbed arsenic, which is labile and sensitive to redox conditions, is present at 0.4 – 0.8 mg/kg in northwest provenance aquifer sediment.

This section presents the results of the first regional compilation and data analysis of arsenic measurements in ground water in the upper Midwest. The data sets used in these analyses were described in Chapter 3.

5.2 Results

5.2.1 Public Water System Wells

Figure 26 presents the compilation of arsenic concentrations in public water systems and the lateral extent of northwest provenance Late Wisconsinan drift in the upper Midwest, USA. Visual inspection of Figure 26 provides a compelling argument that there is a relationship between the presence of this sediment and elevated arsenic concentrations in ground water.

The public water system arsenic concentrations were evaluated on the basis of location inside or outside of the footprint of the northwest provenance Late Wisconsinan drift. The proportion of public water system sample locations with arsenic concentrations exceeding 10 μg/l was then calculated for each group. Table 18 presents a summary of this indicator analysis. The comparison rejects the hypothesis that these two proportions are equal ($z = 11.46$, P-value < 10^{-27}, or ≈ 0); thus, the two populations are different.

Table 19 summarizes available information regarding well depth and aquifer type for sample locations. Many public water system sample locations are not associated with a particular well. Instead, the sample locations provide a sample of water blended from two or more sources. Many of the sample locations with unknown aquifer and well depth information are from such sample locations.

Table 20 presents additional arsenic concentration differences within well types for wells with known depths and located within the northwest provenance Late Wisconsinan drift. Depth ranges were chosen based upon quartile ranges for the two different well types. The shallowest

and deepest depth ranges represent the lower and upper quartiles, while the middle depth range represents the middle 50% of depth ranges.

The proportions of both bedrock wells and glacial drift wells exceeding 10 μg/l As within the footprint are different from their counterparts located outside of the footprint (bedrock $z = 4.13$, P-value <0.001; glacial $z = 9.68$, P-value ≈ 0). The shallowest bedrock wells located within the footprint are significantly impacted with arsenic, as are the glacial drift wells in the middle depth range. Glacial drift wells are significantly deeper within the footprint than outside of the footprint; the populations are different ($z = 7.09$, P-value ≈ 0).

Figure 27 presents directional indicator variograms of the upper Midwest region's public water system arsenic measurements. The directional variograms, which are perpendicular to one another, have similar sills, but the apparent nugget effect is approximately six times larger in southwest to northeast, or 45 degree direction (b) when compared to the northwest to southeast, or -45 degree direction (a). As illustrated by the variograms, public water system arsenic measurements are spatially correlated on a scale of 150 kilometers; therefore, one or more of the variables governing the release of arsenic are correlated at this length scale: this is a regional phenomenon. Nearest-neighbor analysis shows that elevated arsenic concentrations are clustered, not randomly distributed.

Figure 28 presents arsenic and iron measurements available for approximately 300 upper Midwest public water system sample locations. Arsenic and iron are very weakly correlated ($R^2 = 0.176$, P-value ≤ 0.001).

5.2.2 All Types of Wells

Figure 29 presents the compilation of arsenic concentrations in ground water and the lateral extent of northwest provenance Late Wisconsinan drift in the upper Midwest, USA. Again, visual inspection provides a compelling argument that there is a relationship between the presence of this sediment and elevated arsenic concentrations in ground water.

The ground water arsenic concentrations were evaluated on the basis of location inside or outside of the footprint of the northwest provenance Late Wisconsinan drift. The proportion of ground water sample locations with arsenic concentrations exceeding 10 μg/l was then calculated for each group. Table 21 presents a summary of the indicator analysis for all wells (and subsets of wells). The comparison of all wells inside and outside of the drift rejects the hypothesis that the proportions are equal ($z = 32.8$, P-value $< 10^{-227}$ or $= 0$); thus the two populations are different. Table 22 summarizes available information regarding well depth and aquifer type for sample locations.

Table 23 presents additional arsenic concentration differences within well types for wells of known depth located within the northwest provenance Late Wisconsinan drift. As for public water system wells discussed in the previous section, depth ranges were chosen based upon quartile ranges for the two different well types.

For all wells, the proportions of both bedrock wells and glacial drift wells exceeding 10 μg/l As within the footprint are different from their counterparts located outside of the footprint (bedrock $z = 4.00$, P-value <0.001; glacial $z = 22.7$, P-value $= 0$). As with public water system wells, the shallowest bedrock wells located within the footprint are significantly impacted by arsenic, as are the glacial drift wells in the middle depth range. Glacial drift wells are significantly deeper

within the footprint than outside of the footprint; the populations are different ($z = 12.72$, P-value ≈ 0).

Figure 30 presents a directional indicator variogram of the upper Midwest region's ground water arsenic measurements. As illustrated by the variogram, ground water arsenic measurements are spatially correlated on a scale of more than 200 kilometers. Nearest-neighbor analysis indicates that elevated arsenic concentrations are clustered, not randomly distributed.

5.3 Discussion

Visual inspection of the regional mapping of arsenic concentrations and the lateral extent of the northwest provenance Late Wisconsinan drift provides a compelling argument that there is a relationship between the two. The statistical analyses provide undeniable evidence of a relationship. Within the footprint, significantly more sample locations exceed 10 µg/l arsenic compared to outside the footprint. Inside the footprint, a higher percentage of wells finished in glacial sediments have elevated arsenic concentrations compared with bedrock wells. Additionally, a higher percentage of the shallowest bedrock wells overlain by northwest provenance Late Wisconsinan drift have elevated arsenic compared with other bedrock wells. Glacial drift wells within the footprint are significantly deeper than glacial drift wells outside of the footprint. The use of deeper wells implies that the northwest provenance Late Wisconsinan drift is fairly continuous, thick, and not very permeable, which is consistent with the reported characteristics of this drift.

Elevated arsenic concentrations are not spatially random, as evidenced by their spatial correlation over lengths of 150 kilometers as well as their geographic clustering. The northwest to southeast directional variogram captures the fact that elevated arsenic concentrations mirror the ice flow direction of Late Wisconsinan ice advances from the northwest. The long-distance spatial correlation of the data eliminates localized phenomena, such as pyrite oxidation induced by the presence of a well, or an arsenic 'roll-front,' as probable regional-scale arsenic mobilization mechanisms.

Northwest provenance Late Wisconsinan sediment does not have particularly high arsenic concentrations when compared with sediment of northeastern provenance. Additionally, existing data suggest that sediment arsenic concentrations are not correlated with ground water arsenic concentrations. It is nonetheless proposed that the presence of the northwest provenance Late Wisconsinan drift is the cause of the widespread area of elevated arsenic concentrations in ground water in the upper Midwest study area. The physical characteristics of this drift – its fine grained matrix, entrained organic matter, and biological activity associated with consuming organic matter – are consistent with sediment characteristics associated with reductive arsenic mobilization mechanisms, such as reductive dissolution and reductive desorption (reduction of As(V) to As(III) followed by desorption of As(III) species, or reduction of Fe(III) species to less adsorptive non-aqueous Fe(II) species). The presence of this significant geologic feature and its depositional history are consistent with the observation that elevated arsenic concentrations are spatially related in the direction of ice flow on a scale of 150 kilometers.

Glacial drift wells constructed within the northwest provenance Late Wisconsinan sediment are relatively deep. Age-dating of glacial drift well water in west-central Minnesota indicates that most wells have water that is hundreds to thousands of years old (Ekman and Alexander, 2002). Rodvang and Simpkins (2001) observe that ground water in aquifers beneath North American Quaternary till is older than the practice of intensive agriculture. The observed well depths and

age dating results suggest that the water in the upper Midwestern glacial drift wells is reduced. Water sampling results from glacial drift public water system and domestic wells in Minnesota suggest that the water is, indeed, reduced. These results are illustrated in Figures 16 and 17.

The oxidation state of arsenic is sensitive to the redox state of the solution. Processes within an aquifer influence the redox state not only of arsenic, but also of iron and sulfur, which influence distributions of arsenic (Hering and Kneebone, 2002; Hounslow, 1980; Thorton, 1996). As illustrated in Figure 28, significant concentrations of iron are present in upper Midwestern ground water. Additionally, iron concentrations in ground water are weakly correlated to arsenic concentrations in ground water. This relationship is suggestive of arsenic being coincidentally mobilized with iron when iron oxides reductively dissolve.

Root *et al.* (2005) observe elevated arsenic concentrations in bedrock wells in southeast Wisconsin. The bedrock is overlain by glacial drift older than the Late Wisconsinan. The vast majority of both till and bedrock samples collected in their study had less than 8 mg/kg arsenic. Only three samples had arsenic concentrations exceeding 8 mg/kg; the highest measured arsenic value in this study was 21 mg/kg. Reductive dissolution and desorption are the proposed arsenic mobilization mechanisms in these wells, based on measured redox conditions, iron and sulfate concentrations, and the lack of a relationship between arsenic and potentially competing anions.

The evidence presented in this chapter and Chapter 4 suggests that mechanisms similar to those in southeast Wisconsin are at work within the footprint of the northwest provenance Late Wisconsinan sediment and in the bedrock overlain by the sediment.

5.4 Summary

Elevated arsenic concentrations in ground water are related to the presence of northwest provenance Late Wisconsinan drift in the upper Midwest, USA. Within the footprint of this sediment, 23.8% of sample locations exceed 10 µg/l arsenic compared to only 4.3% outside the footprint. Glacial drift wells and shallow bedrock overlain by the glacial sediments are most impacted by arsenic. Elevated arsenic concentrations are spatially related to one another over significant distances – more than 150 kilometers. Elevated arsenic is not randomly distributed.

Evidence suggests that the distinct physical characteristics of the northwest provenance Late Wisconsinan drift cause the geochemical conditions necessary to mobilize arsenic. These fine-grained, comparatively organic-rich, biologically active sediments create a geochemical environment that is favorable to a regional-scale mobilization of arsenic in ground water via reductive mobilization mechanisms such as reductive dissolution and reductive desorption. This study highlights an important and often unrecognized phenomenon: high-arsenic sediment is not necessary to cause arsenic-impacted ground water – when 'impacted' is now defined as greater than 10 µg/l.

Most of the data used in this analysis were collected for other purposes; therefore, the cost of conducting this analysis was relatively low. In spite of the low cost, the results have enormous value and consequence. A regional-scale environmental problem was observed and characterized. Significant knowledge gaps that inhibit planning, such as the lack of information tying sampling results to a specific well, were identified. An important result of this analysis is demonstration of the value of finding and using existing sampling results to cost-effectively observe and characterize regional-scale environmental problems. Regional-scale problems cannot be observed with only local-scale data analysis.

A more detailed discussion of the observed differences between arsenic concentrations in public water system wells and other types of wells is presented in the next chapter.

6.0 Well Characteristics Influencing Arsenic Concentrations in Ground Water

6.1 Introduction

The results presented in the previous chapter showed that there are differences in the prevalence of elevated arsenic concentrations in different types of wells, even in the same geographic area. Warner (2001) noted that well characteristics may affect arsenic concentrations in ground water, but provided no elaboration. Kim (2002) observed that arsenic concentrations in public water supply wells are lower than arsenic concentrations in domestic wells in Michigan. Ryker (2003) presented the differences in nationwide data sets between arsenic concentrations in public water system wells versus domestic wells. McMahon (2001) discussed the important biogeochemical reactions that take place in the unique interface environment between an aquifer and the overlying confining unit. Because chemical gradients develop between aquifers and aquitards, the aquifer/ confining unit interface sustains greater biogeochemical activity than either the aquifer or the confining unit. Of specific interest to this study are the reducing environments that are created at the interface.

This chapter examines observed relationships between arsenic concentrations and well construction practices in upper Midwestern wells, provides hypotheses and supporting information to explain the observed differences, and suggests potential regulatory action in arsenic-affected areas to reduce the number of arsenic-affected domestic wells.

6.2 Results

Figures 26 and 29 present the compilation of arsenic concentrations in ground water and the lateral extent of northwest provenance Late Wisconsinan drift in the upper Midwest, USA. Table 21 present a summary of arsenic measurements segregated into groups by location relative to the northwest provenance Late Wisconsinan drift, well use, and aquifer type. Even excluding the local MARS results from the analysis, it is clear that public water system wells are less impacted by arsenic contamination than other types of wells. Within the footprint of the northwest provenance Late Wisconsinan drift, 27.7% of non-PWS wells (23.2% excluding MARS wells) are impacted by arsenic contamination, compared to only 12% of PWS wells. The proportions are different ($z = 15.85$, P-value ≈ 0).

Table 22 presents a summary of available well depths for the sampled wells, also segregated by well location, use, and aquifer type. Inside the footprint of the northwest provenance Late Wisconsinan drift, glacial drift PWS wells are significantly deeper than other types of glacial drift wells ($z = 9.08$, P-value ≈ 0). Although bedrock PWS wells are deeper, on average, than other types of wells, the difference in bedrock well depths is not statistically significant ($z = 1.36$, P-value $= 0.173$).

Well construction characteristics were examined using the MARS local-scale data set. The MARS wells were linked to the geologic information in the CWI. All MARS wells were domestic-use glacial sediment wells. Arsenic concentrations were segregated by well characteristics such as well screen length, well screen proximity to the upper confining unit (the northwest provenance Late Wisconsinan drift), and sediment characteristics of the aquifer intersected by the well screen, as reported by the driller. Table 24 presents a summary of arsenic and iron concentrations in MARS wells, segregated by well characteristics. Figure 31 provides an illustration of the well characteristics of interest.

Domestic wells that have screens that are less than 8 feet long and set within 4 feet of the upper confining till unit have an average arsenic concentration of 20 µg/l, with 60% of wells exceeding 10 µg/l. Domestic wells with longer screens set further from the upper confining unit average only 12 µg/l arsenic. Only 40% of those wells exceed 10 µg/l. The two arsenic concentration populations are different ($z = 2.94$, P-value <0.0033). Iron concentrations also differ between the two types of well characteristics ($z = 2.27$, P-value $= 0.025$). Wells with screens that intersect gravel in addition to or instead of sand have lower average arsenic concentrations and a lower probability of having elevated arsenic. These two arsenic concentration populations are also different ($z = 2.70$, P-value <0.0069), but the average iron concentrations are not different between these groups. The pe readings are similar in each group of wells.

6.3 Discussion

The results presented thus far can be summarized as follows:

- Elevated ground water arsenic concentrations in the upper Midwest are not related to anthropogenic arsenic sources.
- Elevated ground water arsenic concentrations in the upper Midwest are not random. Elevated arsenic concentrations are spatially correlated over a very long distance, 150-200 kilometers, and high arsenic concentrations are clustered together.
- Arsenic concentrations in ground water are not correlated to arsenic concentrations in sediment.
- Elevated arsenic concentrations are more likely to be found in any well located within the footprint of the northwest provenance Late Wisconsinan drift than in similar wells outside of the footprint.
- Elevated arsenic concentrations are more likely to be found in glacial drift wells within the northwest provenance Late Wisconsinan drift than in bedrock wells within the footprint.
- Elevated arsenic concentrations are more likely to be found in shallow bedrock wells located within the footprint of the northwest provenance Late Wisconsinan drift than in deeper bedrock wells within the footprint.
- Elevated arsenic concentrations are more likely to be found in domestic and monitoring wells when compared to public water system wells.
- Elevated arsenic concentrations are more likely to be found in domestic wells with short screens set in proximity to the upper confining unit than in wells with any other combination of screen length and screen placement.
- Elevated arsenic concentrations are less likely to be found in domestic wells that have long screens set away from the upper confining unit.
- Elevated arsenic concentrations are less likely to be found in domestic wells that draw water from a gravel aquifer than a sand aquifer.

At first glance, these observations may seem unrelated. The observations are, however, completely consistent with known reductive arsenic mobilization mechanisms, known biogeochemical reactions that occur at the interface between an aquifer and the overlying confining unit, and known characteristics of the northwest provenance Late Wisconsinan sediment. The observations also have important ramifications for public policy development related to arsenic contamination in water supply wells.

Reductive arsenic mobilization mechanisms, such as reductive dissolution of metal hydroxides and reductive desorption (i.e. As (V) species being reduced to As (III) species), are sensitive to the surface area of the hydroxides (Houben, 2003a; Pierce and Moore, 1982; Schwertmann and Cornell, 2000). Larger particles (i.e. gravel) have less surface area per volume than smaller particles (i.e. sand); thus, larger particles have less surface area available for metal hydroxide coatings to form and adsorb arsenic. Less adsorbed arsenic yields a smaller amount of aqueous arsenic in equilibrium with adsorbed arsenic. Additionally, less adsorbed arsenic results in less potential for mobilization of arsenic at concentrations of concern via reductive mobilization mechanisms.

The confining till unit in western Minnesota is present across the upper Midwest region, as illustrated in Figure 2. This northwest provenance Late Wisconsinan till has physical characteristics that can create geochemical conditions favorable to arsenic mobilization via reductive mechanisms such as reductive dissolution of metal hydroxides and reductive desorption. The widespread presence of organic material and biological activity in this till, as discussed in Chapter 2, is suggestive that geochemical conditions favorable to arsenic mobilization are likely to be present in proximity to the till, which is the upper portion of an aquifer. McMahon (2001) discusses the important biogeochemical iron reduction reactions that take place in the unique interface environment between an aquifer and the overlying confining unit. This study shows that the aqueous iron concentrations are higher in domestic wells with short screens set in proximity to the confining unit when compared to long screens set away from the confining unit. The pe readings are similar in each group of wells. The results indicate that the reactions discussed in McMahon (2001) likely influence the geochemistry of the upper portions of western Minnesota glacial aquifers.

Elevated arsenic concentrations are spatially correlated over a very long distance. The concept of 'moving a well over' to avoid arsenic contamination, as might reasonably be considered if ground water contamination is due to anthropogenic contamination, is not a scientifically appropriate response in the case of naturally occurring arsenic. Consideration of the three-dimensional problem and its associated three-dimensional processes is crucial.

The construction of a domestic well is often priced by the foot, both for drilling costs and for the cost of the screen. Cost-effective domestic well construction, therefore, means constructing the shallowest well with the shortest screen that will provide adequate water quantity. This construction practice often results in domestic wells with short screens set just below an upper confining unit, often till, as illustrated by the right-hand well in Figure 31. Although cost-effective at the time of drilling, this well construction practice has the unforeseen and unfortunate effect of placing the well screen in the portion of the aquifer most likely to be affected by active arsenic mobilization processes.

Public water systems have the responsibility for providing a consistent, reliable water supply to their customers at a reasonable price. Public water systems, therefore, invest time and money in planning and constructing wells to ensure that the well will provide an adequate supply of water to meet water supply requirements into the foreseeable future. The emphasis of public water systems on a reliable, consistent water supply results in the targeting of aquifers that will provide a large quantity of water. By necessity, public water systems tap coarser, larger aquifers, and they install wells with long screens. Until recently, most US public water systems probably gave little thought to trying to drill a well that would be expected to have low arsenic concentration. A fortunate outcome of the decades-old heuristic for constructing public water system wells has

coincidentally resulted in tapping lower-arsenic aquifers and constructing wells that are apparently less vulnerable to arsenic contamination.

Regulatory agencies could consider developing guidelines that would change common domestic well-drilling practices. Changing routine well-drilling practices in known high-arsenic areas of the region may have the benefit of reducing the number of families exposed to arsenic from their drinking water. Well drillers could be encouraged to routinely set well screens further away from a till unit overlaying the sandy aquifer and to use longer screens in domestic wells. Although both of these construction changes would mean an increase in up-front costs to homeowners, incorporating these changes could protect a significant number of families from exposure to arsenic from their drinking water. Even though effective arsenic treatment systems are available for home use, eliminating the source of arsenic exposure is a more effective and permanent solution. Eliminating the source of arsenic exposure would also eliminate the expense of ongoing treatment system maintenance and reduce the need for further water testing.

6.4 Summary

Arsenic contamination is more common in domestic wells and in monitoring wells than in public water system wells. Additionally, arsenic contamination is more prevalent in domestic wells with a short screen set in proximity to an upper confining unit, such as till.

Public water system wells have distinctly different well construction practices and well characteristics when compared to domestic and monitoring wells. Well construction practices such as seeking a thick, coarse aquifer and installing a long well screen, yield good water quantity for public water system wells. These well construction practices also coincidentally often yield low arsenic. Coarse aquifer materials have less surface area for adsorbing arsenic and, thus, less arsenic available for potential mobilization. Wells with long screens set away from an upper confining unit are at lower risk of exposure to geochemical conditions conducive to arsenic mobilization via reductive mechanisms such as reductive dissolution of metal hydroxides and reductive desorption of arsenic. Changes in routine domestic well construction practices to exploit deeper parts of an aquifer and use a longer screen could reduce the number of domestic wells that are affected by arsenic contamination in the upper Midwest.

Based on the results presented thus far, it is likely that reductive arsenic mobilization mechanisms are causing the widespread arsenic contamination in upper Midwestern ground water. Although unsupported with direct evidence, indirect evidence indicates that biogeochemical reactions likely play an important role.

7.0 Temporal Variability of Arsenic Concentrations in Minnesota Ground Water

Several questions related to the temporal variability of arsenic concentrations in ground water were addressed during this research. The questions were generally related to the following areas of concern:

- Will arsenic concentrations change systematically in a newly-constructed well?
- What is the 'normal' arsenic variability in a public water system well?
- Is there any temporal pattern to arsenic concentration variability in public water system wells?

Sampling schemes were designed to better understand temporal arsenic concentration variability in Minnesota ground water. Long-term arsenic variability sampling consisted of sampling three wells to examine potential hourly, daily, weekly, monthly, or seasonal arsenic concentration trends. Samples were collected at these three wells at four different time scales: hourly, daily, weekly, and monthly. Short-term arsenic variability sampling was conducted at 11 public water system wells to examine arsenic variability that may be related to the wells' presence and operation. Short-term arsenic variability sampling consisted of collecting four samples over the course of an hour, during which the well pump operated continuously, and then collecting a final sample several hours after the well pump had been shut off. Detailed sample collection methods were described in Chapter 3.

7.1 Temporal Variability in Newly Constructed Domestic Wells

7.1.1 Introduction

Some variability has been noted in arsenic concentrations measured in domestic wells in Minnesota, and pyrite cycling is one arsenic mobilization mechanism hypothesized to be causing elevated arsenic concentrations in Minnesota ground water (Minnesota Department of Health, 2001). Pyrite oxidation has been documented to cause extremely high concentrations of arsenic (i.e., arsenic greater than 1,000 μg/l) in ground water (Schreiber et al., 2000; Smedley and Kinniburgh, 2002). In these settings of pyrite oxidation, arsenic concentrations reportedly increase over time as the pyrite is exposed to air and oxidizes, releasing arsenic, iron, and sulfur. The release of sulfur causes extremely low pH water (i.e., pH 2) as sulfuric acid forms in water and causes very high arsenic concentrations (Schreiber *et al.*, 2000).

If pyrite oxidation were occurring in Minnesota domestic wells, then it would be expected that the arsenic concentration would increase over the time of well operation. Research was conducted to find out whether or not arsenic concentrations change systematically over time in newly-constructed domestic wells in Minnesota.

7.1.2 Results

Figure 32 illustrates arsenic concentration variability in newly-constructed wells. The initial sample is the filtered sample for wells that were sampled on the date of well drilling.

The sample results shown in Figure 32 are linearly related with a slope of 0.9849, effectively 1:1. There is, therefore, no temporal trend in arsenic concentrations in newly-constructed wells. A trend would have been discernible from a linear regression line with a slope of notably less than 1:1 (decreasing arsenic concentration over time) or greater than 1:1 (increasing arsenic concentration over time). Moreover, none of the water from newly constructed wells had an

extremely low pH. All pH measurements were circumneutral. Based on the lack of temporal arsenic concentration trends and the absence of low pH water in newly-constructed wells, pyrite oxidation can be ruled out in the 17 study wells.

Figure 33 presents filtered and unfiltered arsenic concentrations for samples collected immediately following well development on the day of well drilling. Each pair of samples was collected at the same time at the same well. At two of the seven wells, sample locations A and B on Figure 33, the arsenic concentration in the unfiltered sample is significantly less than the arsenic concentration in the filtered sample. It was hypothesized that excess carbonate sediment in the unfiltered sample neutralized the acid preservative, thus allowing precipitation of iron and adsorption of arsenic (Bose and Sharma, 2002; De Vitre et al., 1991; Pierce and Moore, 1982; Sracek et al., 2004; Welch et al., 2000).

The pH was checked in the suspect unfiltered samples and was found to be over 5, which is significantly higher than pH 2, the target pH and the measured pH in the filtered sample of the pair. At pH 5, iron precipitates out of solution, and arsenic adsorbs to the precipitated iron oxides.

7.1.3 Discussion

There is no temporal arsenic concentration trend in 17 newly-constructed domestic wells in Minnesota. At two of seven wells sampled on the date of drilling, the measured arsenic concentration in the unfiltered sample was significantly less than the measured arsenic concentration in the filtered sample.

The research results have provided answers to two important questions related to promulgation of a rule to test all new domestic wells in Minnesota for arsenic.

First, these results indicate that an arsenic sample can be collected from a new well whenever it is most convenient to do so. Arsenic concentrations in new wells do not increase or decrease systematically over time.

Second, these results indicate that if a sample is collected on the day that the well is drilled, it is crucial that the sample be collected appropriately. Samples collected on the day that the well is drilled must be collected after the well has been sufficiently developed to ensure that formation water, not drilling fluid, is sampled. Samples collected on the day that the well is drilled must be filtered or otherwise collected (i.e., decanted) to ensure that carbonate-rich sediment will not interfere with the sample's required low-pH preservation.

7.2 Long-Term Temporal Variability in Public Water Supply Wells

7.2.1 Introduction

Numerous public water systems in Minnesota have noted arsenic concentration variability over time (Peterson, 2003). Arsenic compliance sampling is only required at public water systems every three years, however, so very little is known about potential trends or causes of arsenic concentration variability. Because the more stringent arsenic drinking water standard will soon be enforced, there is new interest in gaining a better understanding of arsenic concentration fluctuations over time and determining how many samples are sufficient to declare that a system is not in compliance.

7.2.2 Results

Hourly, daily, weekly, and monthly arsenic sampling results for three public water system wells are presented in Figure 34. Although there is no temporal pattern of arsenic concentration variability in these wells over the period of sampling, there *is* concentration variability, as shown in Table 25. At the sampled wells, the magnitude of the differences presents no regulatory significance. The results do point out, however, that there is some variability in arsenic concentrations in public water system wells. The standard deviation is as high as 3.5 µg/l for well 240652 during the daily sampling, and the standard deviation is near or above 1.0 µg/l for the averages of all samples collected at each well. As discussed in Chapter 4, virtually all of the arsenic in raw water samples is dissolved arsenic; the total arsenic and filtered arsenic results were effectively identical.

7.2.3 Discussion

There is some random variability in arsenic concentrations in public water system wells. When it is crucial to accurately determine average arsenic concentrations – for example, at a well that fluctuates above and below the regulatory arsenic limit of 10 µg/l – it may be worthwhile to collect more than the prescribed number of samples. The cost of making a Type II error – failing to reject the hypothesis that the average arsenic concentration is more than 10 µg/l – is much higher than the cost of additional sample analyses. Using the results of this study as an example, a power-function test (Ross, 1987), as illustrated in Table 26, can be used to determine the sample size required to accept the hypothesis that the arsenic concentration is, indeed, more than 10 µg/l. A power of 0.8 gives reasonable confidence that a Type II error will be avoided (StatSoft, 2004). For a standard deviation of 0.5 µg/l, four samples are almost enough to differentiate between a population with a mean of 10 µg/l versus a population with a mean of 11 µg/l. If the standard deviation is 3.5 µg/l, however, 100 samples are needed to differentiate between a population with a mean of 10 µg/l versus 11 µg/l. The more variable the data set (i.e., the larger the standard deviation), the more samples are required to accurately determine the population mean.

7.3 Short-Term Temporal Variability in Public Water Supply Wells

7.3.1 Introduction

Some Minnesota public water system operators reported that arsenic concentration was dependent upon the timing of sample collection (Peterson, 2003). Anecdotal evidence from these local operators suggested that samples collected after purging the well for a period of time have a higher arsenic concentration than samples collected after just a few minutes of well purging. In contrast, Gotkowitz et al. (2004) reported increases in arsenic concentrations in wells when the well was *not* pumped. Research was needed to verify the reported arsenic concentration variability and then either support or refute one of three hypothesized arsenic mobilization mechanisms: pyrite oxidation, reductive dissolution, or reductive desorption.

The pyrite oxidation hypothesis would be supported if the arsenic concentration started out high and then decreased over a short period of time, and an increase in pH from acidic to circumneutral was seen (Schreiber *et al.*, 2000; Williams, 2001). The reductive dissolution mechanism hypothesis (reduction of Fe(III) to $Fe(II)_{aq}$) would be supported if the arsenic concentration increased over time with an increasing and relatively high iron content (Bose and Sharma, 2002). The reductive desorption hypothesis would be supported if the arsenic

concentration increased over time while the iron content was low, and the arsenic concentration increase was primarily due to an increase in As(III) species (Jones *et al.*, 2000; Langner and Inskeep, 2000; Zobrist *et al.*, 2000). Increases in arsenic concentration over time would indicate that the area near the well is enriched with metal hydroxides that adsorb arsenic. Adsorbed arsenic is labile and particularly sensitive to small changes in geochemical conditions (Kinniburgh and Smedley, 2001b).

7.3.2 Results

As shown in Figure 35(A), seven public water system wells tested for short-term arsenic concentration variability did not exhibit any significant arsenic concentration variability over the five-hour period of sampling. Figure 36(A) illustrates iron concentration changes at the same wells over the same sampling period. In most wells, iron concentrations do not appreciably fluctuate, and there is no discernible iron variability pattern that is common among these wells. Figure 37(A), a pe-pH diagram, illustrates the measured pH and converted ORP field readings relative to theoretical arsenic speciation fields at equilibrium. The pe was negative (-0.5 or lower) at the beginning of pumping in all but one of these wells, and the pe decreased as the well pumps ran. The pH increased at some wells and decreased at other wells over the sampling period. In these wells, the percentage of As(III) at each well remained relatively steady at 80% to 100% As(III) over the one-hour sampling period. All seven of these wells used submersible pumps.

Four public water system wells tested for short-term arsenic concentration variability did have notable arsenic concentration variability over time, as shown in Figure 35(B). In all of the wells with arsenic concentration variability over time, the arsenic concentration was less than 10 µg/l shortly after pumping started, and it increased relatively rapidly during the first 20 minutes of pumping. Arsenic concentrations then increased more slowly through the remaining 40 minutes of sampling, decreasing again to less than 10 µg/l within four hours after cessation of pumping. Neither nitrate nor nitrite was detected in any of the wells.

Table 27 presents selected water chemistry results for the wells with notable arsenic concentration variability. In wells 209387, 228735, and 242000, most of the increase in arsenic concentration was due to an increase in As(III) species. As illustrated in Figure 36(B), in these same three wells, iron concentrations decreased over the one-hour sampling period and increased after the period of no pumping. Dissolved oxygen and pe both decreased over the one-hour sampling period, while pH increased. The initial pe was positive or only slightly negative in these three wells. Figure 37(B) shows a pe-pH diagram illustrating the measured field parameters relative to theoretical arsenic speciation. These three wells had turbine pumps.

In well 228735, the arsenic concentration increase was not attributable to As(III) species, and iron concentrations increased over the one-hour sampling period. The initial pe in this well was -0.8, similar to the initial pe in the wells that did not exhibit arsenic concentration variability. This well used a submersible pump.

The sediment extraction results, presented in Chapter 4, show that 0.4-0.8 mg/kg of the arsenic present in aquifer sediment is labile arsenic, that is, arsenic adsorbed to or coprecipitated with oxides coating sediment grains. See Table 16.

Speciation modeling shows that decreases in pe result in an increased percentage of As(III) species. In the example speciation models, pe values of 0.5, 0.0, -0.5, and –2.0 (Models 1 - 4,

Table 7) result in 6.3%, 39.7%, 86.8%, and 100% As(III) species, respectively. The pe range from 0.5 to -0.5 appears to be a crucial transition range. At circumneutral pH, the speciation of arsenic changes from being dominated by As(V) species to being dominated by As(III) species. Adsorption modeling shows that As(III) species adsorbs less strongly than As(V) species in a circumneutral pH range. In the example adsorption model, only 2% of the total arsenic present as As(V) species were in the aqueous phase (Model 5). By comparison (Model 6), over 8% of the As(III) species were in the aqueous phase, all other model parameters being equal. Additionally, iron oxy-hydroxide minerals are not stable at low pe. Geochemical modeling results are consistent with observed changes in arsenic concentration, given changing arsenic speciation and changes in redox conditions.

7.3.3 Discussion

Seven public water system wells tested for short-term arsenic concentration variability did not exhibit any significant arsenic concentration variability over the five-hour period of sampling. The pe calculated from field ORP measurements was -0.5 or lower at the beginning of pumping in all but one of these wells. The negative pe readings indicated that As(III) species should dominate; sampling results confirm that As(III) species are, indeed, predominant.

Four public water system wells did have notable arsenic concentration variability over time. The pe in three of these four wells was initially positive or only slightly negative and, as the well pump operated, the pe decreased through the crucial pe range for arsenic speciation changes from As(V) to As(III). Our results are opposite of the findings of Gotkowitz *et al.* (2004), where ORP measurements increased when the well pump ran. When their well pump did not run, arsenic concentrations increased while ORP measurements decreased. They attributed arsenic concentration increases to biologically-induced reductive mechanisms within the stagnant borehole water. Although the arsenic variability observed in the current study has not previously been reported for public water system wells, the arsenic concentration variability is consistent with well-documented reductive arsenic mobilization mechanisms, which are briefly discussed here.

Arsenic is naturally present in a wide variety of geological materials. Under a wide range of geochemical conditions, arsenic is associated with minerals such as iron oxides, iron hydroxides, and other metal oxides/hydroxides. Arsenic adsorption occurs when the ionic complexes of As(V) ($HAsO_4^{-2}$ and $H_2AsO_4^{-1}$) and neutral and ionic complexes of As(III) (H_3AsO_4 and $H_2AsO_3^{-1}$) are adsorbed to iron and other metal hydroxide solid surfaces (Hem, 1985; Holm and Curtiss, 1988; Hounslow, 1980; Kinniburgh and Smedley, 2001b; Korte, 1991; Ryker, 2003; Sullivan and Aller, 1996; Yan *et al.*, 2000). Metal hydroxides are ubiquitous in aquifers throughout the world (Zachara *et al.*, 2001). Labile arsenic is adsorbed onto metal oxides or coprecipitated with metal oxides; arsenic minerals and arsenic coprecipitated with minerals other than metal oxides are strongly held and are not as readily available to release under normal ground water conditions (Smedley and Kinniburgh, 2002).

The oxidation state of arsenic is sensitive to the redox state of the solution. Processes within an aquifer influence the redox state not only of arsenic, but also of iron and sulfur, which influence distributions of arsenic (Hering and Kneebone, 2002; Hounslow, 1980; Thorton, 1996). Processes such as carbonate dissolution and biological activity, which control pH and redox states of fluids infiltrating through tills or clay, have been well documented for numerous localities (Keller *et al.*, 1991a; Lawrence *et al.*, 2000; Simpkins and Parkin, 1993; Yan *et al.*,

2000). Correlations between ground water arsenic concentration and redox are noted in the literature (Holm and Curtiss, 1988; Kim *et al.*, 2002; Kinniburgh and Smedley, 2001b; Korte, 1991; Saxena *et al.*, 2004; Schreiber *et al.*, 2000; Sukop, 2000; Warner, 2001).

The sediment extraction results show that 0.4-0.8 mg/kg of the arsenic present in aquifer sediment is arsenic adsorbed to sediment grains. Following the Hering and Kneebone (2002) calculation described in Chapter 5, mobilization of only 0.4% of 0.4 mg/kg or 0.2% of 0.8 mg/kg of the labile adsorbed arsenic accounts for the measured increases in arsenic concentration in public water system wells. Geochemical modeling indicates that the presence of As(III) species is favored at lower pe values, and desorption of As(III) species is also favored.

A well introduces air (oxygen) into the aquifer around the well. Even more significantly, pumping a well can lower the water table such that an unsaturated zone is created around a well (Gotkowitz *et al.*, 2004). The introduction of oxygen into the aquifer changes the water chemistry and thus can change the concentration of dissolved arsenic in water (Ryker, 2003). The arsenic concentration in the aquifer can significantly increase if arsenic-rich sulfide minerals are oxidized (Schreiber *et al.*, 2000). In contrast, oxygenation of the aquifer immediately surrounding a well may effectively lower arsenic concentrations by providing oxidized iron to which arsenic can adsorb (Tyrrel and Howsam, 1997).

Kanivetsky (2000) relates elevated arsenic concentrations in Minnesota to processes involving adsorption/desorption of arsenic to iron oxides. In Bangladesh, widespread arsenic contamination has been attributed by some authors to biogeochemical redox changes resulting in iron oxide reduction leading to arsenic mobilization (Akai *et al.*, 2004; Nickson *et al.*, 2000; Zheng *et al.*, 2004).

Geochemical modeling results are consistent with arsenic concentration changes observed in this study. Speciation modeling shows that decreases in pe result in an increased percentage of As(III) species. In the example speciation models, pe fluctuations from 0.5 to -0.5 appear to be key: over this pe change at circumneutral pH, the speciation of arsenic changes from being dominated by As(V) species to being dominated by As(III) species. Adsorption modeling shows that As(III) species sorbs less strongly than As(V) species in a circumneutral pH range. Additionally, iron oxy-hydroxide minerals are not stable at low pe.

Reductive desorption and reductive dissolution, which were hypothesized as potential relevant arsenic mobilization mechanisms, are the mechanisms supported by the field data and geochemical modeling. Reductive desorption is proposed as the mechanism to explain the observed water chemistry changes in three of the four previously described wells with notable arsenic concentration variability during pumping. Reductive dissolution is proposed as the mobilization mechanism in one well with notable temporal arsenic concentration variability. A schematic illustrating reductive desorption and reductive dissolution mechanisms is presented in Figure 38.

7.3.3.1 Reductive Desorption

The relevant equation governing reduction of As(V) to As(III) is the following (Meng *et al.*, 2003):

$$HAsO_4^{2-} + 4H^+ \; 2e^- = H_3AsO_3 + H_2O \qquad pK = 28.065$$

$$pe = 0.5\ pK - 2\ pH$$

The preceding relationship necessitates that if As(V) is being reduced to As(III) as the pe decreases, then the pH must increase. As is illustrated in Figure 37, the field data are consistent with the equilibrium requirements for this arsenic reduction equation.

After the well starts pumping, reduced water is drawn to the well. The reduced water has lower iron and sulfur concentrations, likely due to precipitation of iron sulfide minerals such as pyrite. Pyrite was observed growing in glacial sediment in this study (Chapter 4), and has been observed growing in glacial aquifer sediment in Minnesota by others (Berndt and Soule, 1999). The reduced water may also have low arsenic due to coprecipitation of arsenic with pyrite, but it is impossible to measure directly. As the reduced water flows into the zone influenced by the well, arsenic adsorbed to sediment grains near the well is desorbed after a short lag time. The increase in arsenic concentration is primarily due to an increase in As(III) species, which adsorb less strongly to iron oxides than As(V) species and do not adsorb appreciably to other metal oxides. The mobilization mechanism is likely reductive desorption: As(V) species are reduced to As(III) species and then desorb due to reduced adsorption capacity, or iron oxide adsorptive capacity is reduced as Fe(III) minerals are reduced to non-aqueous Fe(II). The As(III) desorption mechanism may also be simple desorption.

After the well stops pumping, the dissolved arsenic concentration decreases slightly due to adsorption. The dissolved iron concentration increases as some iron hydroxides dissolve in the temporarily-reduced aquifer environment. After the higher redox zone around the well equilibrates, both the arsenic concentration and the iron concentration return to their initial concentrations and redox states.

7.3.3.2 Reductive Dissolution

An equation governing reduction of solid precipitates of Fe(III) to aqueous Fe(II) is the following (Bose and Sharma, 2002):

$$Fe(OH)_{3\,(s)} + 3H^+ + e^- = Fe^{2+} + 3H_2O \qquad pK = 26.632$$

$$pe = K + \log[Fe^{2+}] - 3pH$$

The relationship necessitates that if Fe(III) is being reduced to Fe^{2+} as the pe decreases, then the pH must increase. As is illustrated in Figure 37 and in Table 27, the field data are consistent with the equilibrium requirements for iron reduction. At one sampling location, aqueous iron increased as pe decreased and pH increased.

After the well starts pumping, reduced water is drawn to the well. As the reduced water flows into the zone influenced by the well, iron oxides precipitated on sediment grains near the well are reduced and mobilized. The increase in arsenic concentration is not due to an increase in As(III) species, suggesting that adsorbed As(V) species are being co-mobilized with iron.

After the well stops pumping, the dissolved arsenic and iron concentrations decrease again due to adsorption and precipitation of metal oxides.

7.4 Summary

Arsenic concentrations do not change systematically in newly-constructed, glacial sediment domestic wells in Minnesota, so a new well may be sampled whenever it is most convenient. If an arsenic sample is collected on the day that the well is drilled, it must be filtered or otherwise

collected (i.e., decanted) to ensure that carbonate-rich sediment will not interfere with the sample's required low-pH preservation.

There is no discernible pattern of long-term arsenic concentration variability in the three sampled public water system wells. In addition, no 'normal' arsenic variability in public water system wells was established in this study. Standard deviations for hourly to monthly time scale sampling ranged from 0.5 µg/l to 3.5 µg/l. These results illustrate that four sample results are insufficient to confidently declare a public water system out of compliance if the well has significant arsenic variability and an average arsenic concentration just over 10 µg/l.

There is a pattern to arsenic concentration variability in some public water system wells due to reductive arsenic mobilization mechanisms. Four of eleven sampled public water system wells in Minnesota had notable arsenic concentration variability over a short period of time. In these wells, the arsenic concentration was less than 10 µg/l shortly after pumping started, but the arsenic concentration increased over time to a level exceeding 10 µg/l. In these wells, the arsenic concentration decreased to below 10 µg/l again four hours after pumping stopped. The arsenic concentration variability can be explained by reductive arsenic mobilization mechanisms.

The pe in three of these four wells had initial pe readings that were positive or only slightly negative, and the pe moved through the crucial positive-to-negative range, where the speciation of arsenic changes from being dominated by As(V) species to being dominated by As(III) species. Six of the seven wells that did not exhibit short-term temporal changes in arsenic concentration did not have pe measurements that traveled through the positive-to-negative pe range. Three of the four wells with arsenic concentration variability used turbine pumps. All of the remaining wells used submersible pumps.

The results of the short-term arsenic variability sampling strongly point to reductive desorption and reductive dissolution as active arsenic mobilization mechanisms.

8.0 Practical Applications and Regulatory Implications

As described throughout the previous chapters, this research has resulted in practical applications of immediate use. There were also findings of potential regulatory significance. These practical applications and regulatory implications are reiterated in this chapter.

8.1 'Site Investigation' Sampling

The technique of site investigation has been widely and successfully used at hazardous waste sites to delineate the extent of contamination around an anthropogenic release, primarily with the goal of remediation design and implementation (Golian, 1988). A typical site investigation includes tasks such as land use review, soil/sediment boring and analysis, monitoring well installation, well and surface water sampling and analysis, and three-dimensional synthesis of results to quantify the extent of contamination and recommend remediation options, if necessary.

A similar approach, as was described in Chapters 3 and 4, was applied to investigate the extent of naturally occurring arsenic contamination. However, rather than identifying a 'source,' or where the contamination *is*, the goal of a site investigation around a high-arsenic public water supply well is identifying where the arsenic *isn't*. With respect to regional-scale, naturally occurring ground water arsenic contamination, avoiding a 'source', in the traditional, localized, high-concentration sense of the word, is not the appropriate goal. Rather, this type of site investigation seeks to identify a different aquifer, either at a different elevation or in a different nearby geographic location, which will not have high arsenic due to dissimilar geochemical conditions.

Based on the promising 'site investigation' results presented in Chapter 4 for Climax and Cosmos, the Minnesota Department of Health has to begun routinely work with communities with arsenic-impacted wells to conduct a site investigation prior to approving an expensive arsenic treatment plant. From 2002 through the present, more than a dozen site investigations have been conducted by the Minnesota Department of Health. In most communities, site investigation results indicated that drilling a new well may be a viable, low-cost compliance option. As an example, representatives of the Polk County community of Nielsville worked with the Minnesota Department of Health to conduct a site investigation. As a result of the site investigation, Nielsville drilled a new, low-arsenic well during 2004.

8.2 New Well Sampling

As of early 2005, the Minnesota Department of Health was in the process of promulgating updated well rules. One proposed well rule change would require sampling all new domestic wells in Minnesota for arsenic. Research results presented in Chapter 7 and in a report to the Minnesota Department of Health (Erickson and Barnes, 2004c) indicate that an arsenic sample could be collected from a new well whenever it is most convenient to do so.

Research results also indicate that if a sample is collected on the day that the well is drilled, it is crucial that the sample be collected appropriately. Samples collected on the day that the well is drilled must be collected after the well has been sufficiently developed to ensure that formation water, not drilling fluid, is sampled. Samples collected on the day that the well is drilled must also be filtered or otherwise collected (i.e., decanted) to ensure that carbonate-rich sediment will not interfere with the sample's required low-pH preservation.

8.3 Temporal Variability Sampling

The results presented in Chapter 7 and in a report to the Minnesota Department of Health (Erickson and Barnes, 2004a) show that additional sampling – above and beyond minimal compliance sampling – can be of tremendous benefit. Results show that some public water system wells have predictable, explainable variations in arsenic concentration that occur over an hour-long period of pumping. Routine quarterly and annual sampling did not reveal the pattern; systematic frequent sampling did.

Public water systems with predictable and explainable arsenic concentration variability could, as an arsenic compliance option, consider exploiting this variability by making a change in well operations. A viable, low-cost compliance option could involve the use of the variable-concentration well on an intermittent basis using a timer. Although additional water sampling may be necessary to demonstrate that changing well operations is a consistent and reliable method of maintaining a low arsenic concentration, the results of this research present a promising, low-cost potential compliance solution.

Long-term variability sampling results indicate that additional arsenic sampling may be warranted at some public water system wells. Although there was no discernible pattern of long-term arsenic concentration variability in the three sampled public water system wells, standard deviations for hourly to monthly time scale sampling ranged from 0.5 µg/l to 3.5 µg/l. These results indicate that additional arsenic sampling may sometimes be necessary. Four sample results are insufficient to confidently declare a public water system out of compliance if the well has significant arsenic variability and an average arsenic concentration just over 10 µg/l.

8.4 Domestic Well Construction Methods

As described in Chapter 6, regulatory agencies could consider developing guidelines that would change common domestic well-drilling practices to potentially reduce the likelihood of arsenic-impacted well water. Well drillers could be encouraged to routinely set well screens further away from a till unit overlaying the sandy aquifer and to use longer screens in domestic wells. Although both of these construction changes would mean an increase in up-front costs to homeowners, incorporating these changes could protect a significant number of families from exposure to arsenic from their drinking water. Even though effective arsenic treatment systems are available for home use, eliminating the source of arsenic exposure is a more effective and permanent solution. Eliminating the source of arsenic exposure would also eliminate the expense of ongoing treatment system maintenance and reduce the need for further water testing.

9.0 Summary, Regulatory Implications, and Future Work

9.1 Summary

Arsenic contamination in upper Midwestern ground water is widespread, naturally occurring, and associated with the lateral extent of northwest provenance Late Wisconsinan glacial drift. Within the footprint of this sediment, 1,690 of 7,101 (23.8%) sample locations exceed 10 µg/l arsenic compared to only 186 of 4,333 (4.3%) outside the footprint. Glacial drift wells and shallow bedrock overlain by this glacial sediment are most impacted by arsenic contamination. Elevated arsenic concentrations are spatially related to one another over significant distances – more than 150 kilometers. Elevated arsenic is not randomly distributed. Evidence suggests that the distinct physical characteristics of the northwest provenance Late Wisconsinan drift cause the geochemical conditions necessary to mobilize arsenic. This fine-grained, comparatively organic-rich, biologically-active sediment creates a geochemical environment that is favorable to a regional-scale mobilization of arsenic in ground water via reductive mobilization mechanisms such as reductive dissolution and reductive desorption.

Arsenic concentrations are positively correlated to analytes like iron and manganese, and negatively correlated to analytes like chloride and bromide. In this study, there was no correlation between arsenic and carbonate, sulfate, TOC, or ammonium, and there was a weak negative correlation between phosphorous and arsenic. Arsenic present in ground water is aqueous, and most of the arsenic present in Minnesota ground water is As(III). No extremely low pH waters were encountered.

Arsenic concentrations measured in sediment in this study are not particularly high, 0.6 mg/kg to 10.6 mg/kg. Sediment and ground water arsenic concentrations from the same sample location are not correlated. A small but significant concentration of sediment arsenic is adsorbed onto or coprecipitated with iron hydroxides; this arsenic is labile arsenic. This study highlights an important and often unrecognized phenomenon: high-arsenic sediment is not necessary to cause arsenic-impacted ground water – when 'impacted' is now defined as greater than 10 µg/l.

Arsenic contamination is more common in domestic wells and in monitoring wells than in public water system wells. Additionally, arsenic contamination is more prevalent in domestic wells with a short screen set in proximity to an upper confining unit, such as glacial till. The geochemical environment at the interface between the confining unit and the aquifer is conducive to arsenic mobilization.

Public water system wells have distinctly different well construction practices and well characteristics when compared to domestic and monitoring wells. Public water system well construction practices such as seeking a thick, coarse aquifer and installing a long well screen, yield good water quantity. These well construction practices also, coincidentally, often yield low arsenic concentrations.

Arsenic concentrations do not change systematically in newly-constructed, glacial sediment domestic wells in Minnesota. Over the course of nine months, there was no discernible pattern of arsenic concentration variability in three public water system wells.

There is a pattern to arsenic concentration variability in some public water system wells due to reductive arsenic mobilization mechanisms. Four of eleven sampled public water system wells in Minnesota had notable arsenic concentration variability over a short period of time. In these wells, the arsenic concentration was less than 10 µg/l shortly after pumping started, but the

arsenic concentration increased over time to a level exceeding 10 µg/l. In these wells, the arsenic concentration decreased to below 10 µg/l again four hours after pumping stopped. The arsenic concentration variability can be explained by reductive arsenic mobilization mechanisms.

The pe in three of these four wells had initial pe readings that were positive or only slightly negative, and the pe moved through the crucial positive-to-negative range, where the speciation of arsenic changes from being dominated by As(V) species to being dominated by As(III) species. Six of the seven wells that did not exhibit short-term temporal changes in arsenic concentration did not have pe measurements that traveled through the positive-to-negative pe range. Three of the four wells with arsenic concentration variability used turbine pumps. All of the remaining wells used submersible pumps.

Several arsenic mobilization mechanisms were presented in Chapter 2 as possible mechanisms responsible for elevated arsenic in upper Midwestern ground water. Based on these research results, the following mechanisms are likely to play an important role in arsenic mobilization in the upper Midwest:

- Adsorption/desorption to iron hydroxides
- Reductive dissolution of iron hydroxides
- Microbially-mediated release of arsenic

The following arsenic mobilization mechanisms were either refuted or not supported based on the results of this research:

- Anthropogenic sources
- Anion competition for adsorption/desorption sites to various metal hydroxides
- Aging of iron hydroxides, resulting in a decreased number of adsorption sites
- Competition with or complexation with various organic species
- Release from or coprecipitation with sulfide minerals (e.g. pyrite)

Most of the data used in this analysis were collected for other purposes; therefore, the cost of conducting this analysis was relatively low. In spite of the low cost, the results have considerable consequence. A regional-scale environmental problem was identified, and significant knowledge gaps that inhibit planning, such as the lack of information tying sampling results to a specific well, were exposed. An important result of this analysis is demonstration of the value of finding and using existing sampling results to cost-effectively observe and characterize regional-scale environmental problems. Regional-scale problems cannot be observed with only local-scale data analysis.

9.2 Regulatory Implication

This research has better defined the areas in the upper Midwest region and in Minnesota that are most at-risk for arsenic contamination. The types of domestic wells most likely to be affected by arsenic contamination have also been better defined. Public health education can be focused in areas that are most likely to be affected by high-arsenic ground water. High-arsenic areas have the greatest need for testing drinking water for arsenic. Additionally, new guidelines could be developed to change common domestic well-drilling practices. Well drillers could be encouraged to routinely set well screens further away from the till unit overlaying the sandy

aquifer and to use longer screens in domestic wells. These well construction changes could prevent a significant number of families from being exposed to arsenic from their drinking water.

Although it was hypothesized that arsenic concentrations in a new well would change over time because constructing a well changes the geochemical environment of the aquifer, this hypothesis proved to be false. Arsenic concentrations in new wells vary over time in a manner similar to arsenic concentrations in older wells. This result has provided the answer to one of the questions that had been delaying the promulgation of updated well rules to test all new domestic wells in Minnesota for arsenic: If an arsenic sample is required for a new well, when should the well be sampled so that the measurement is representative of the typical arsenic concentration? It is now known that an arsenic sample can be collected from a new well whenever it is most convenient because arsenic concentrations in new wells do not increase or decrease systematically over time. Based on these results, after a lengthy delay, the Minnesota Department of Health is again moving forward in the process to promulgate a rule to test all new wells in the state for arsenic.

The research also confirmed that there is some arsenic concentration variability in public water system wells over a long period of time. For most public water systems, the observed arsenic concentration variability will not affect the system's status of being in or out of compliance with the 10 µg/l arsenic standard. At wells that fluctuate at or near the 10 µg/l limit, however, the variability could play a crucial role in determining the system's categorization. The Minnesota Department of Health could consider establishing a site-specific sampling regime to determine whether the system's average arsenic concentration is indeed above 10 µg/l. Four quarterly samples with large concentration differences will not, with a satisfactory degree of confidence, determine the well's true average arsenic concentration. Additional sampling requirements should be determined and sampling conducted before forcing a public water system to invest in a costly but perhaps unnecessary treatment plant or other compliance option.

In collaboration with Minnesota Department of Health engineers and hydrogeologists, the author identified two potential low-cost public water system arsenic rule compliance options (drilling a new well and changing a well's pumping regime), developed methodologies for evaluating the viability of these low-cost options, and proved that the methodologies are effective in evaluating these low-cost compliance options on a community-by-community basis. The Minnesota Department of Health is already using both the 'site investigation' methodology and a prescribed temporal sampling scheme on a regular basis in Minnesota communities that have elevated arsenic concentrations in their water supply. Implementing a viable, low-cost arsenic compliance option is preferable to building an unnecessary and expensive community water treatment plant.

9.3 Future Work

This project provided better understanding of the causes for elevated arsenic concentrations in ground water in Minnesota and in the upper Midwest. Several hypotheses are offered to explain observed patterns of elevated arsenic. In the future, the following investigations could be conducted to further support or to refute the hypotheses presented here:

1) Collect sediment and water samples from new wells constructed in differing geologic materials throughout the region. Preliminary results indicate that there is no direct relationship between sediment arsenic and water arsenic in northwest provenance Late Wisconsinan sediment. No other types of sediment were examined, however. A broader sampling scheme may reveal potential relationships between sediment arsenic concentrations and water arsenic

concentrations that are not related strictly to total arsenic concentration. Other sediment characteristics, such as adsorption characteristics, could also be examined to see whether there are important physical characteristics that influence arsenic mobilization.

2) Collect sediment and water samples from new wells to look for biological activity that may be influencing arsenic mobilization from sediment to water. It is hypothesized that the widespread presence of organic matter in northwest provenance Late Wisconsinan sediment fosters active biological activity, which creates a geochemical environment conducive to arsenic mobilization, especially near till-aquifer boundaries. No biogeochemical experiments were performed during this work to directly support this hypothesis.

3) Construct a series of well nests in known high-arsenic areas to more closely examine the hypothesized relationship between well characteristics, such as screen length and screen proximity to the upper confining till unit, and an increased probability of elevated arsenic concentration in ground water.

4) Examine arsenic concentrations and well construction characteristics in future newly-constructed wells in Minnesota. The proposed well rule changes would require testing all new domestic wells for arsenic beginning in 2006. Approximately 15,000 new wells are constructed in the state each year. The new arsenic and well construction results would provide significant additional data with which to further evaluate the observed relationship between elevated arsenic concentration and certain well construction characteristics.

5) Collect an initial arsenic sample and a series of additional arsenic samples from future newly-constructed wells to further evaluate the potential for arsenic concentration changes over time in newly-constructed wells. Only 19 new wells were sampled during this project, and the wells were only sampled twice, several months to one year apart.

6) Conduct additional tests on wells with relatively high arsenic concentrations. The wells sampled in this study represent a relatively narrow range of possible arsenic concentrations in domestic wells. No wells with very high arsenic concentrations (more than 100 μg/l), which are known to be present in Minnesota, were sampled as part of this study. It is possible that wells with very high arsenic concentrations are affected by a different, local arsenic mobilization mechanism.

10.0 Tables

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Table 1

Selected chemical reactions governing arsenic speciation and dissociation in water

Description	Reaction	Log K
As(III)/As(V) Couples [a]	HAsO42- + 4H+ + 2e- = H3AsO3 + H2O H2AsO4- + 3H+ + 2e- = H3AsO3 + H2O	28.065 21.130
As(III) dissociation [b]	H3AsO3 = H2AsO3- + H+	-9.17
As(V) dissociation [b]	H3AsO4 = H2AsO4- + H+ H2AsO4- = HAsO42- + H+ HAsO42- = AsO43- + H+	-2.30 -6.99 -11.80

[a] (Meng et al., 2003)
[b] (Nordstrom and Archer, 2003)

Table 2
Examples of identified arsenic release mechanisms

Mechanism	Example Location(s)	Maximum Arsenic	Minerals	Example Reference(s)
Oxidation of sulfide minerals	Mining areas Wisconsin, USA	5,100 µg/l 5,000 µg/l	Arsenopyrite Pyrite	(Williams, 2001) (Schreiber *et al.*, 2000)
High pH desorption	Southwestern USA and South Dakota	600 µg/l	Iron oxides/hydroxides	(Bexfield and Plummer, 2003; Carter *et al.*, 1998)
Reductive desorption	West Bengal, India and Bangladesh	3,200 µg/l	Iron oxides/hydroxides	(Kinniburgh and Smedley, 2001b)
Anthropogenic source	Perham, Minnesota Superfund Site	1,260 µg/l	Arsenic pesticides	(US Environmental Protection Agency, 2002)
Evaporative concentration	Nevada, USA	1,200 µg/l	Various	(Welch and Lico, 1998)
Thermal water discharge	Wyoming, USA	2,475 µg/l	N/A	(Langner *et al.*, 2001)
Anion competition	Laboratory Bangladesh	4,719 µg/l >50 µg/l	Iron oxides/hydroxides	(Anawar *et al.*, 2004; Stollenwerk, 2003; Zheng *et al.*, 2004)
Oxide mineral aging	Laboratory	5,000 µg/l	Various iron oxides	(Smedley and Kinniburgh, 2002)
Microbially mediated reduction	Laboratory Field - Bangladesh	0.75-20 mg/l 100 µg/l	Iron oxides/hydroxides	(Akai *et al.*, 2004; Jones *et al.*, 2000; Langner and Inskeep, 2000; Zobrist *et al.*, 2000) (Harvey *et al.*, 2002)
Carbonate complexation	Laboratory Model	275 µg/l 200 µg/l	Orpiment/Realgar Ferrous iron	(Kim *et al.*, 2000) (Appelo *et al.*, 2002)
Organic matter/ carbon complex. and competition	Laboratory	80 µg/l 7.5 g/l	Hematite Goethite	(Redman *et al.*, 2002) (Grafe *et al.*, 2001)

Table 3

Iron oxides present in aquifer systems

Mineral	Formula	Specific Surface Area (m^2/g)	Crystallinity
HFO	FeO(OH)	600	Low
Goethite	α-FeO(OH)	54	High
Magnatite	Fe_3O_4	90	High

Table 4
Public water systems participating in arsenic variability research in Minnesota

Public Water System Name	Well ID	Sampling Scheme
Albany	228734	Short-term
Albany	228735	Short-term
Cosmos	222103	Long-term
Cosmos	241459	Long-term
Climax	240652	Long-term
Deerwood	232353	Short-term
Frost	217007	Short-term
Hanley Falls	545003	Short-term
Lake Lillian	209497	Short-term
LaSalle	138797	Short-term
Lowry	242000	Short-term
School Sisters of Notre Dame (Mankato)	209387	Short-term
School Sisters of Notre Dame (Mankato)	209388	Short-term
Winsted	228799	Short-term

Table 5
Sequential Extraction Procedure

Step	Extractant	Target Phase	Possible Mechanisms
PO_4	1 M NaH_2PO_4, pH 5, 16 and 24 hr, 25°C one repetition of each time duration + one Milli-Q water wash	Adsorbed As	Anion exchange of PO_4 for AsO_4 and AsO_3
HCl	1 N HCl, 1 h, 25°C one repetition + one Milli-Q water wash	As coprecipitated with acid volatile sulfides, carbonates, Mn oxides, and very amorphous Fe oxyhydroxides	Proton dissolution; Fe-Cl complexation
Ox	0.2 M ammonium oxalate/oxalic acid, pH 3, 2 hr, 25°C, in the dark one repetition + one Milli-Q water wash	As coprecipitated with amorphous Fe oxyhydroxides	Ligand-promoted dissolution

(Keon *et al.*, 2001)

Table 6
Detection limits for analyzed parameters

Trace Elements		
Analyte	**Detection Level**	**Unit**
Li	0.05	µ
B	5	µg/l
Al	1	µg/l
P	1	µg/l
S	100	µg/l
Cl	500	µg/l
Cr	0.05	µg/l
Fe	3	µg/l
Mn	0.01	µg/l
Co	0.01	µg/l
Ni	0.05	µg/l
Cu	0.05	µg/l
Zn	0.1	µg/l
As	0.05	µg/l
Br	0.5	µg/l
Se	0.05	µg/l
Rb	0.01	µg/l
Sr	0.05	µg/l
Mo	0.2	µg/l
Cd	0.02	µg/l
Cs	0.01	µg/l
Ba	0.01	µg/l
W	0.02	µg/l
Tl	0.02	µg/l
Pb	0.02	µg/l
U	0.01	µg/l
Anions		
Fluoride	0.005	mg/l
Chloride	0.005	mg/l
Nitrite-N	0.005	mg/l
Bromide	0.005	mg/l
Chlorate	0.01	mg/l
Nitrate-N	0.002	mg/l
Phosphate-P	0.005	mg/l
Sulfate	0.01	mg/l
EDTA-preserved As and Fe		
As	0.05	µg/l
Fe	10	µg/l
Other		
Total Alkalinity	10	mg/l
Ammonium N	0.02	mg/l as N
Total Organic Carbon	1.0	mg/l

Table 7
Geochemical modeling input parameters

Input Parameter	Speciation		Adsorption	
	Model 1	Models 2-4	Model 5	Model 6
pH	7.0	7.0	7.0	7.0
pe	0.5	0, -0.5, -2.0	N/A	N/A
As V (mol)	1.0 E -6	1.0 E -6	1.0 E -5	N/A
As III (mol)	1.0 E -6	1.0 E -6	N/A	1.0 E -5
Model	N/A	N/A	2-Layer FeOH	2-Layer FeOH
Ionic Strength	N/A	N/A	1.0 E -3	1.0 E -3

Table 8
Summary of statewide arsenic sampling results for Minnesota

Location Description	Count	Average As (µg/l)	Median As (µg/l)	Maximum As (µg/l)	Count ≥10 µg/l	% Wells ≥10 µg/l
All Data	3,303	3.9	1.1	156.6	319	9.7%
Inside Footprint	2,179	5.1	1.5	156.6	308	14.1%
Outside Footprint	1,124	1.5	1.0	42.0	11	1.0%

Table 9
Statistically significant correlation coefficients between As and specified analyte, GWMAPS (n=954)

Analyte	Pearson		Spearman	
	Correlation Coefficient	Probability	Correlation Coefficient	Probability
Sr	0.317	<0.0001	0.379	<0.0001
P	0.157	<0.0001	0.378	<0.0001
Fe	0.183	<0.0001	0.368	<0.0001
Si	0.272	<0.0001	0.350	<0.0001
K	0.158	<0.0001	0.346	<0.0001
Mo	0.339	<0.0001	0.322	<0.0001
Li	0.447	<0.0001	0.321	<0.0001
Na	0.110	0.001	0.318	<0.0001
B	0.125	0.000	0.316	<0.0001
Mn	0.037	0.253	0.307	<0.0001
Alkalinity	0.250	<0.0001	0.294	<0.0001
Mg	0.308	<0.0001	0.247	<0.0001
Spec Cond	0.137	<0.0001	0.239	<0.0001
Ca	0.257	<0.0001	0.232	<0.0001
SO_4	0.272	<0.0001	0.202	<0.0001
Co	0.044	0.171	0.170	<0.0001
Se	-0.014	0.670	0.161	<0.0001
Ba	0.046	0.158	0.127	<0.0001
Rb	0.101	0.002	0.097	0.003
V	0.144	<0.0001	0.029	0.367
NO_3	-0.068	0.036	-0.269	<0.0001
Eh	-0.119	0.000	-0.241	<0.0001
DO	-0.090	0.005	-0.216	<0.0001
Cs	-0.037	0.250	-0.095	0.003
Sn	-0.060	0.062	-0.093	0.004
Bi	-0.091	0.005	-0.092	0.004
Zr	-0.026	0.415	-0.080	0.014
Pb	-0.011	0.738	-0.071	0.028
Al	-0.020	0.539	-0.067	0.037
Ni	0.074	0.022	-0.010	0.755

Table 10
Descriptive statistics for the MARS data set

Analyte	Units	Raw Water (N=453)				
		Mean	Std Dev	Median	Minimum	Maximum
As	µg/l	18.3	21.3	11.7	0.2	145.3
Al	µg/l	17.4	159.1	0.6	0.0	2229
Ba	µg/l	63.01	94.62	28.39	0.02	757.76
B	µg/l	584.9	742.3	289.5	0.0	5895
Cd	µg/l	0.01	0.06	0.00	0.00	0.70
Cr	µg/l	4.0	3.1	3.0	0.0	20
Co	µg/l	0.5	0.6	0.3	0.0	6.5
Cu	µg/l	8.7	31.8	1.8	0.0	392.6
Fe	µg/l	2047	1932	1770	0	15100
Pb	µg/l	0.49	2.61	0.15	0.00	51.68
Mn	µg/l	255.5	258.7	192.2	0.1	1925
Mo	µg/l	6.6	5.8	4.9	0.2	36.4
Ni	µg/l	3.8	3.5	3.0	0.0	30.7
NO_3	µg/l	414	3015	0	0	46000
Se	µg/l	1.0	1.3	0.8	0.0	17.7
Sr	µg/l	687	515	536	0	2914
SO_4	mg/l	407	394	284	0	2431
Tl	µg/l	0.22	0.26	0.11	0.00	1.14
U	µg/l	2.60	5.45	0.80	0.00	63.55
Zn	µg/l	72.8	233.2	7.4	0.3	3237
Br	µg/l	161	237	81	12	2018
Cs	µg/l	0.01	0.02	0.01	0.00	0.26
Cl	mg/l	31	69	10	0	581
Li	µg/l	74.2	62.5	55.3	0.5	379.9
Rb	µg/l	2.5	1.8	2.0	0.0	14.2
W	µg/l	0.90	1.42	0.52	0.00	24.93
pH	pH unit	7.38	0.39	7.35	4.06	8.96
Eh	mV	116	101	100	-195	529
O_2	mg/l	0.45	1.05	0.20	0.00	13.10
Spec Cond	mV	997	672	864	2	8121

Table 11
Statistically significant correlation coefficients between As and specified analyte, MARS raw water (n=453)

Analyte	Pearson		Spearman	
	Correlation Coefficient	P-Value	Correlation Coefficient	P-Value
Mo	0.262	<0.0001	0.441	<0.0001
Fe	0.304	<0.0001	0.374	<0.0001
U	0.018	0.700	0.371	<0.0001
Mn	0.136	0.004	0.314	<0.0001
Sr	0.302	<0.0001	0.305	<0.0001
Co	-0.204	<0.0001	0.297	<0.0001
Ni	0.114	0.015	0.258	<0.0001
Li	0.258	<0.0001	0.204	<0.0001
Cr	0.263	<0.0001	0.170	0.000
Rb	0.154	0.001	0.144	0.002
SO_4^{2-}	0.161	0.001	0.135	0.006
Zn	0.139	0.003	0.004	0.931
Cl	-0.204	<0.0001	-0.288	<0.0001
Br	-0.161	0.001	-0.221	<0.0001
Cu	-0.104	0.027	-0.171	0.000
Cs	-0.061	0.209	-0.142	0.003
pH	0.034	0.469	-0.140	0.003
Al	-0.061	0.198	-0.128	0.006
NO_3	-0.079	0.093	-0.124	0.008
W	-0.044	0.353	-0.097	0.038
B	-0.130	0.007	-0.038	0.433

Table 12
Factor analysis, MARS raw water

Variable	Factor1	Factor2	Factor3	Factor4	Factor5
As	0.286	0.307	0.703	-0.194	0.058
B	0.413	-0.817	0.059	0.034	-0.008
Cr	0.036	0.115	0.542	0.069	0.641
Cu	0.163	-0.131	-0.207	0.606	0.482
Fe	0.272	0.461	0.342	0.374	-0.243
Mn	0.485	0.499	-0.126	-0.118	-0.027
Mo	0.191	-0.445	0.452	-0.437	0.009
Ni	0.575	0.469	-0.217	0.044	0.172
Sr	0.843	0.318	-0.036	-0.118	-0.058
SO_4^{2-}	0.863	0.034	-0.139	-0.131	-0.119
Zn	0.176	0.039	0.429	0.605	-0.450
Br	0.366	-0.845	-0.025	0.002	-0.060
Cl	0.288	-0.784	-0.103	0.078	-0.039
Li	0.892	0.100	-0.071	-0.059	0.054
Rb	0.693	-0.272	-0.025	0.133	0.116
pH	-0.057	-0.774	0.196	0.061	0.002
Variance	3.938	3.791	1.479	1.185	0.979
% Var	24.6%	23.7%	9.2%	7.4%	6.1%
Cumulative %	24.6%	48.3%	57.5%	64.9%	71.0%

Table 13
Summary of sampled wells

Analyte	Public		Domestic			
	Long Temporal	Short Temporal	New	Community	Known	Monitoring
Trace Elements	Y	Y	Y	Y	Y	Y
Dissolved Trace Elements	S	N	S	S	N	Y
Anions	S	Y	Y	N	Y	Y
Total Alkalinity	N	Y	S	N	Y	N
Ammonium	N	Y	S	N	Y	N
Total Organic Carbon	N	Y	S	N	Y	N
Arsenic Species	N	Y	S	N	Y	N
Sediment	N	N	S	N	N	Y
Year(s)	2002-2003	2003-2004	2002-2003	2002	2003	2003-2004

Y = Yes, at all sampling events
S = Yes, at most or some of the sampling events
N = No, not collected at this type of location

Table 14
Selected summary statistics for new data

Variable	N	Units	Mean	Median	Std Dev	Minimum	Maximum
As	98	µg/l	20.04	13.51	18.48	0.10	87.25
Li	98	µg/l	57.8	44.4	46.1	2.4	182.1
B	98	µg/l	412	288	453	16	2857
P	98	µg/l	155	56	414	0	3186
S	98	µg/l	101455	56965	102590	0	380200
Cl	98	µg/l	25473	4734	58090	0	372300
Br	98	µg/l	148	65	190	15	1118
Fe	98	µg/l	1676	1375	1364	0	7264
Mn	98	µg/l	209	155	229	8	1755
Sr	98	µg/l	696	525	548	21	4148
U	98	µg/l	1.59	0.76	2.41	0.00	13.24
NO_3^-	51	mg/l	0.03	0.00	0.15	0.00	1.05
NH_4^+	58	mg/l	1.09	0.98	0.76	0.03	4.46
TOC	58	mg/l	3	3	3	0	26
Tot Alkalinity	57	mg/l	364	360	62	210	570
pH	67	pH unit	7.31	7.31	0.26	6.54	8.08
Conductivity	69	mV	483	441	209	125	996
DO	54	mg/l	0.32	0.26	0.25	0.07	1.68
Eh	65	mV	-35	-50	98	-253	409
% As III	66	percent	83.2%	86.9%	11.8%	49.2%	100%

Table 15
Statistically significant correlations for new data

Analyte	Correlations with Total Arsenic			
	Pearson		Spearman	
	Correlation Coefficient	P-value	Correlation Coefficient	P-value
Li	0.529	<0.0001	0.515	<0.0001
U	0.258	0.010	0.507	<0.0001
DO	0.045	0.746	0.306	0.025
Sr	0.201	0.048	0.281	0.005
Mn	0.097	0.342	0.268	0.008
Br	0.187	0.066	0.203	0.045
S	0.250	0.013	0.173	0.088
pH	-0.213	0.083	-0.250	0.042
P	-0.139	0.171	-0.200	0.048
Analyte	**Correlations with % Arsenic III**			
	Pearson		**Spearman**	
	Correlation Coefficient	**P-value**	**Correlation Coefficient**	**P-value**
P	0.297	0.016	0.277	0.025
NO_3^-	-0.442	0.002	-0.304	0.040
DO	-0.397	0.011	-0.298	0.062

Table 16
Sequential extraction results summary

Well ID	Depth (feet)	Extractant	As (mg/kg)	Fe (mg/kg)
694217	60	PO_4	0.56	109.84
		HCl	0.19	2243.27
		Ox	0.09	843.13
		Total[a]	0.85	3196.24
	63	PO_4	0.32	108.46
		HCl	0.08	1495.70
		Ox	0.19	813.60
		Total[a]	0.58	2417.76
694218	68	PO_4	0.24	119.54
		HCl	0.04	2048.85
		Ox	0.09	972.25
		Total[a]	0.37	3140.64
694217	60	H_2O	0.26	0.13
694217	63	H_2O	0.17	0.38
694218	68	H_2O	0.13	1.98

[a] Total means total adsorbed arsenic plus arsenic coprecipitated with iron minerals

Table 17
Sediment organic carbon results

Well Number	Sample ID	% Organic Carbon
694218	58' (1)	2.76
694218	58' (2)	2.23
694218	58' (3)	2.32
694218	62' (1)	1.21
694218	62' (2)	1.06
694218	62' (3)	0.97
694218	64' (1)	0.17
694218	64' (2)	0.20
694218	64' (3)	0.15

Table 18
Summary of upper Midwest public water system arsenic concentrations

Group	Total Count	Count Exceeding 10 µg/l	% Wells ≥ 10 µg/l
Inside northwest provenance Late Wisconsinan footprint	1764	212	12.0%
Outside northwest provenance Late Wisconsinan footprint	2182	52	2.4%

Table 19
Summary of upper Midwest public water system well depths, aquifer types, and arsenic concentrations

Inside footprint of northwest provenance Late Wisconsinan drift					
Well Type	Count			Median Depth (meters)	% Wells >10 µg/l As
	All	Known Depth	Unknown Depth		
Bedrock	583	526	57	130	7.2%
Glacial Drift	551	474	77	44	16.3%
Unknown	630	57	573	49	12.7%
Outside footprint of northwest provenance Late Wisconsinan drift					
Well Type	Count			Median Depth (meters)	% Wells >10 µg/l As
	All	Known Depth	Unknown Depth		
Bedrock	642	601	41	129	2.2%
Glacial Drift	219	191	28	26	0.5%
Unknown	1321	37	1284	62	2.8%

Table 20
Public water system arsenic concentrations, by depth range and aquifer type

Well Type	Count	Depth Range (m)	% Wells >10 µg/l As
Bedrock	132	800 - 186	1.5%
	263	185 - 92	3.8%
	131	91 - 4[1]	22.1%
Glacial Drift	120	157 - 65	8.5%
	236	64 - 28	27.0%
	118	28 - 7	7.4%

[1] All but four of these wells are more than 30 m deep.

Table 21
Summary of upper Midwest arsenic concentrations, by location and well type

Inside Footprint								
	All Wells		PWS Wells		Other Wells		Other Wells, Excluding MARS	
Aquifer Type	Count	% > 10 µg/l As	Count	% > 10 µg/l As	Count	% > 10 µg/l As	Count	% > 10 µg/l As
Glacial Drift	4,275	30.9%	551	16.3%	3,724	33.1%	2898	27.7%
Bedrock	1,174	7.0%	583	7.2%	591	6.8%	591	6.8%
Unknown	1,652	17.1%	630	12.7%	1,022	19.9%	1022	19.9%
All	7,101	23.8%	1,764	12.0%	5,337	27.7%	4511	23.2%

Outside Footprint						
	All Wells		PWS Wells		Other Wells	
Aquifer Type	Count	% > 10 µg/l As	Count	% > 10 µg/l As	Count	% > 10 µg/l As
Glacial Drift	1,061	7.0%	219	0.5%	842	8.7%
Bedrock	1,528	3.5%	642	2.2%	886	4.4%
Unknown	1,744	3.5%	1,321	2.8%	423	5.7%
All	4,333	4.3%	2,182	2.4%	2,151	6.3%

Other Wells include domestic and monitoring wells

Table 22
Available upper Midwest well depth information

Inside Footprint						
Aquifer Type	All Wells		PWS Wells		Other Wells	
	Count	Median Depth (m)	Count	Median Depth (m)	Count	Median Depth (m)
Glacial Drift	4,063	29	474	44	3,589	27
Bedrock	1,109	106	526	130	583	85
Unknown	523	16	57	49	466	15
Outside Footprint						
Aquifer Type	All Wells		PWS Wells		Other Wells	
	Count	Median Depth (m)	Count	Median Depth (m)	Count	Median Depth (m)
Glacial Drift	1,021	16	191	26	830	14
Bedrock	1,471	137	601	149	870	123
Unknown	93	41	37	62	56	21

Count of the number of wells with known depths in each category

Table 23
Ground water arsenic concentrations, by depth range and aquifer type

Well Type	Count	Depth Range (m)	% Wells >10 µg/l As
Bedrock	277	3-68	16.7%
	555	68-169	5.0%
	277	169-1,028	2.2%
Glacial Drift	1,017	2-15	19.2%
	2,029	15-50	38.0%
	1,017	50-615	26.9%

Table 24
Well characteristics and arsenic concentration for western Minnesota domestic wells

Description	Average As (µg/l)	% >10 µg/l As	Average Fe (µg/l)	Count
Well screen ≤ 8 feet long and distance from screen to till ≤ 4 feet	20	60%	2,484	224
Well screen > 8 feet long and distance from screen to till > 4 feet	12	40%	1,660	71
Well screen intersects sand or clay	18	53%	2,117	754
Well screen intersects gravel	13	41%	1,836	56

Table 25
Summary statistics for long-term temporal sampling

Well ID	Average Arsenic Concentration (µg/l)									
	Hourly		Daily		Weekly		Monthly		All	
	Avg	St Dev	Avg	St Dev	Avg	St Dev	Avg	St Dev	Avg	St Dev
222103	16.5	0.56	15.3	1.16	15.3	0.89	16.3	0.76	16.0	0.95
241459	15.2	1.02	15.3	0.33	13.9	2.07	14.0	2.13	14.7	1.53
240652	31.4	0.57	31.1	3.48	33.2	0.93	33.6	0.91	32.2	1.93

Avg: average
St Dev: standard deviation

Table 26
Example sample size requirements

Standard Deviation	Power	Sample Size
0.5	0.755	4
	0.998	8
	1.000	12
1	0.289	4
	0.680	8
	0.803	10
	0.962	16
2	0.111	4
	0.465	16
	0.807	34
	0.957	56
3.5	0.070	4
	0.229	20
	0.492	48
	0.808	100
	0.953	164

Difference in mean = 1 µg/l

Table 27
Selected results for public water system wells with notable arsenic variability over time

Sample Time	Well 209387						
	Total As	As III	Fe	S	DO	pe	pH
5 min	4.8	3.2	724	15	0.3	0.085	7.22
20 min	12.7	9	595	12.1	0.2	-1.763	7.34
40 min	12.5	9.2	581	11.9	0.1	-2.085	7.38
60 min	12.8	9.4	580	11.9	0.1	-2.203	7.37
5 hour	6.8	NA	977	11.9	NA	NA	NA
Sample Time	**Well 228735**						
	Total As	**As III**	**Fe**	**S**	**DO**	**pe**	**pH**
5 min	5.9	5.1	141	3.7	3.44	0.763	7.22
20 min	10.1	7.2	606	4	0.24	-0.847	7.42
40 min	12	5.2	485	3.9	0.17	-1.559	7.53
60 min	12.4	5.3	476	3.9	0.24	-1.797	7.56
5 hour	7	NA	39	3.4	NA	NA	NA
Sample Time	**Well 228799**						
	Total As	**As III**	**Fe**	**S**	**DO**	**pe**	**pH**
5 min	9.1	6.1	878	10.7	0.33	-0.814	7.12
20 min	13.3	10.6	805	10.1	0.22	-1.593	7.36
40 min	14.6	12.3	783	9.8	0.19	-1.763	7.45
60 min	15	12.8	762	9.3	0.18	-1.831	7.44
5 hour	9.5	NA	841	9.1	NA	NA	NA
Sample Time	**Well 242000**						
	Total As	**As III**	**Fe**	**S**	**DO**	**pe**	**pH**
5 min	8	5.1	1,269	51.7	1.34	-0.153	7.04
20 min	9.5	6.3	1,188	54	0.43	-1.475	6.98
40 min	10.1	6.6	1,164	54.4	0.18	-2.288	7.18
60 min	10.3	7	1,125	55.7	0.18	-2.525	7.22
5 hour	8.2	NA	1,600	NA	NA	NA	NA

NA: not available. As and Fe units are µg/l. S and DO units are mg/l.
Well pump was turned off at T=60 minutes

11.0 Figures

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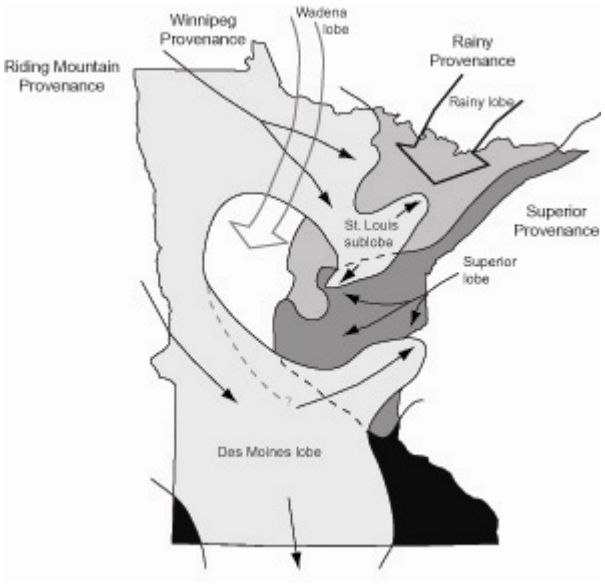


Figure 1 Generalized ice flow direction, source provenance, and ice margin extent in Minnesota

Reprinted with permission from Knaeble and Meyer, 2004.

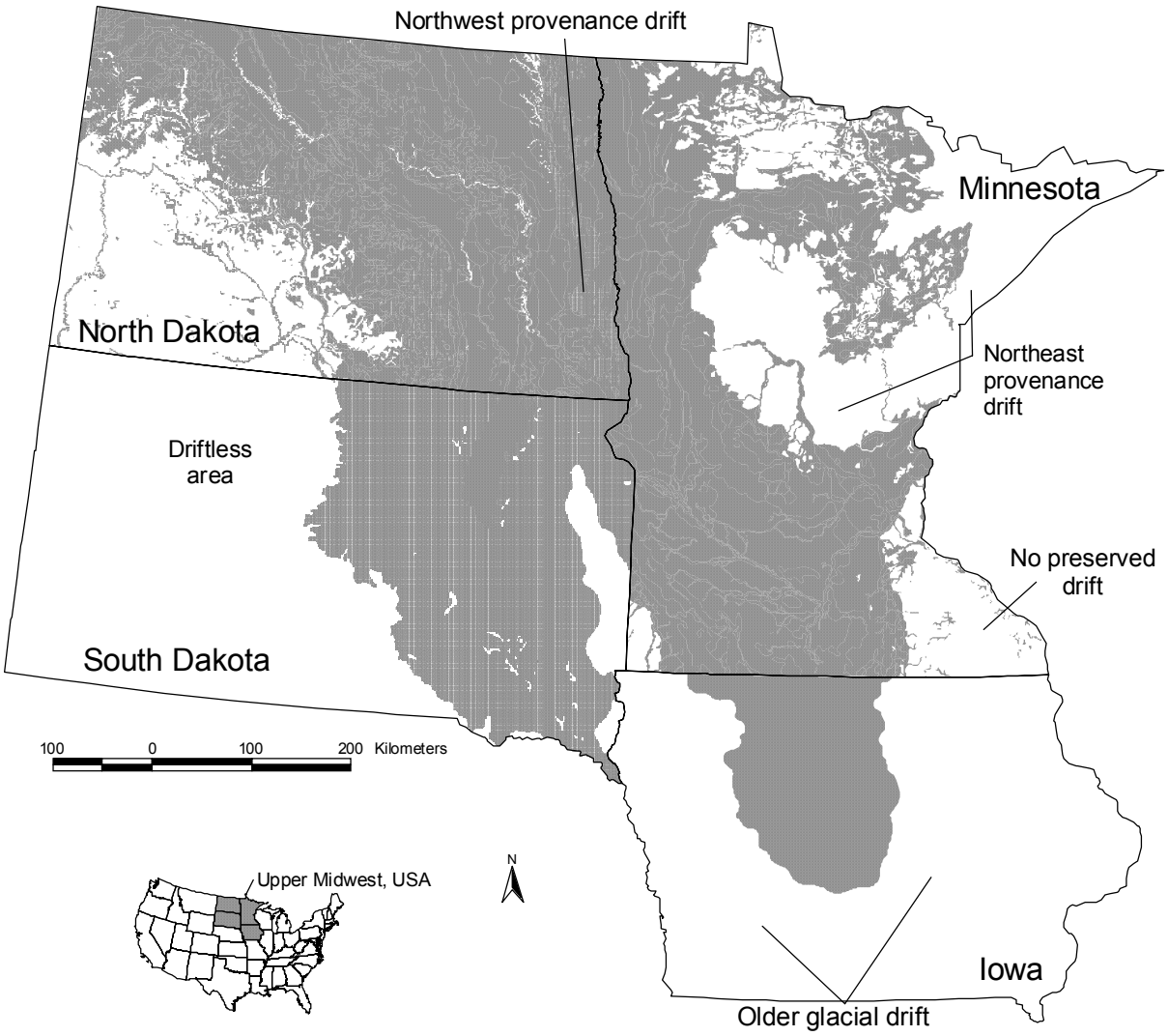


Figure 2 Generalized geologic setting of the study area

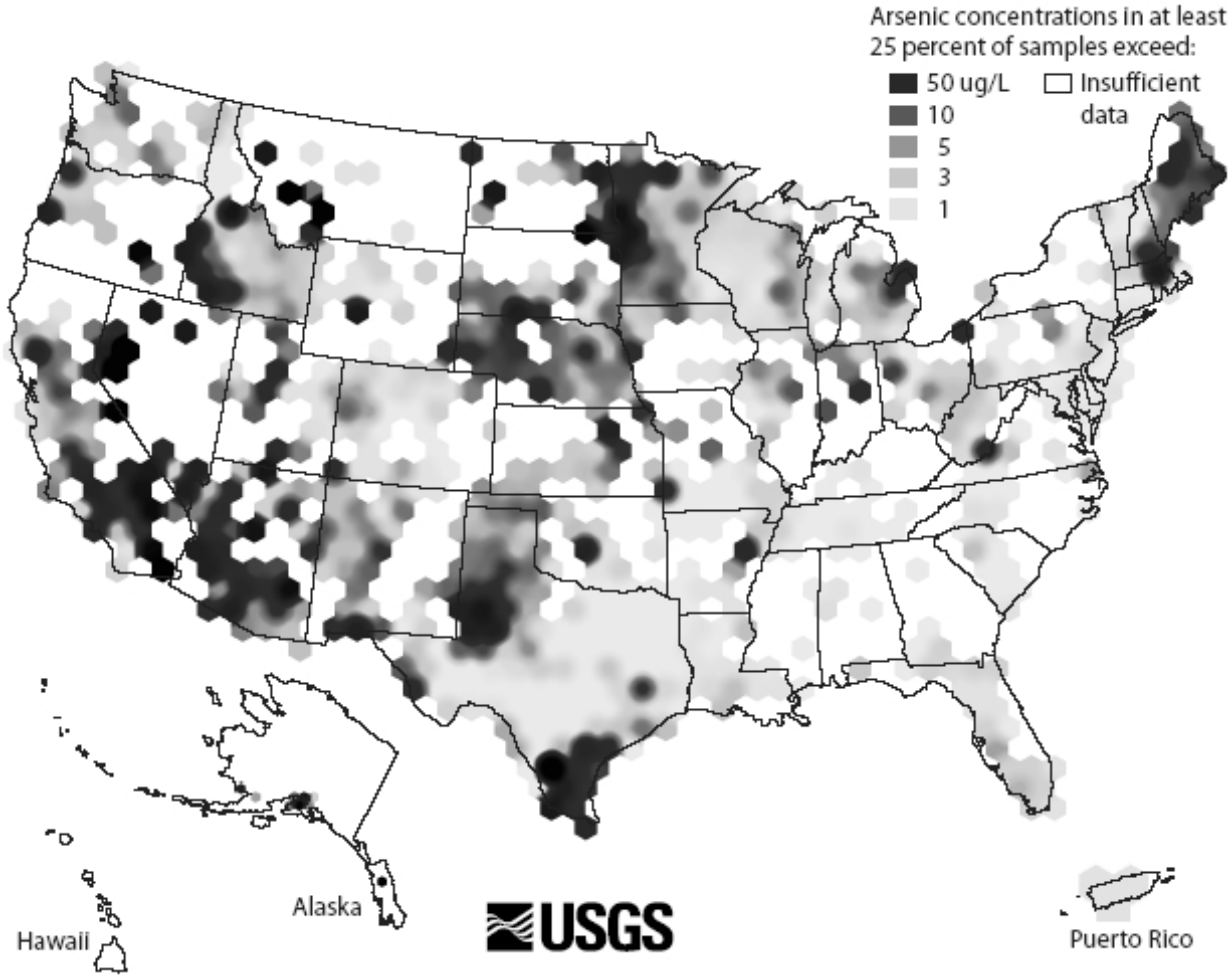


Figure 3 Online USGS map of interpolated arsenic concentrations in the United States

(Ryker, 2001; US Geological Survey, 2005)

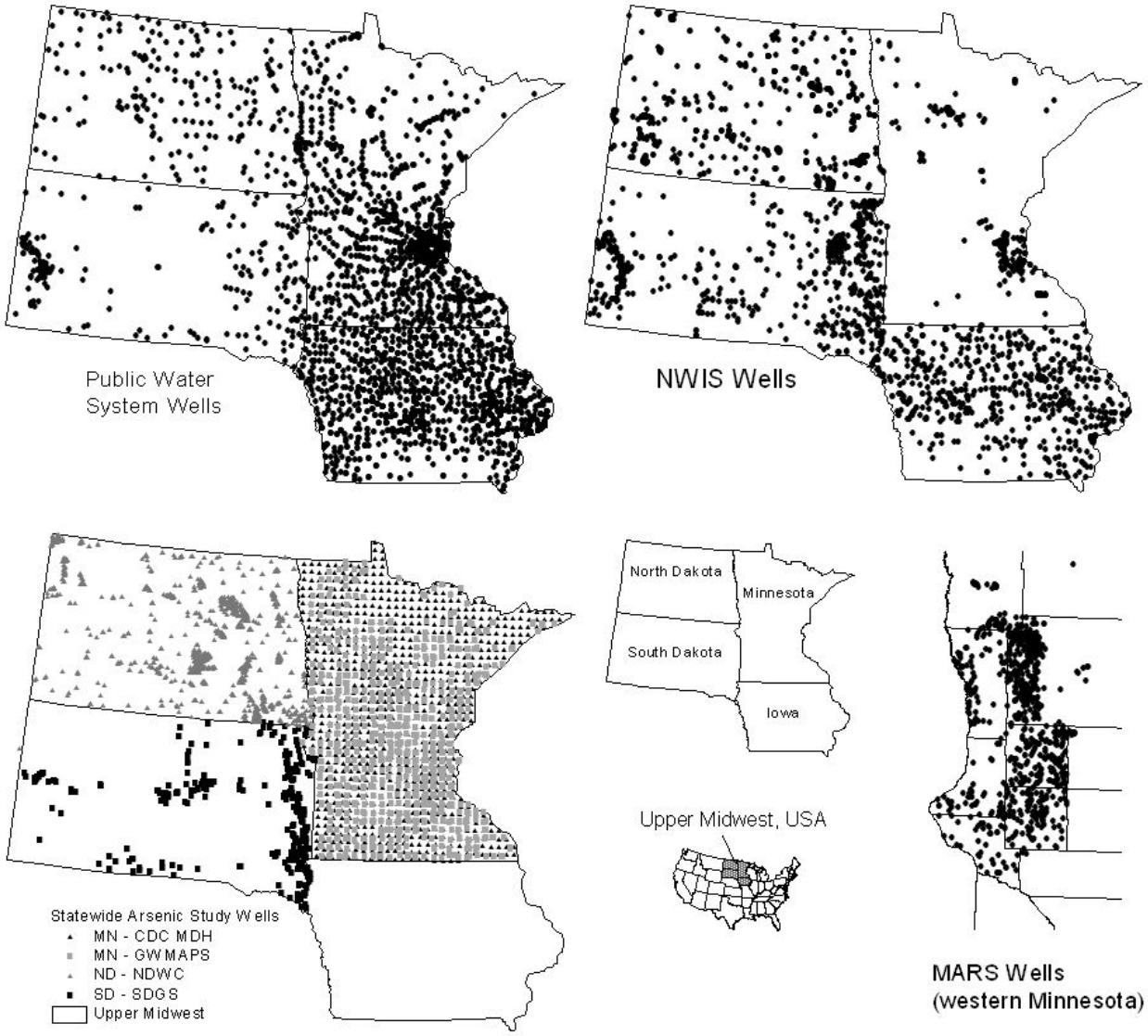


Figure 4 Data sources and locations of ground water sampling points

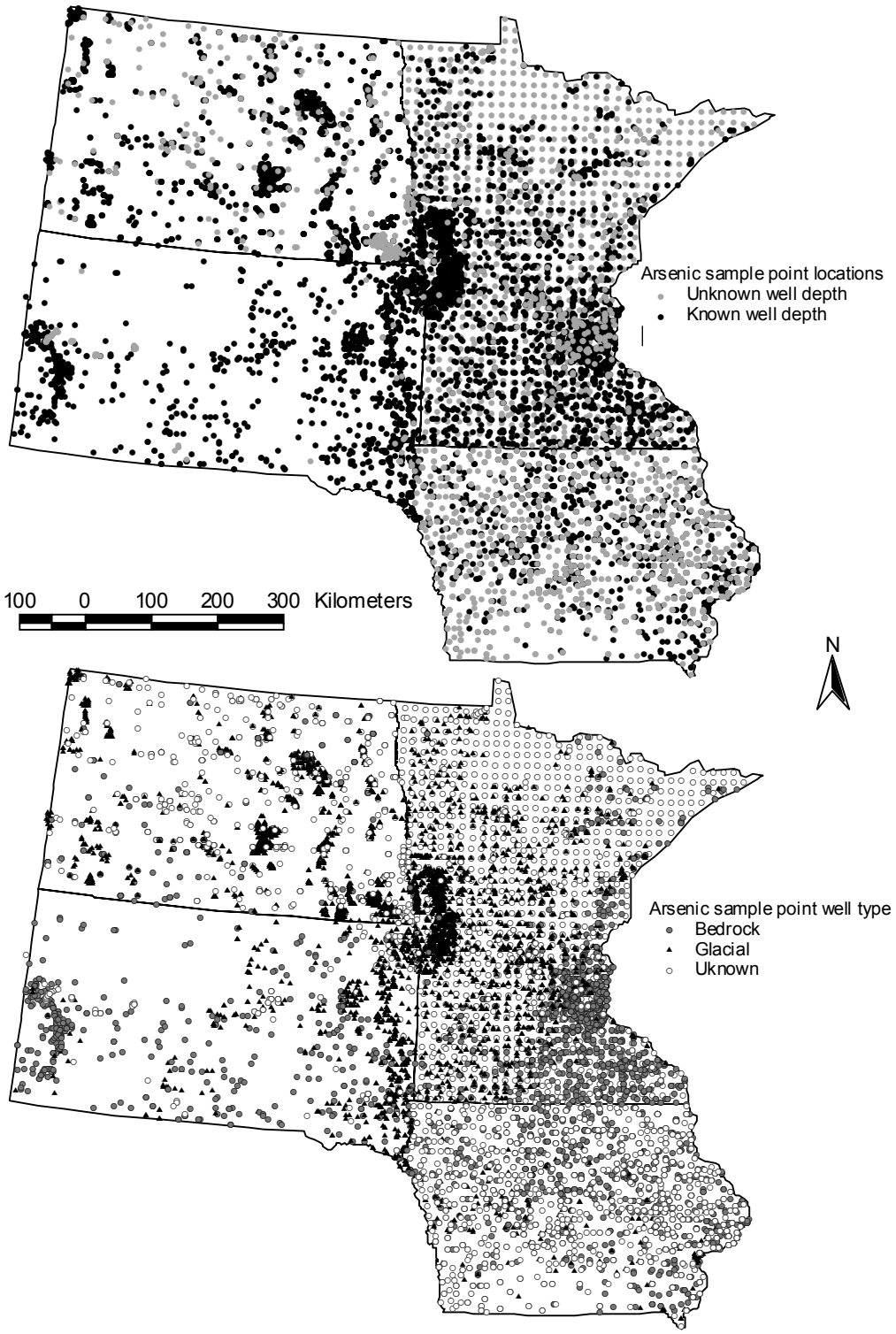


Figure 5 Available depth and aquifer type information

Approximately 8,275 study wells have a known depth, and approximately 3,250 study wells have an unknown depth. There are approximately 2,700 bedrock wells, 5,300 glacial sediment wells, and 3,400 wells of unknown aquifer type included in this study.

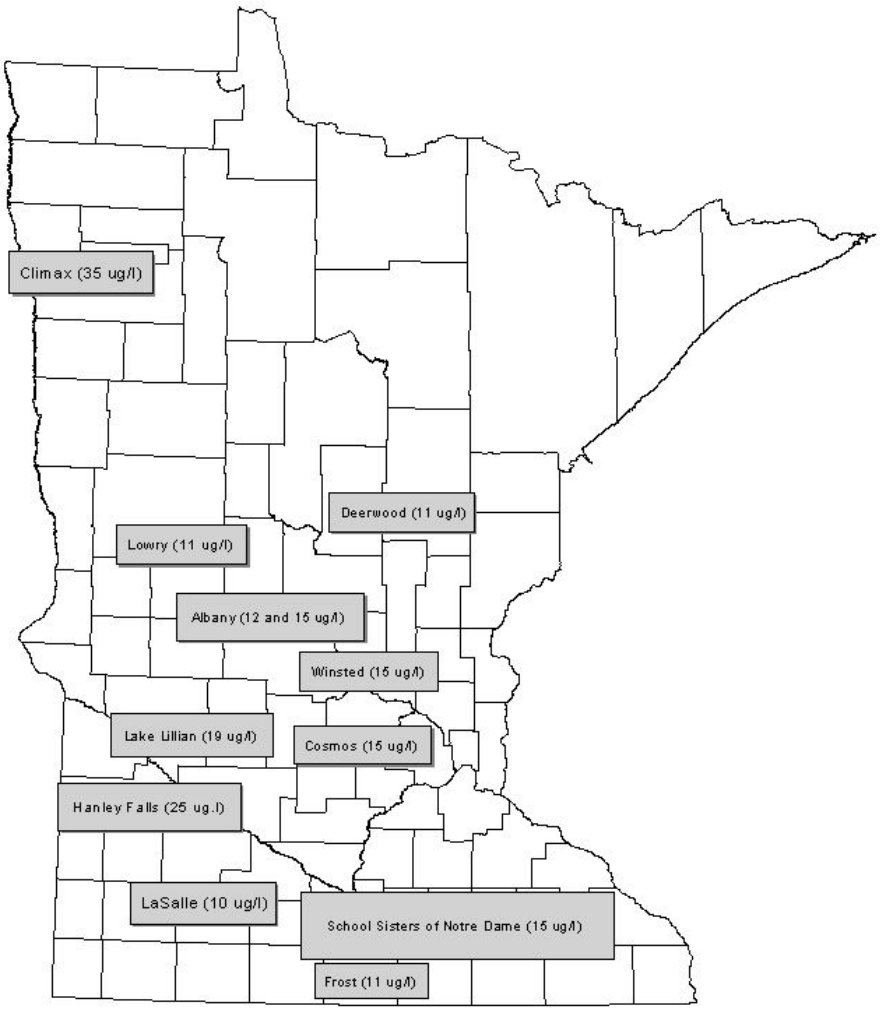


Figure 6 Locations of public water systems participating in arsenic variability research in Minnesota

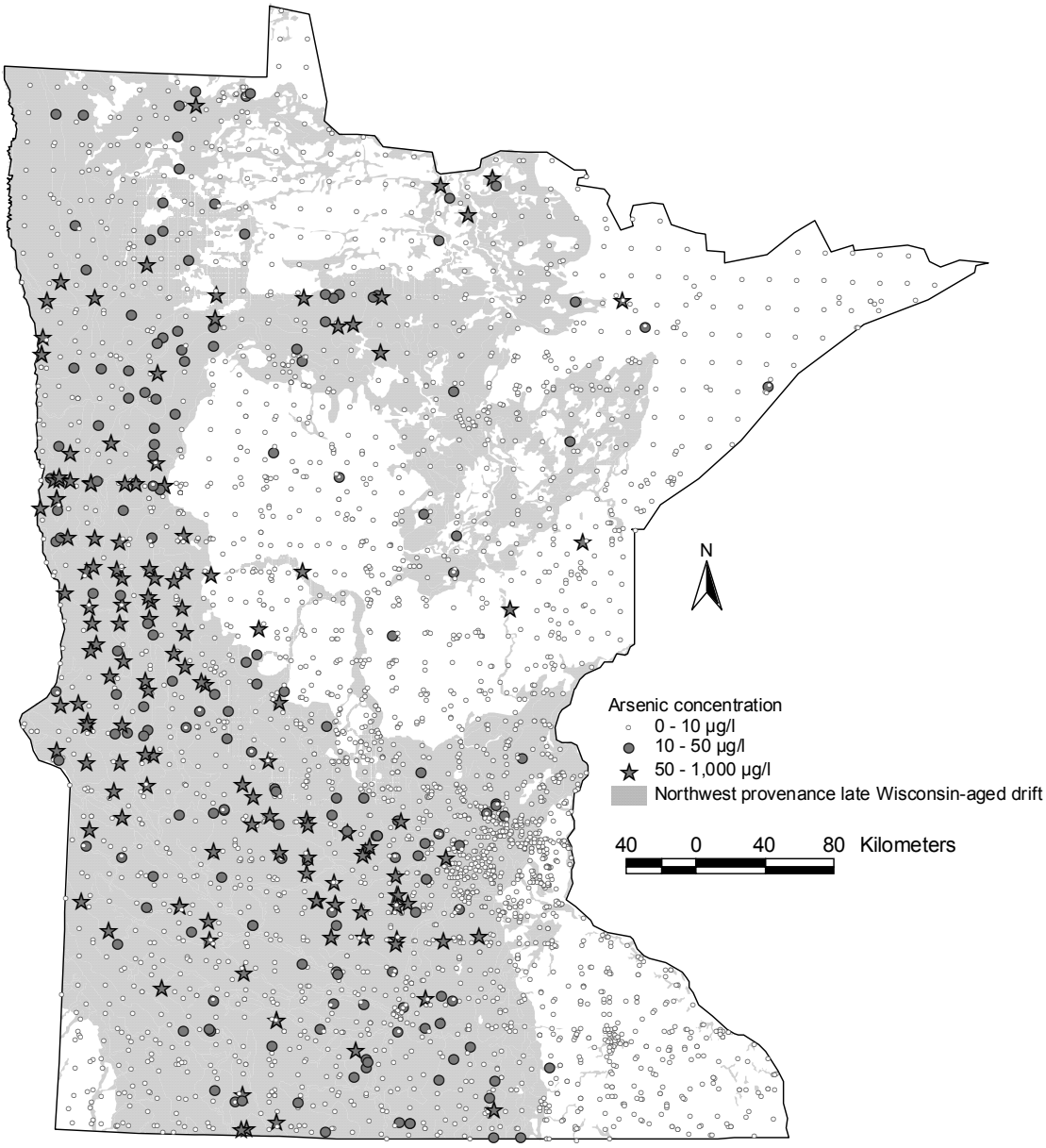


Figure 7 Arsenic concentrations in Minnesota ground water

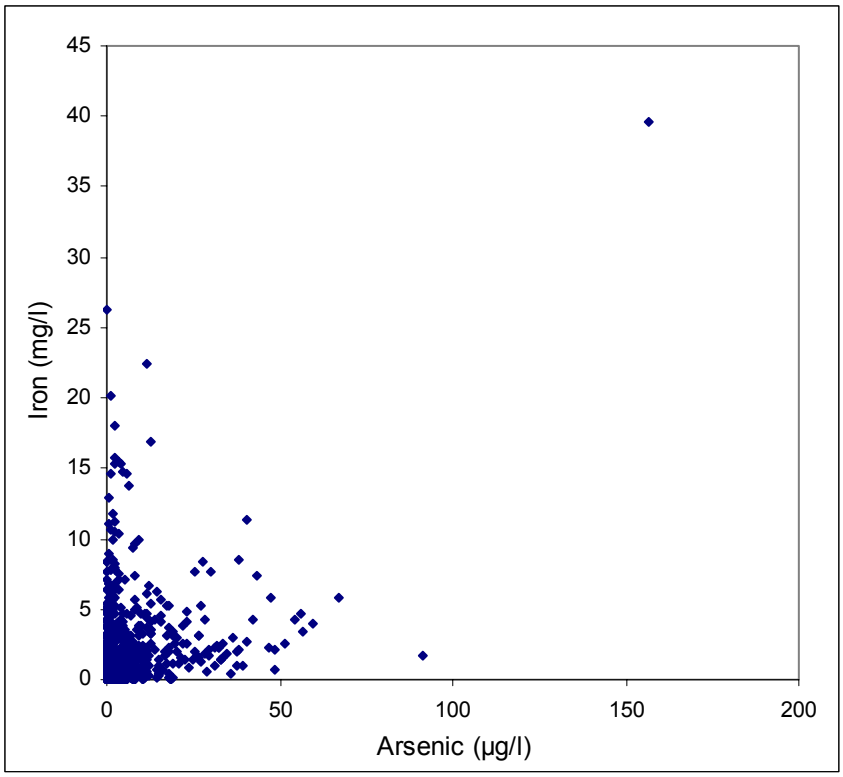


Figure 8 Arsenic and iron concentrations in Minnesota ground water

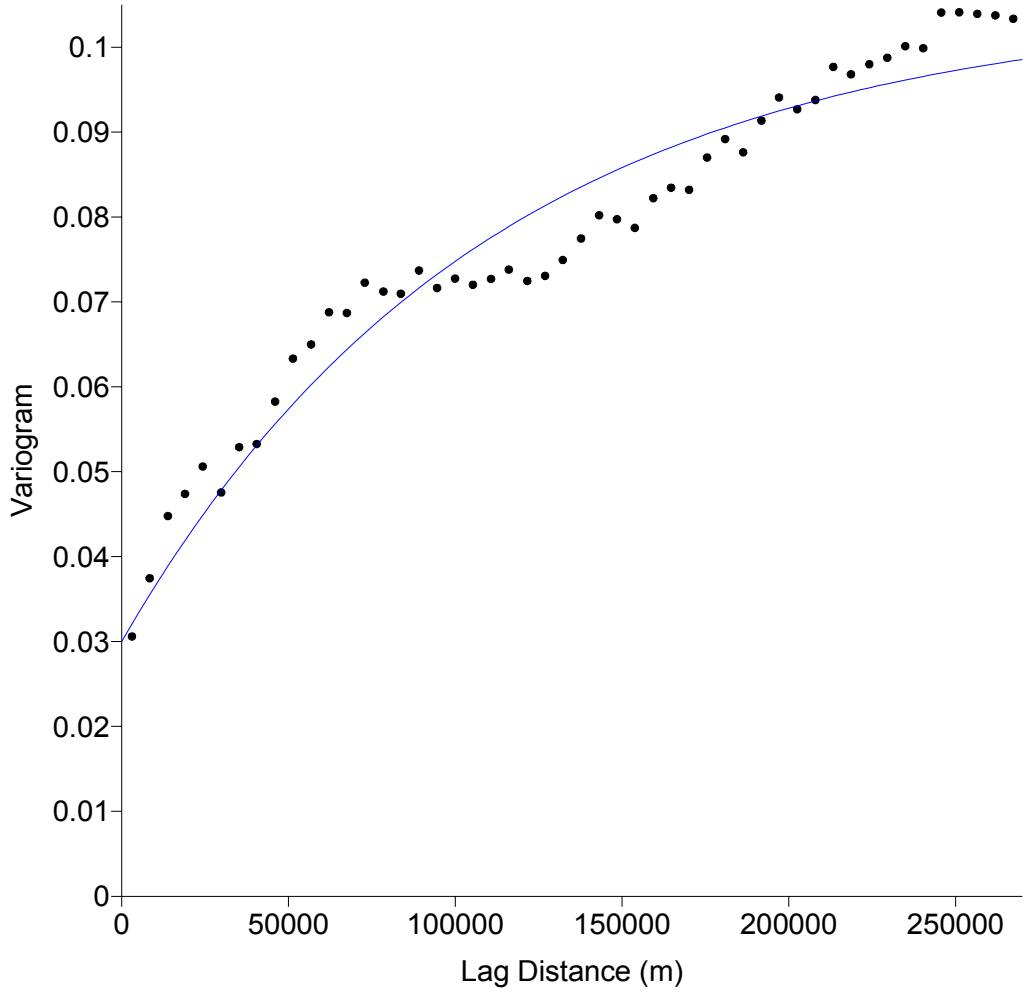


Figure 9 Directional (-45 degrees, 45 degrees tolerance) indicator variogram for Minnesota statewide arsenic measurements

Fitted model combines a nugget effect = 0.03 with an exponential model, scale of 0.075 and length parameter of 100,000 meters. The data are correlated over a distance of more than 250 kilometers.

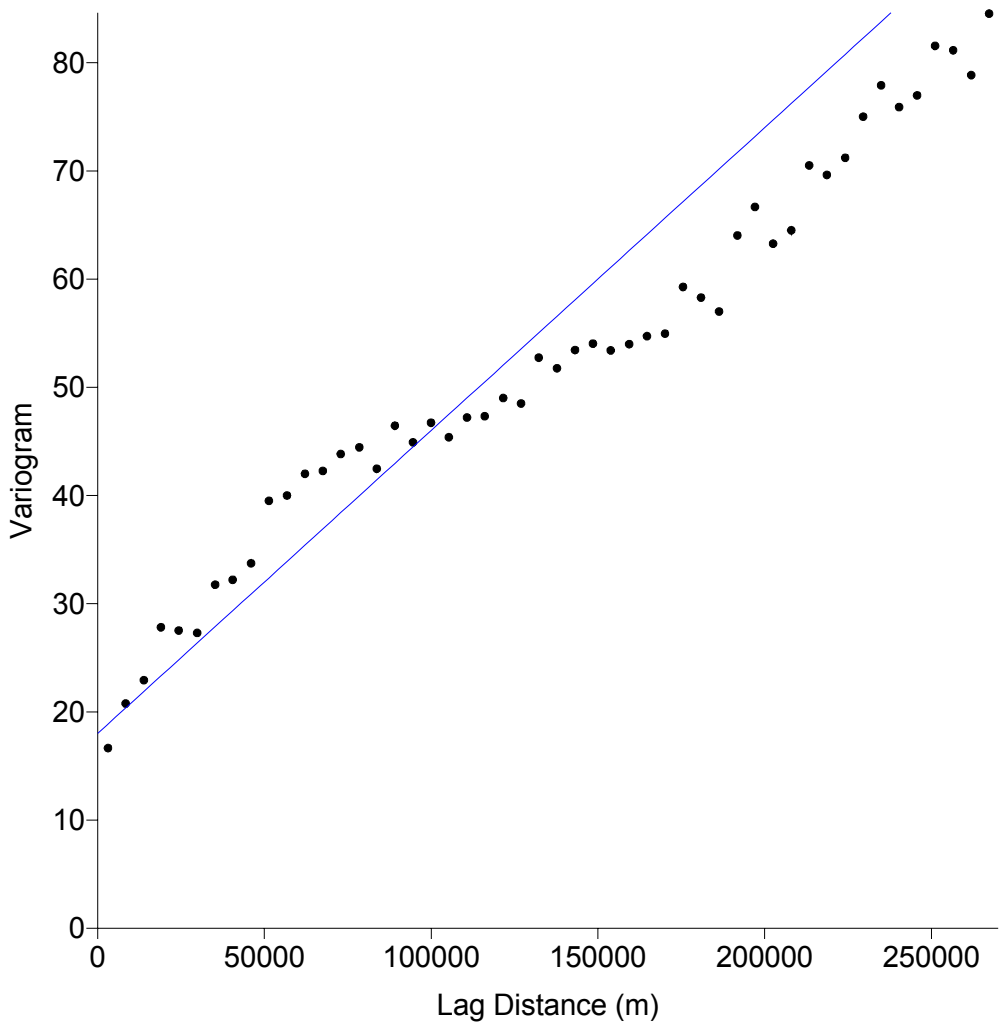


Figure 10 Directional (-45 degrees, 45 degrees tolerance) variogram for Minnesota statewide arsenic measurements

Fitted model combines a nugget effect =18 with a linear model with slope = 0.00028. The data are correlated over a distance of more than 250 kilometers.

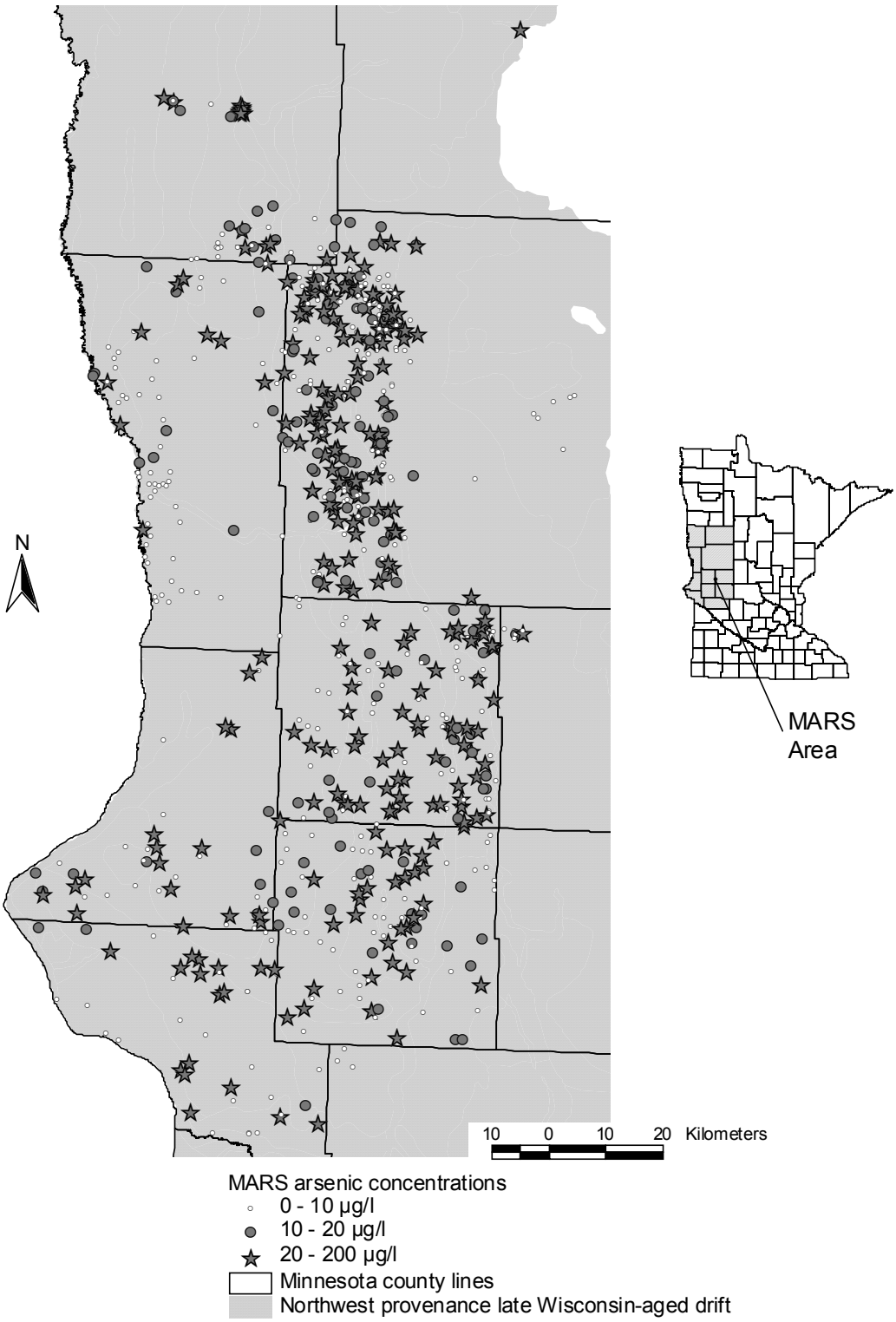


Figure 11 Arsenic concentrations in western Minnesota ground water

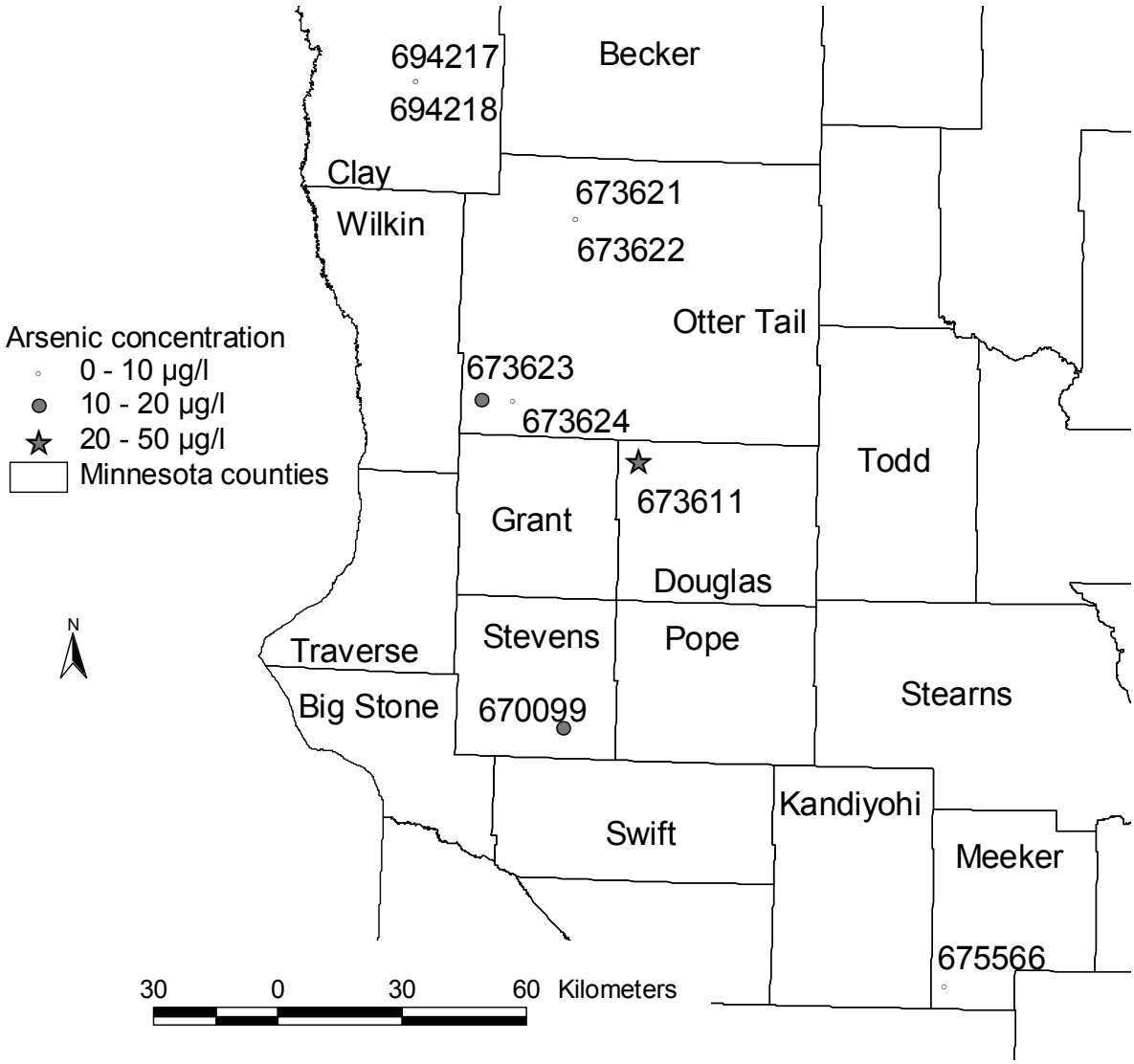


Figure 12 Locations and initial arsenic concentration in new wells constructed in 2002 and 2003 in Minnesota

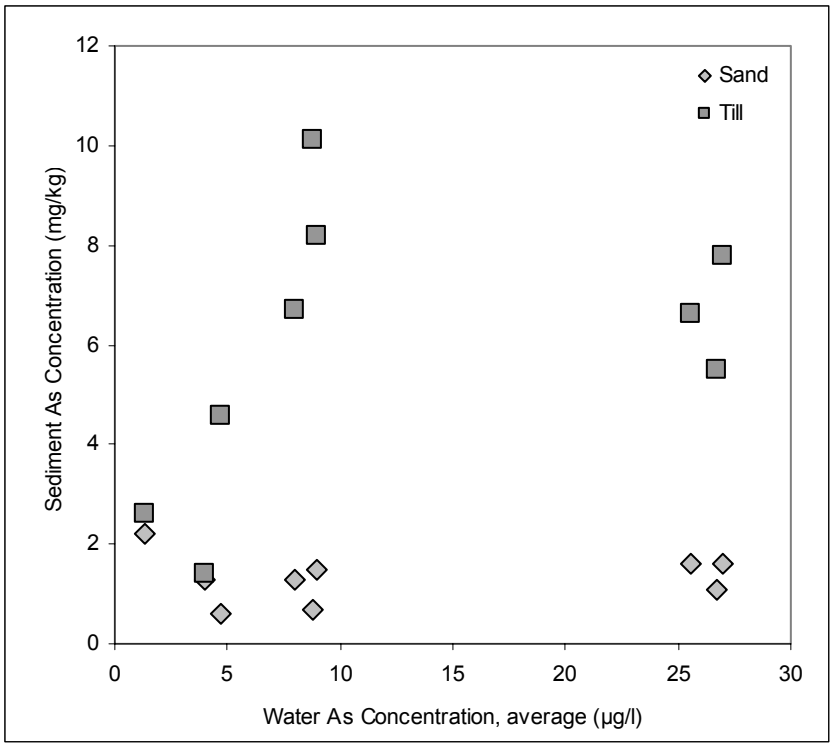


Figure 13 Arsenic concentrations in ground water and sediment

Samples collected from new wells in Minnesota

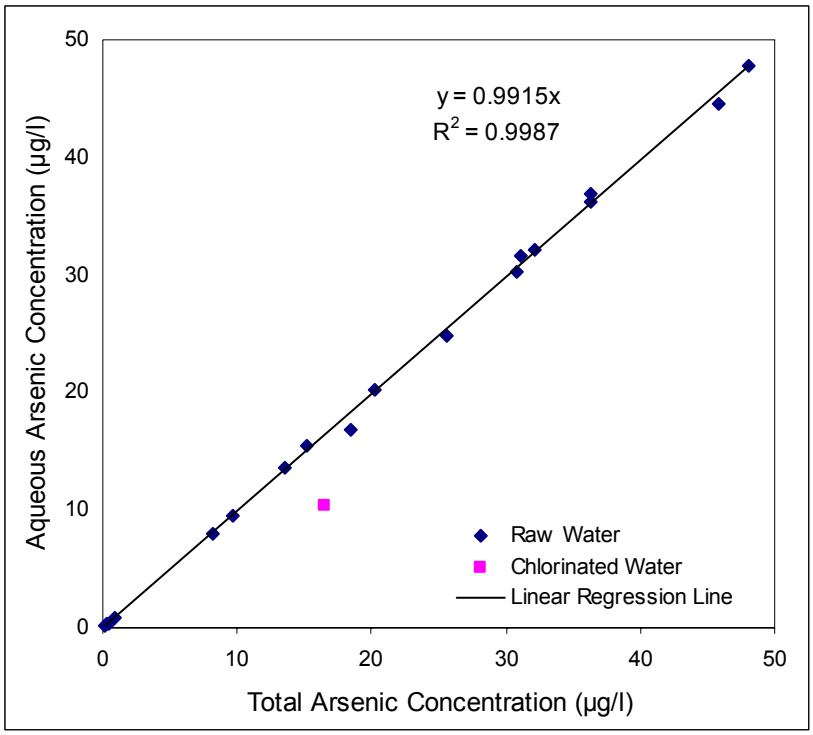


Figure 14 Total and aqueous arsenic concentrations measured in Minnesota ground water

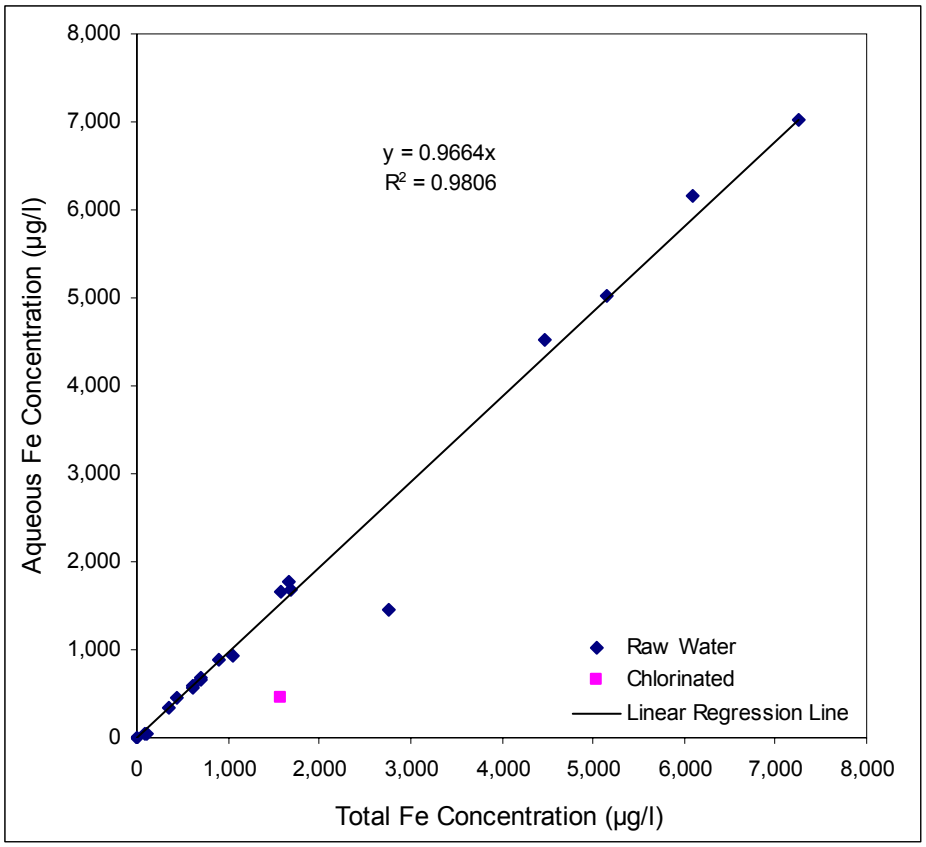


Figure 15 Total and aqueous iron concentrations measured in Minnesota ground water

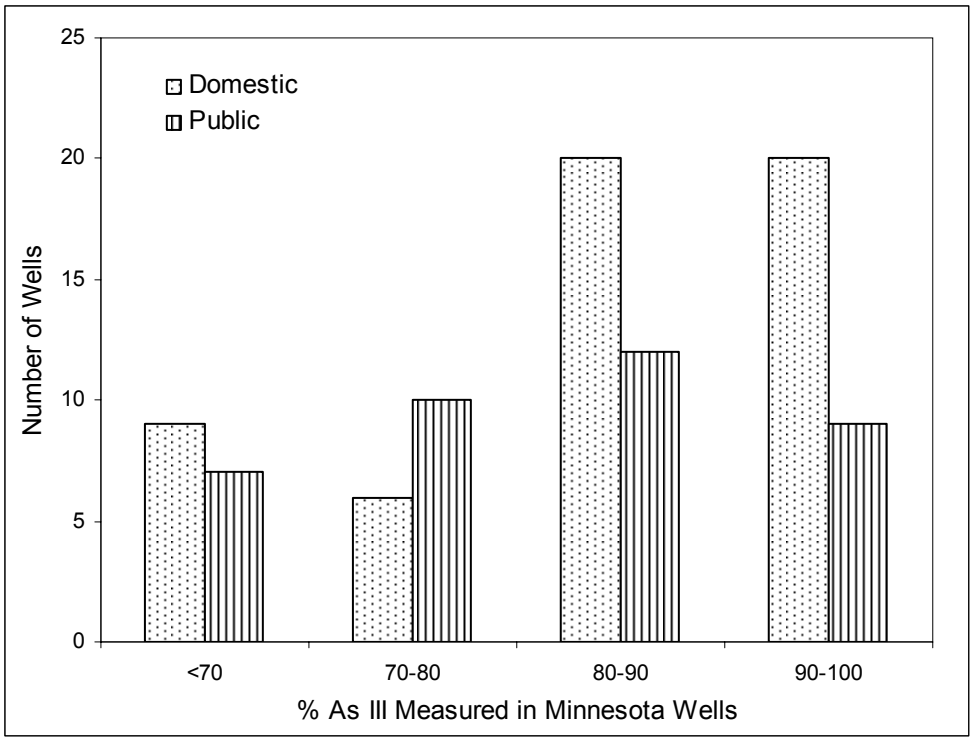


Figure 16 Arsenic speciation results for Minnesota ground water

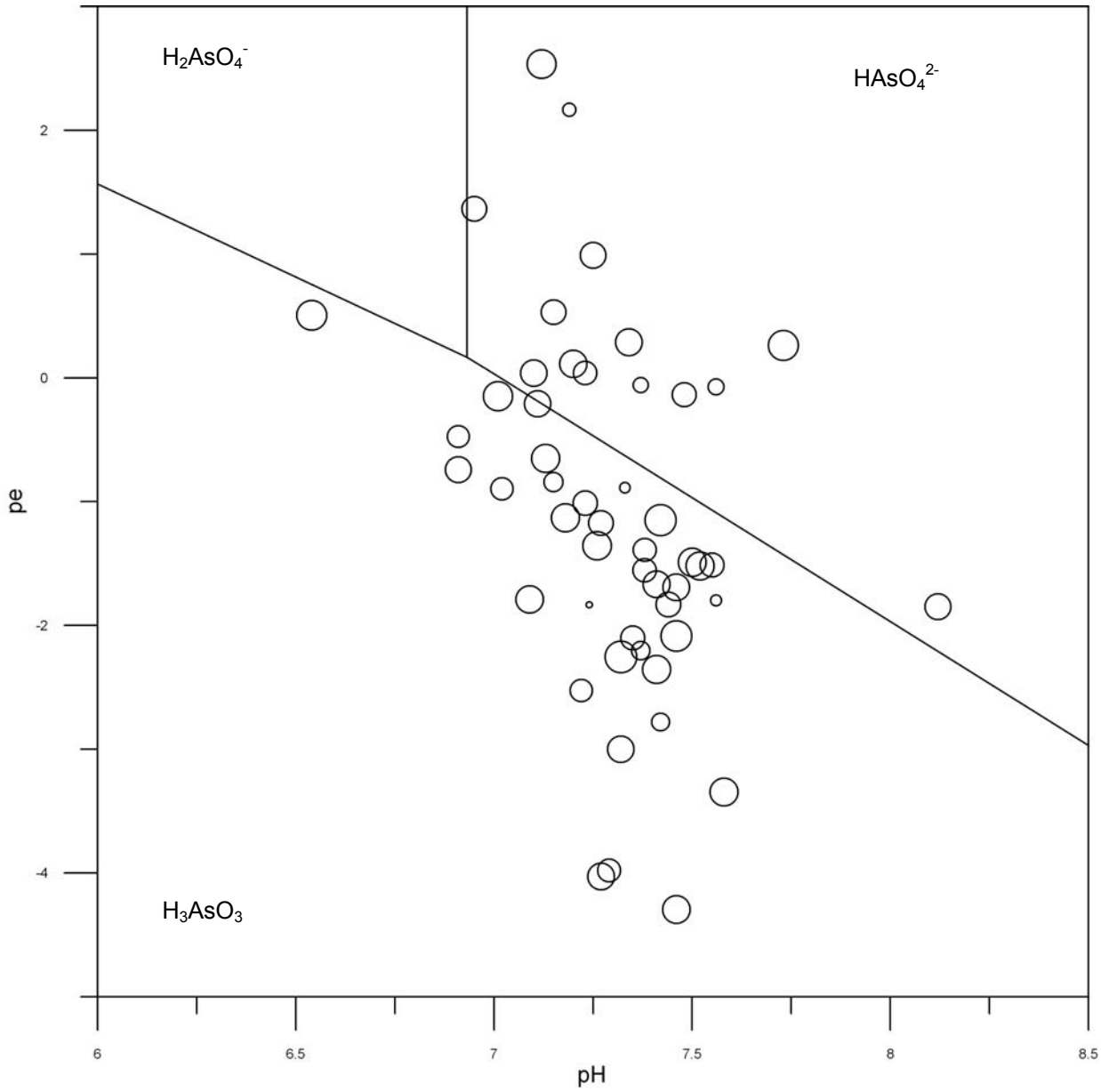


Figure 17 Calculated percent As(III) and measured pe and pH

The smallest bubbles represent 50% As(III), while the largest represent 100% As(III).

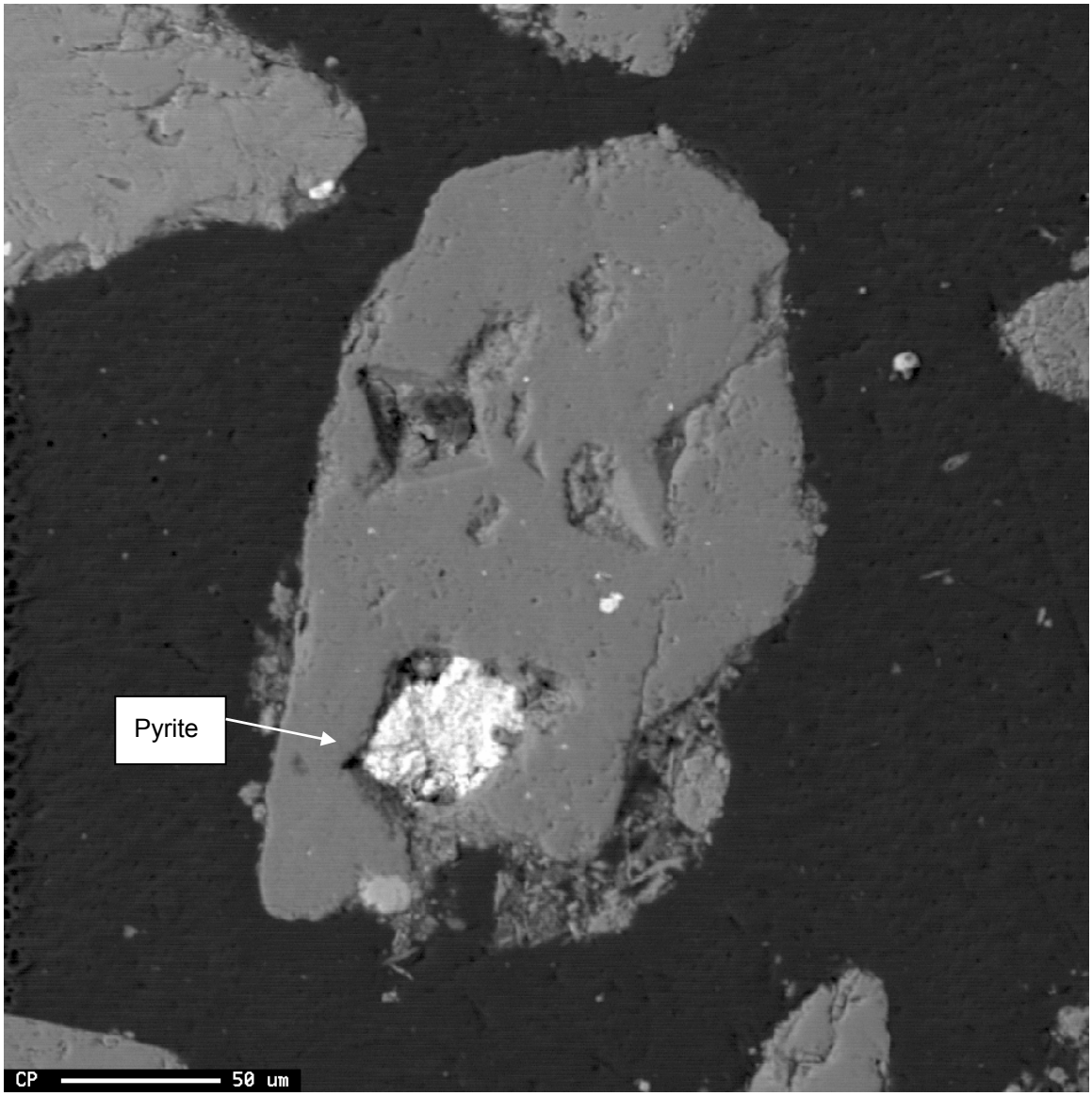


Figure 18 SEM image of pyrite

Sediment sample collected from a northwest Minnesota monitoring well

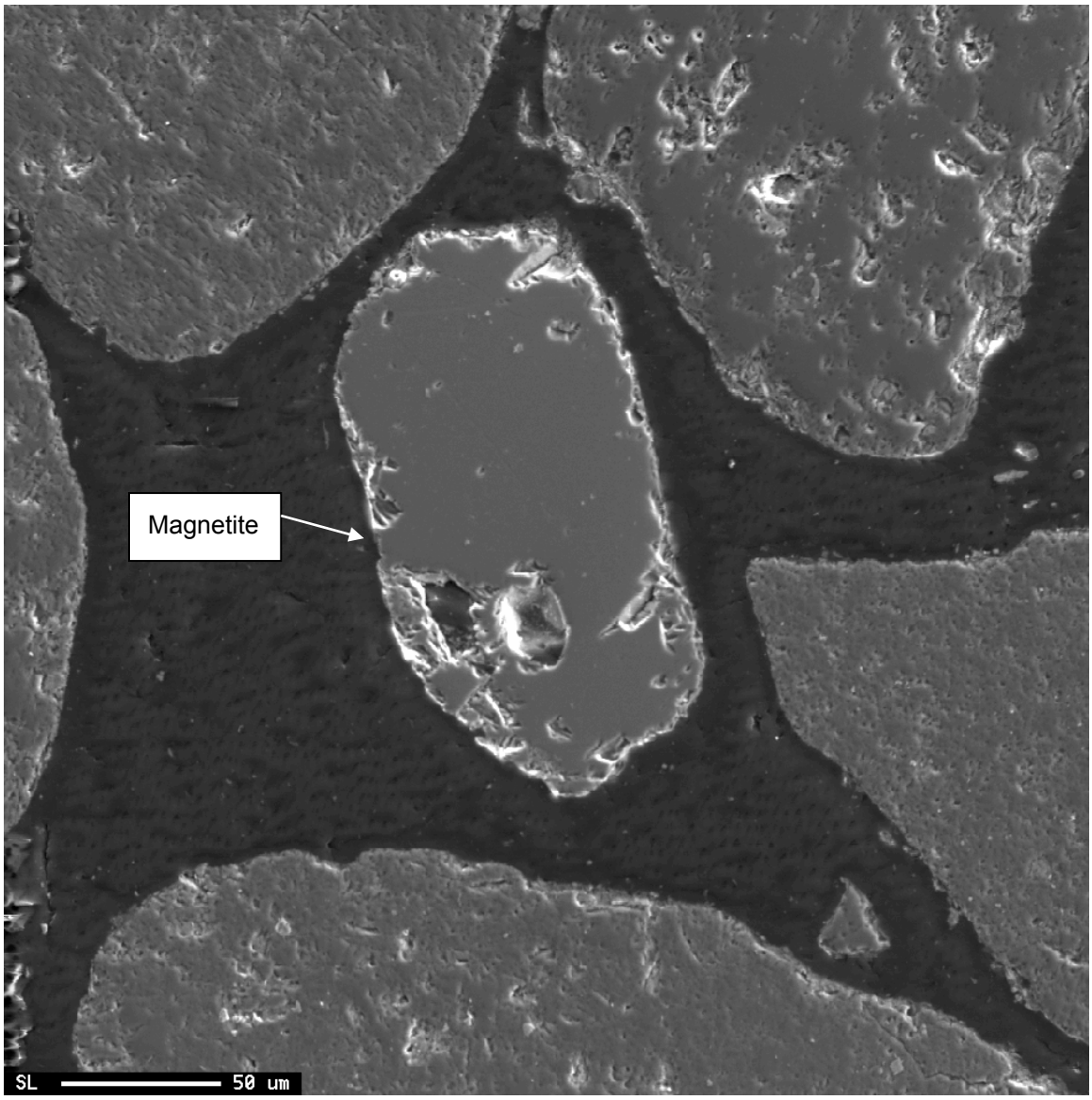


Figure 19 SEM image of magnetite

Sediment sample collected from a northwest Minnesota monitoring well

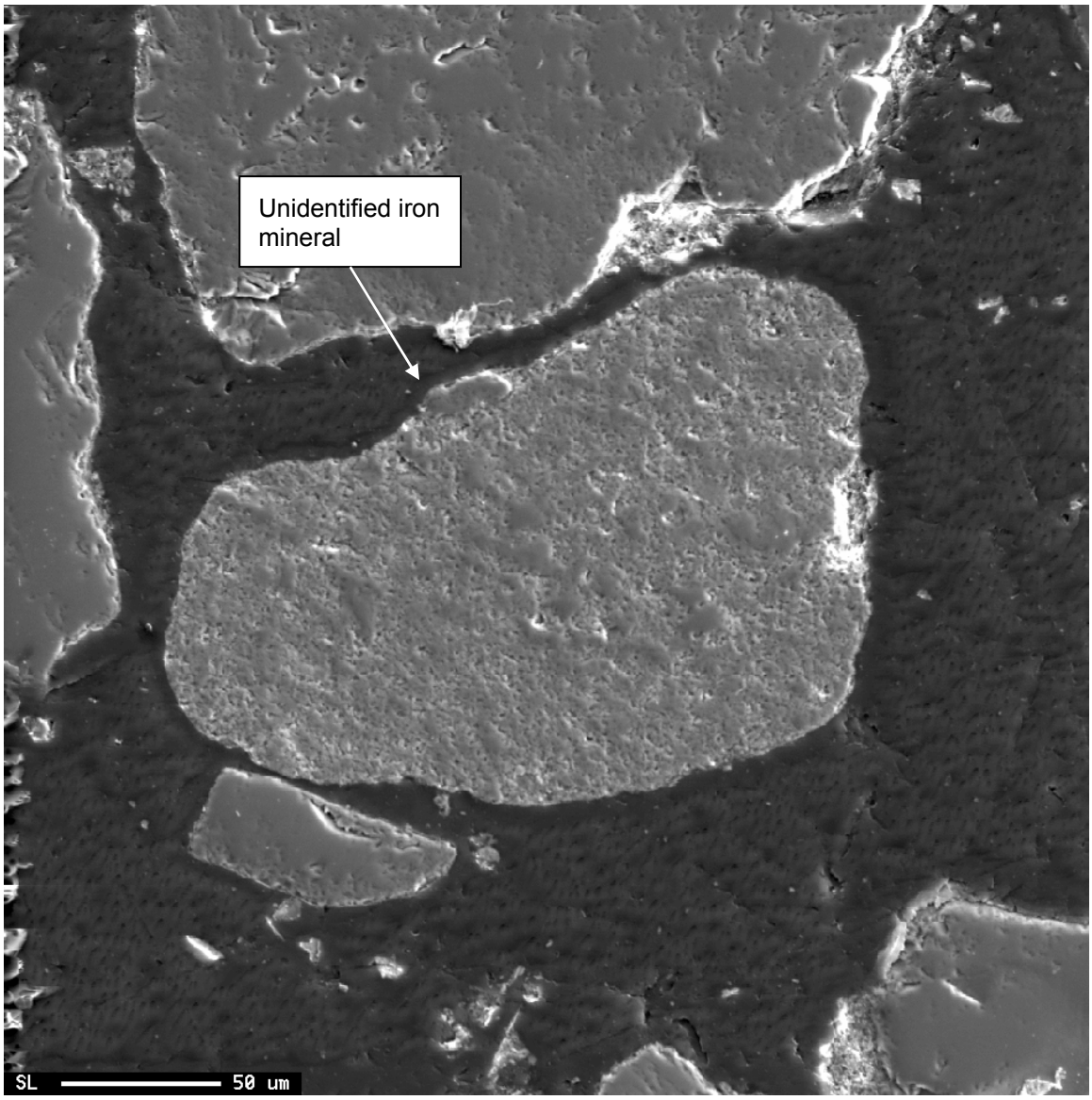


Figure 20 SEM image of unidentified iron mineral

Sediment sample collected from a northwest Minnesota monitoring well

Figure 21 Organic layer from monitoring well core section

The organic layer is black, on the left-hand side of the photograph. The organic layer was present immediately above the brown, sandy aquifer sediment, shown on the right-hand side of the photo.

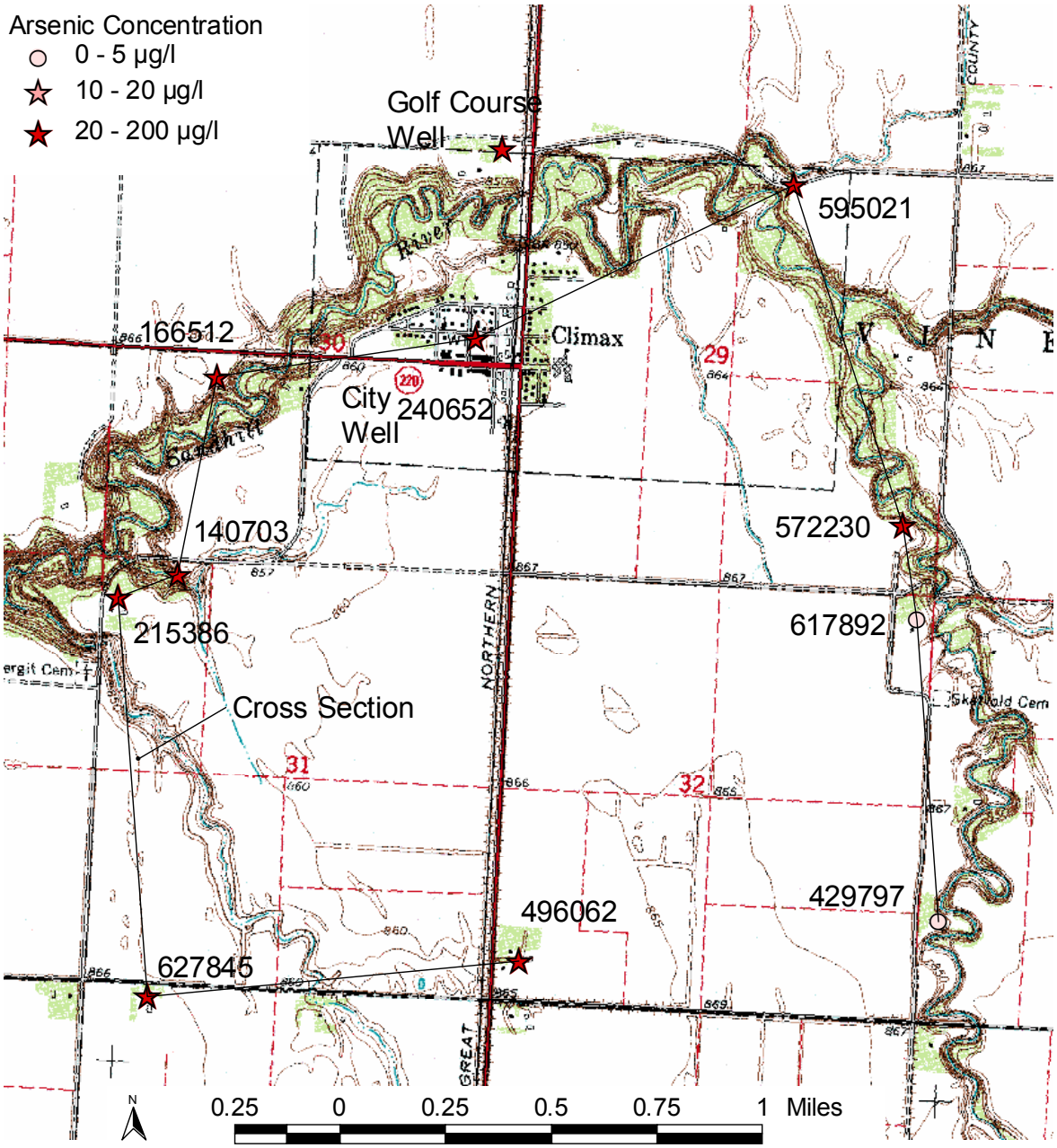


Figure 22 Domestic well sampling results in the Climax area, plan view

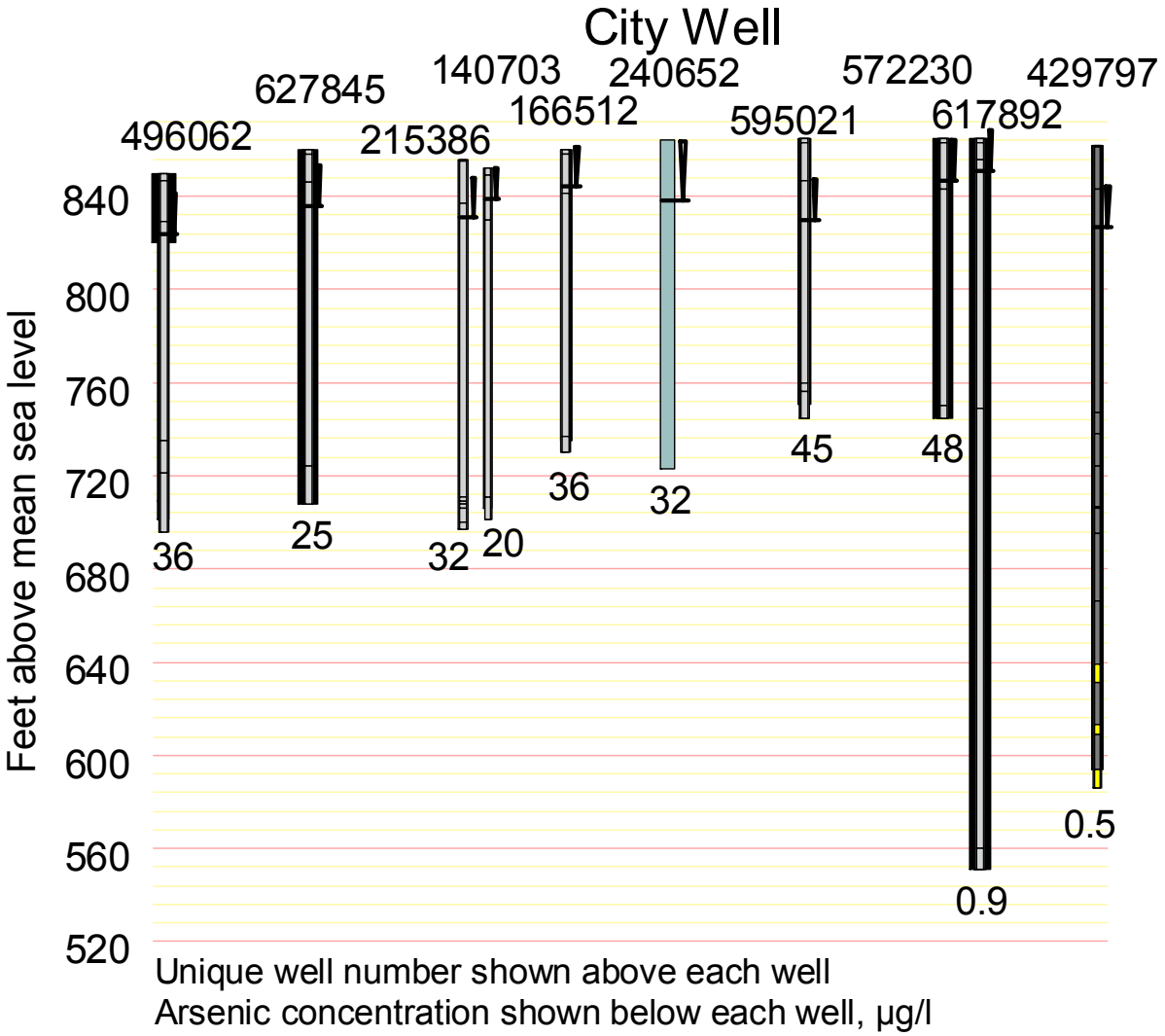


Figure 23 Domestic well sampling results in the Climax area, pseudo cross-section view

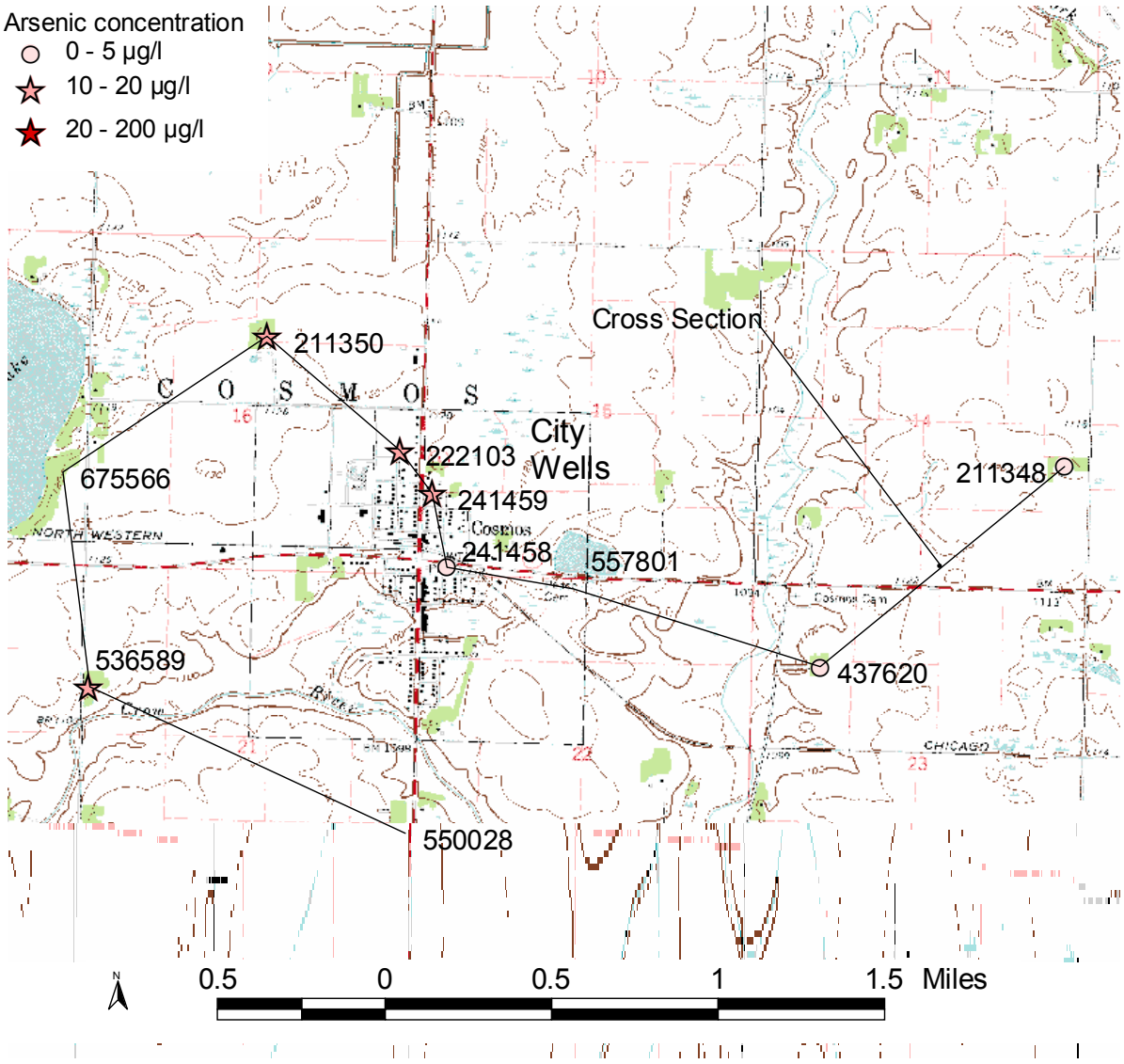


Figure 24 Domestic well sampling results in the Cosmos area, plan view

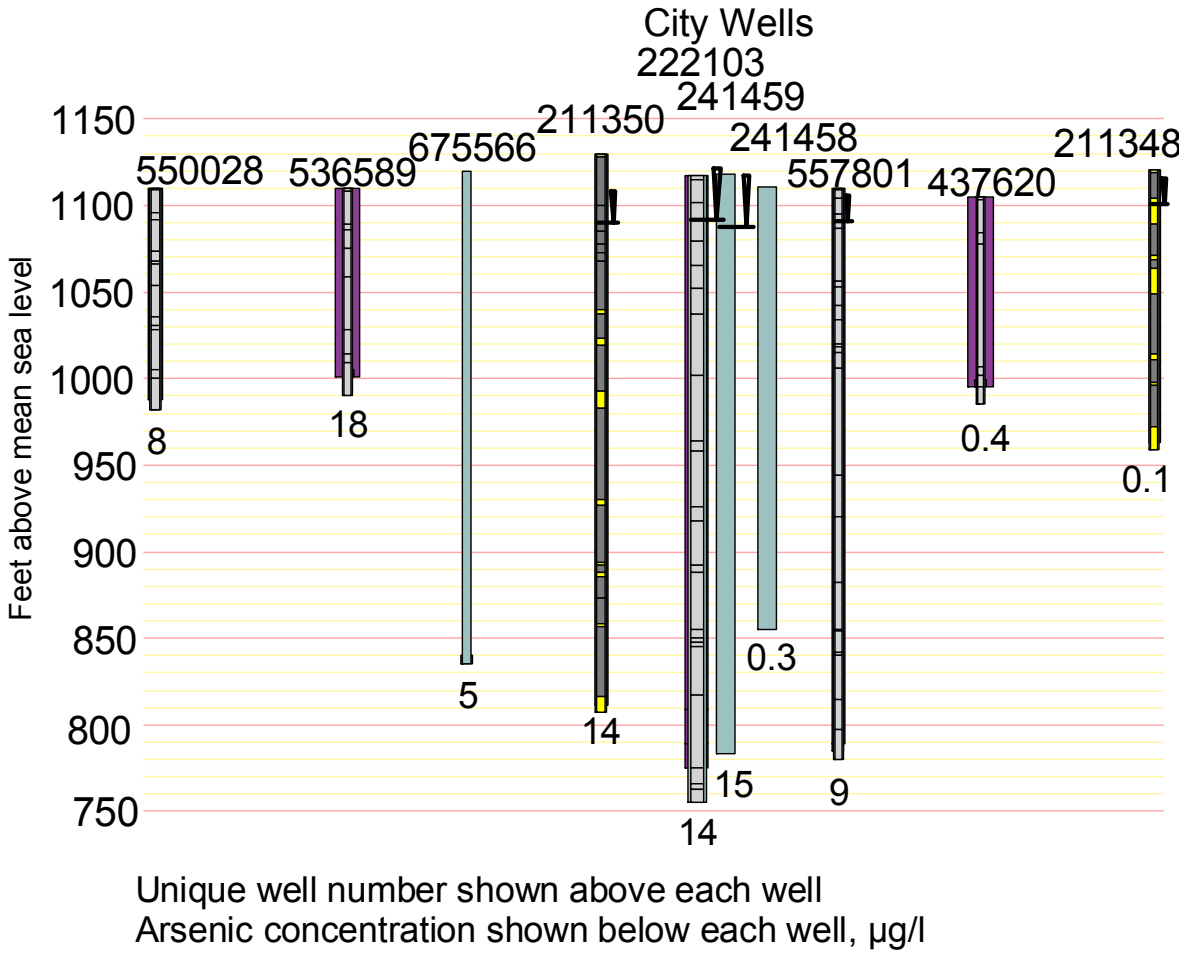


Figure 25 Domestic well sampling results in the Cosmos area, pseudo cross-section view

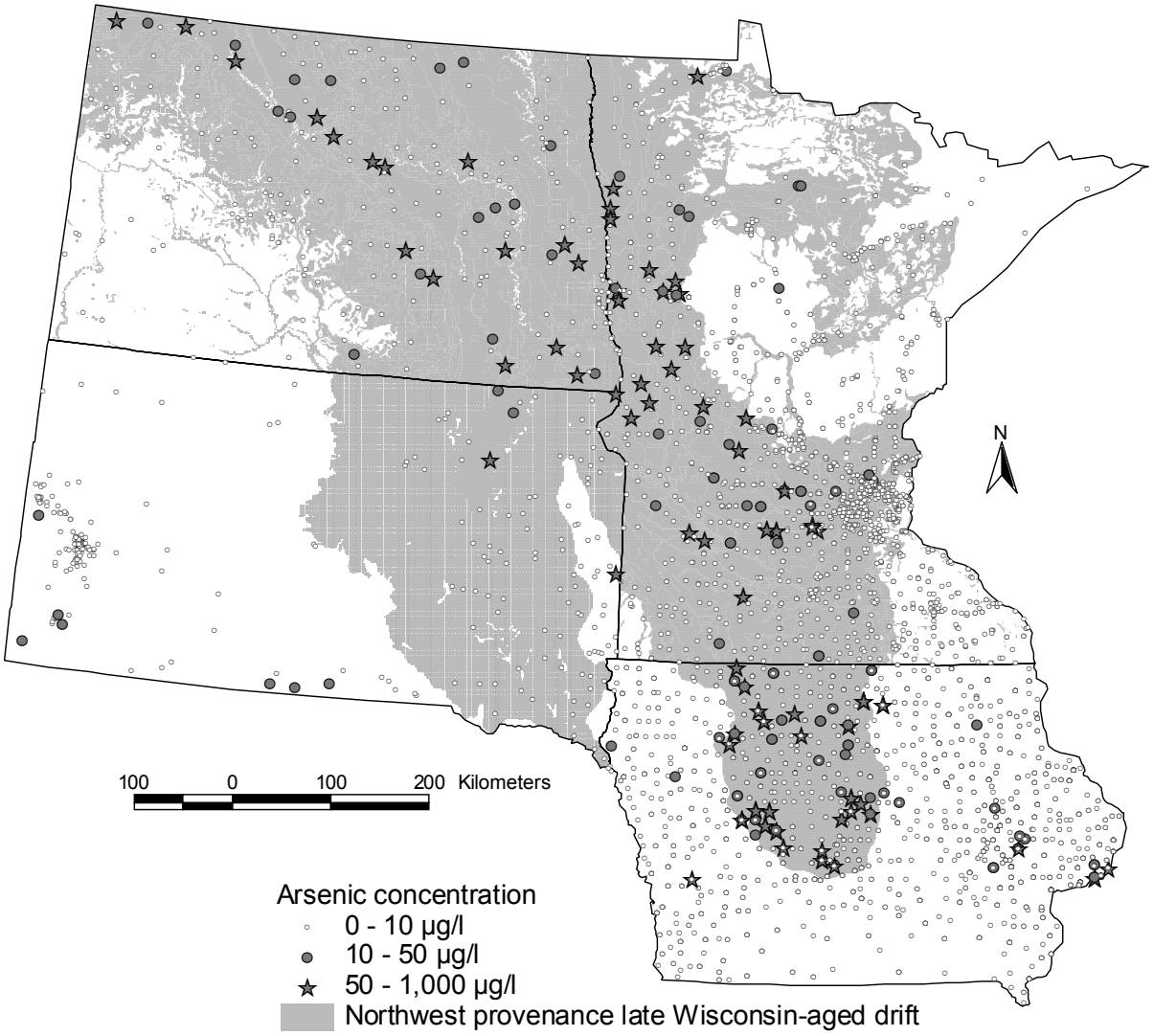


Figure 26 Arsenic concentrations in public water system wells in the upper Midwest, USA

Within the drift footprint, 12.0% of public water system sample locations exceed 10 µg/l arsenic; outside of the footprint, only 2.4% of public water system sample locations exceed 10 µg/l arsenic

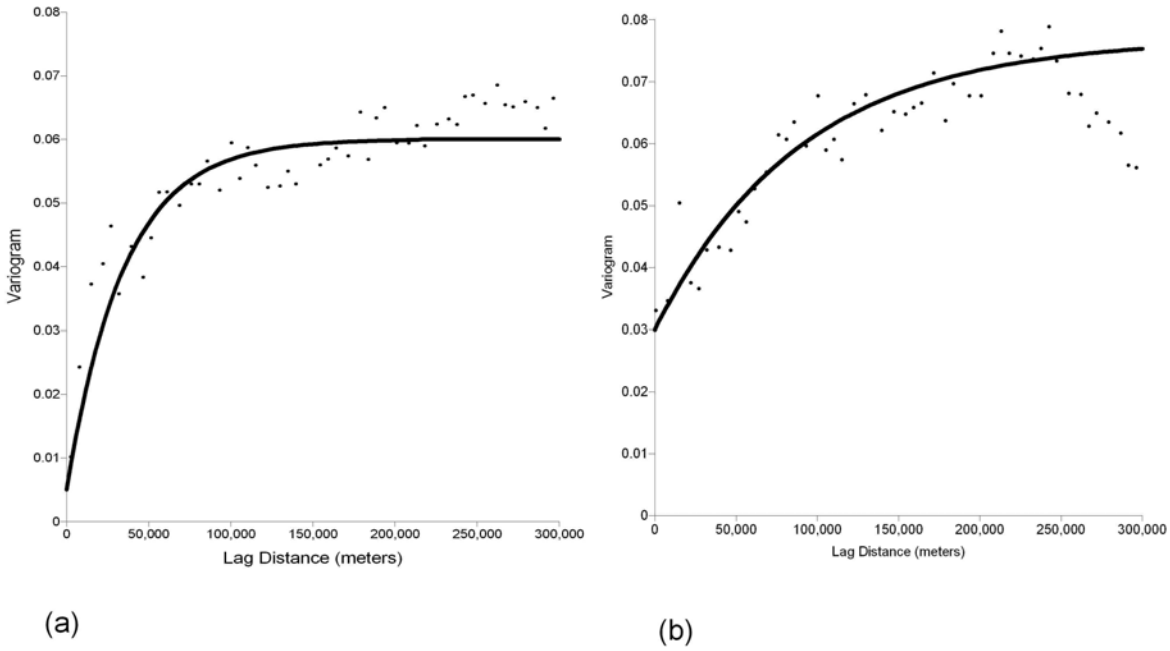


Figure 27 Directional indicator variograms of upper Midwest public water system arsenic measurements

(a) Direction of -45 degrees with 45 degree tolerance. Fitted model combines a nugget effect = 0.005 with an exponential model, scale of 0.055 and length parameter of 35,000 meters. (b) Direction of 45 degrees with 45 degree tolerance. Fitted model combines a nugget effect = 0.03 with an exponential model, scale of 0.047 and length parameter of 90,000 meters.

The data are correlated over a distance of approximately 150 kilometers.

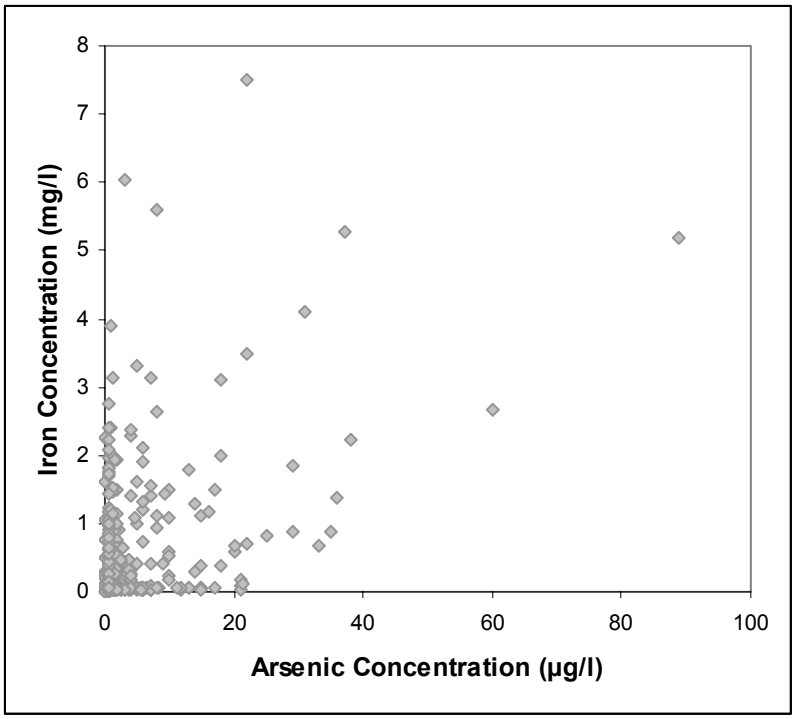


Figure 28 Arsenic and iron concentrations measured in public water system wells in North Dakota, South Dakota, and Iowa

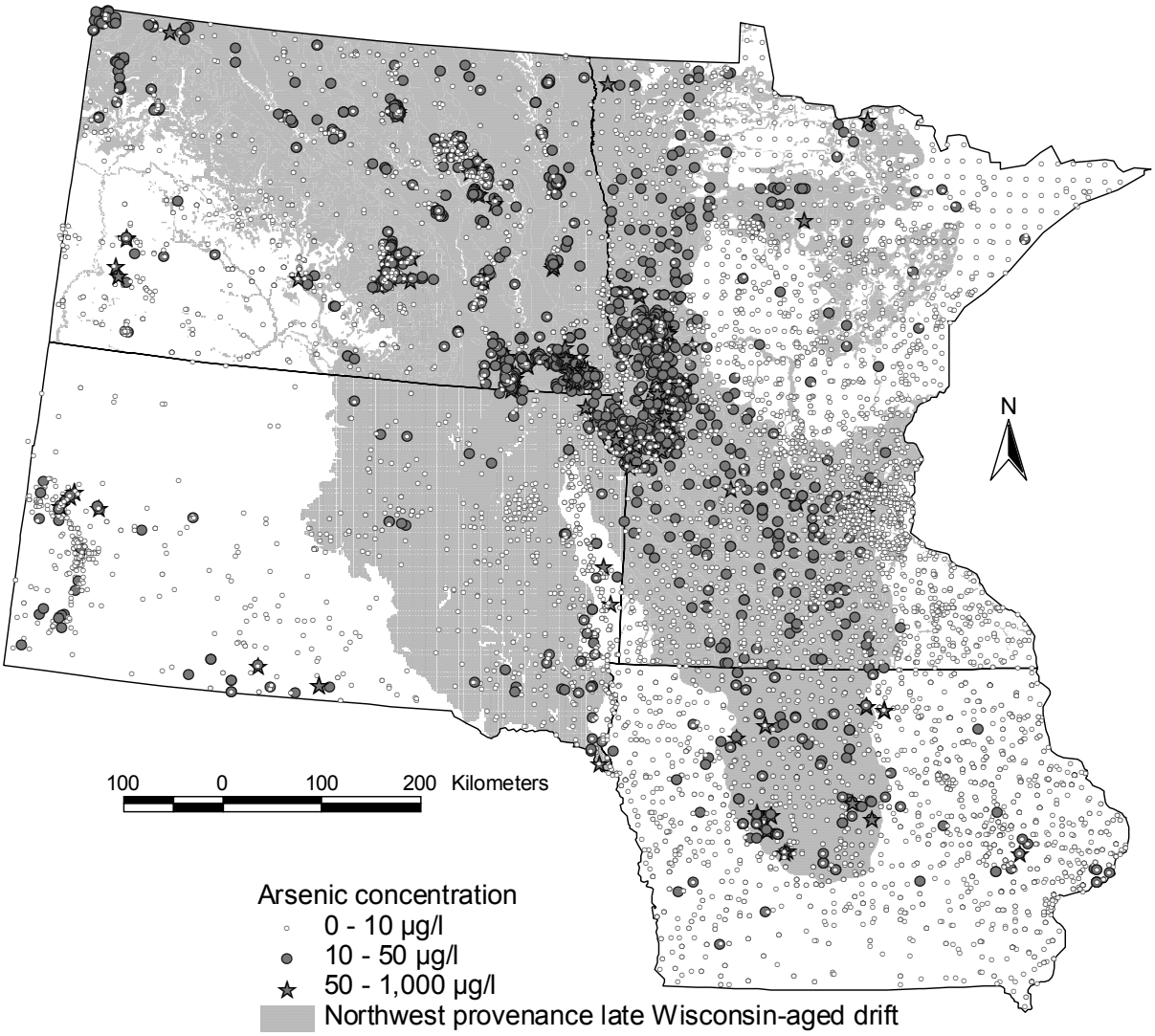


Figure 29 Arsenic concentrations in ground water in the upper Midwest, USA

Within the footprint, 23.8% of sample locations exceed 10 µg/l arsenic; outside of the footprint, only 4.3% of sample locations exceed 10 µg/l arsenic.

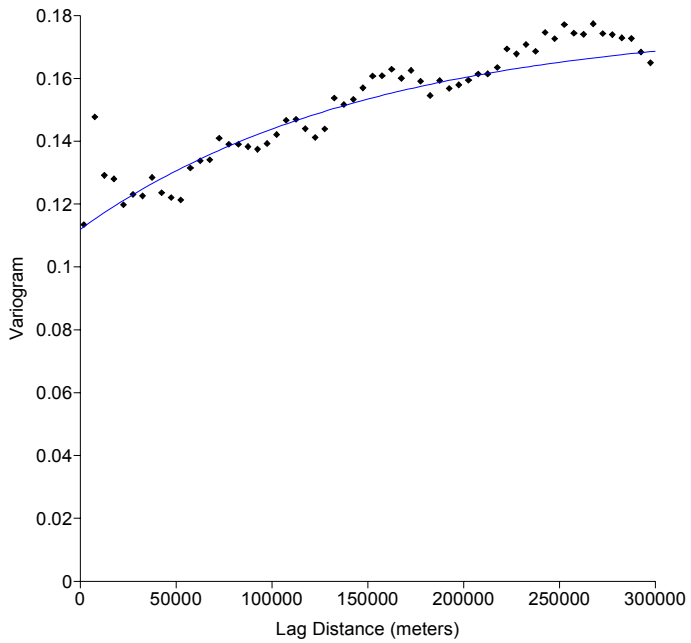


Figure 30 Directional (-20 degrees, 30 degree tolerance) indicator variogram of upper Midwest, USA, ground water arsenic measurements

Fitted model combines a nugget effect = 0.112 with an exponential model, scale of 0.065 and length parameter of 150,000 meters. The data are correlated over a distance of more than 250 kilometers

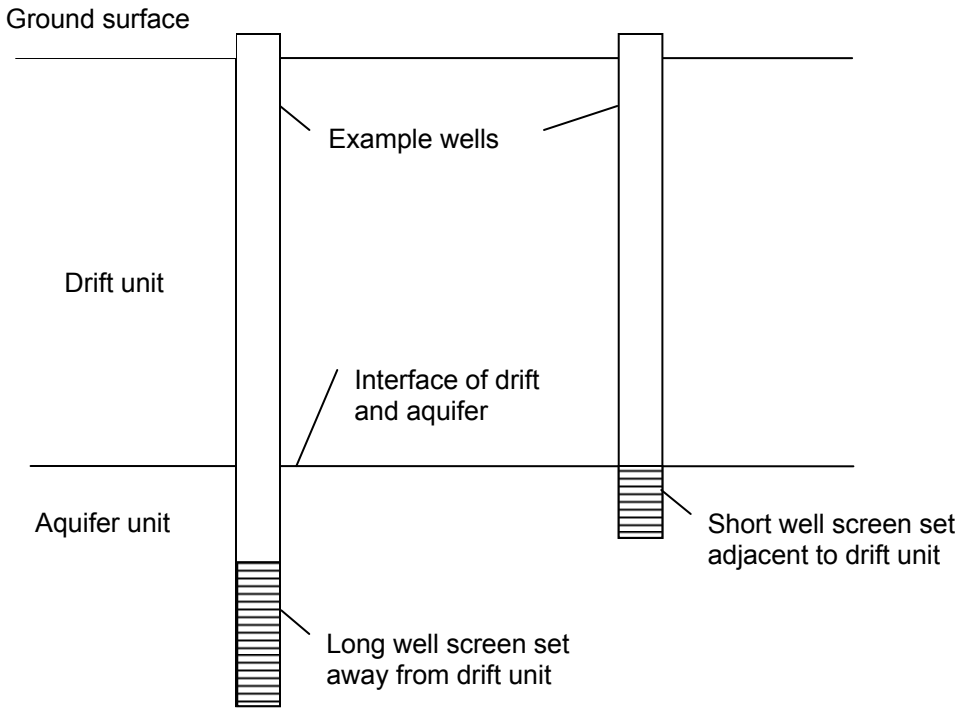


Figure 31 Illustration of well characteristics of interest

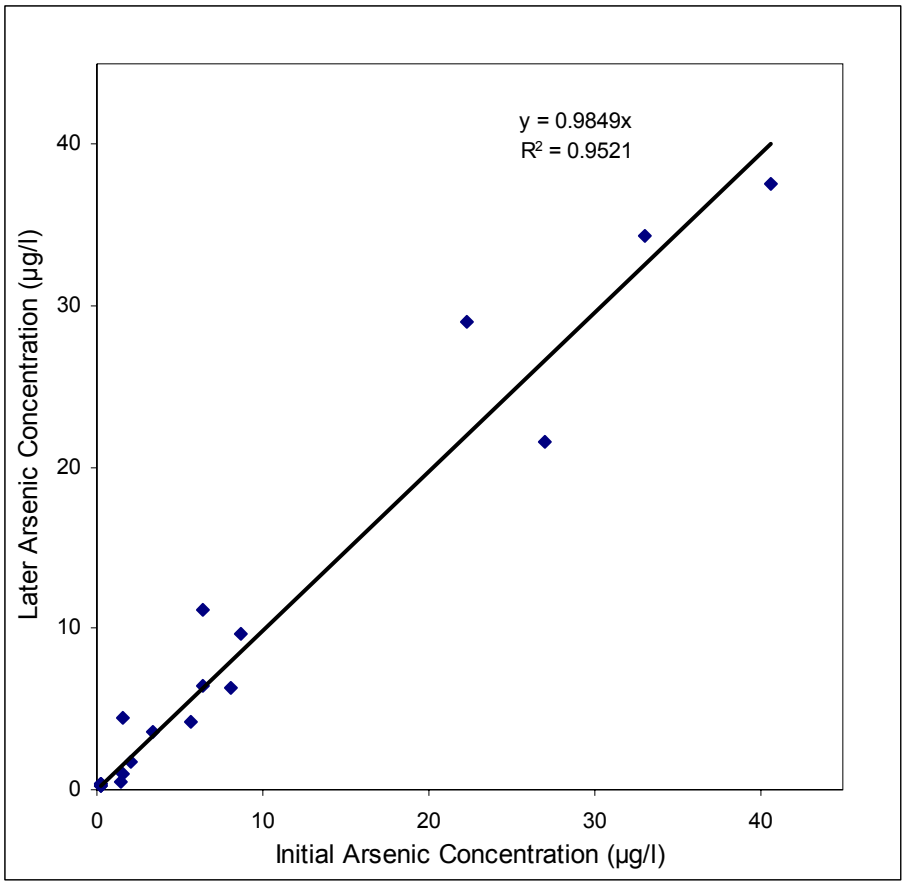


Figure 32 Arsenic concentration measurements in new wells in Minnesota

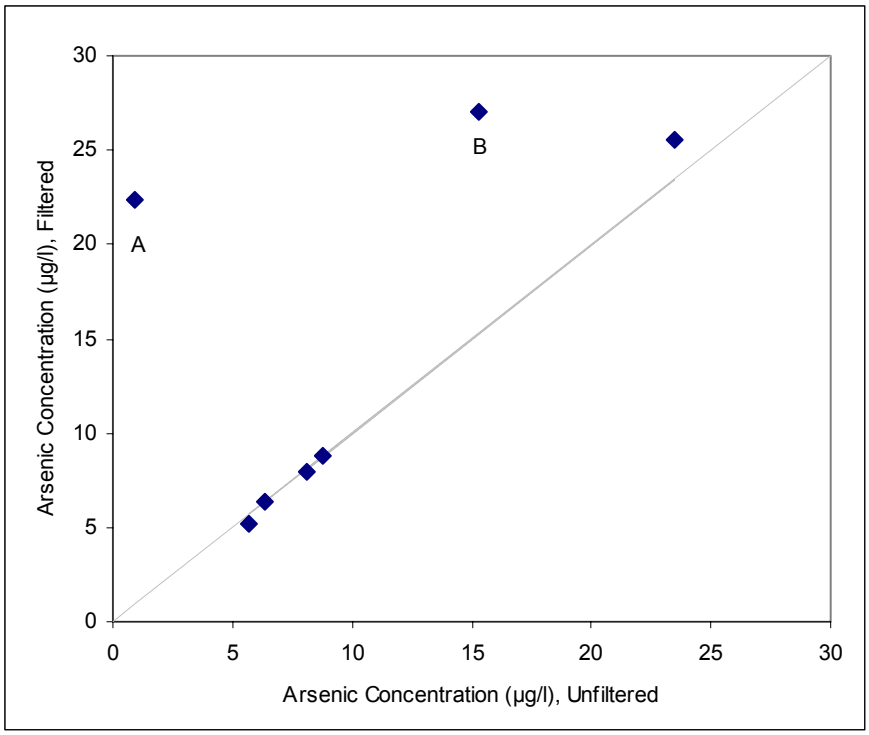


Figure 33 Filtered and unfiltered arsenic concentrations in new domestic wells
Samples were collected on the date of well drilling.

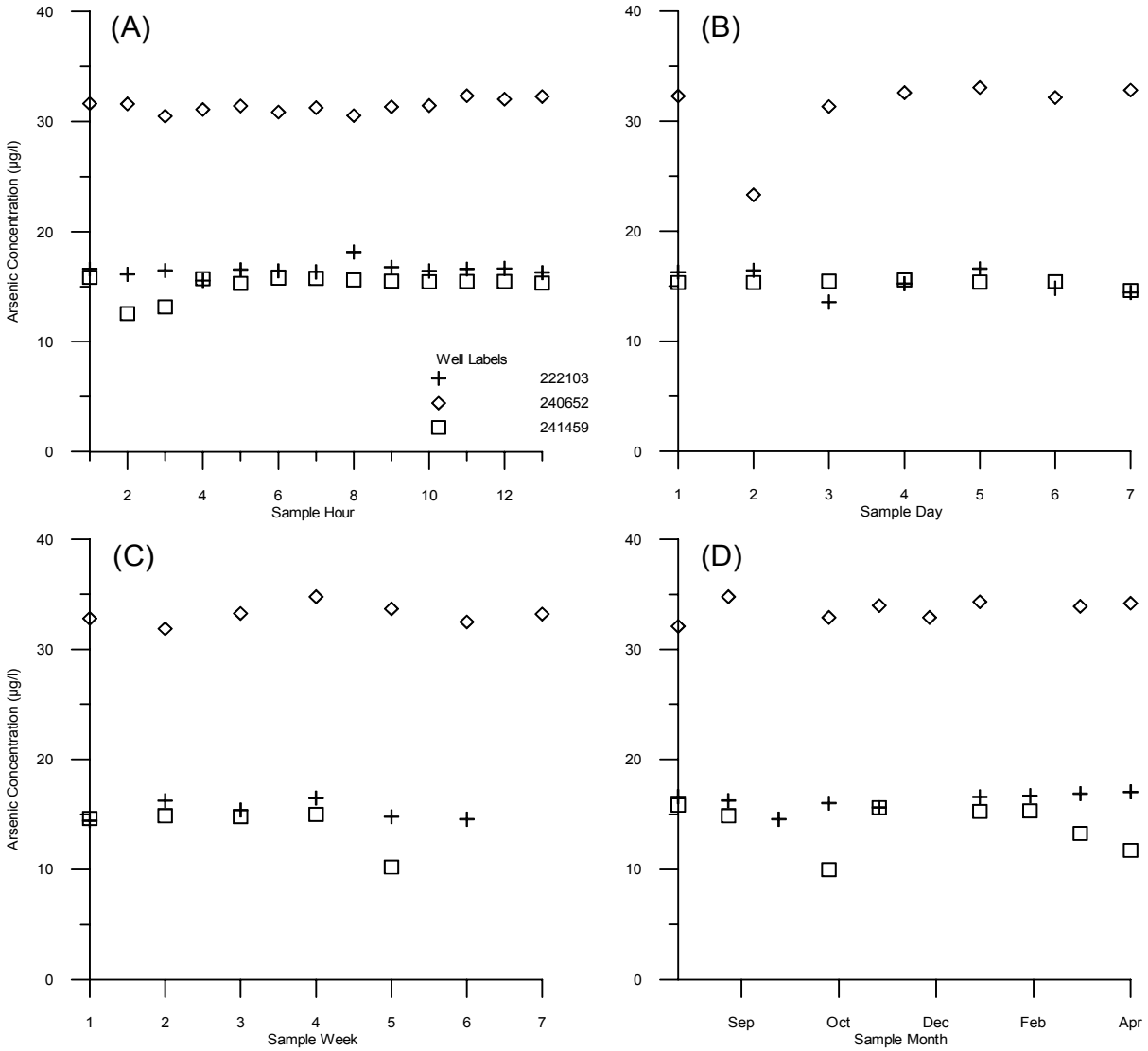
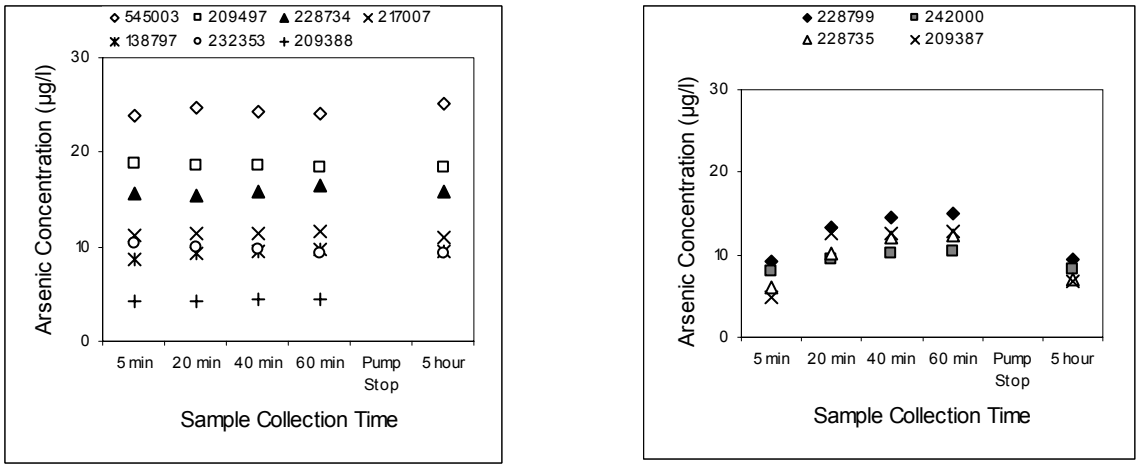


Figure 34 Long-term arsenic variability results

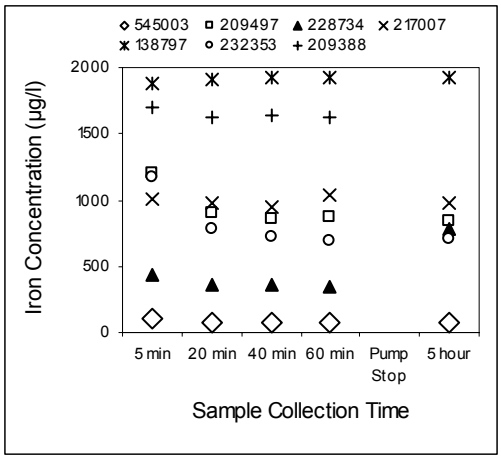
Hourly (A), daily (B), weekly (C), and monthly (D) arsenic sampling results from three Minnesota public water system wells. Samples were collected July 2002 – April 2003.



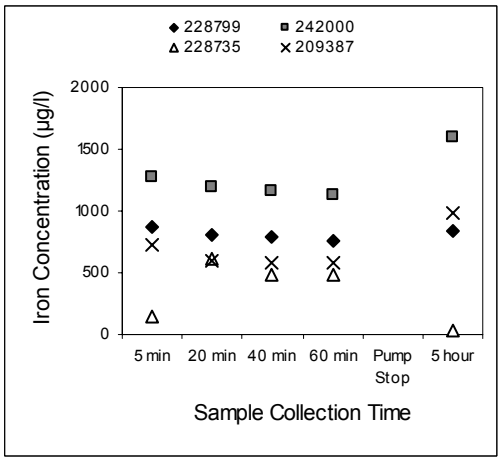
(A) (B)

Figure 35 Short-term arsenic variability results

(A) Seven Minnesota public water system wells have no discernible arsenic concentration variability; (B) four wells do have arsenic variability.



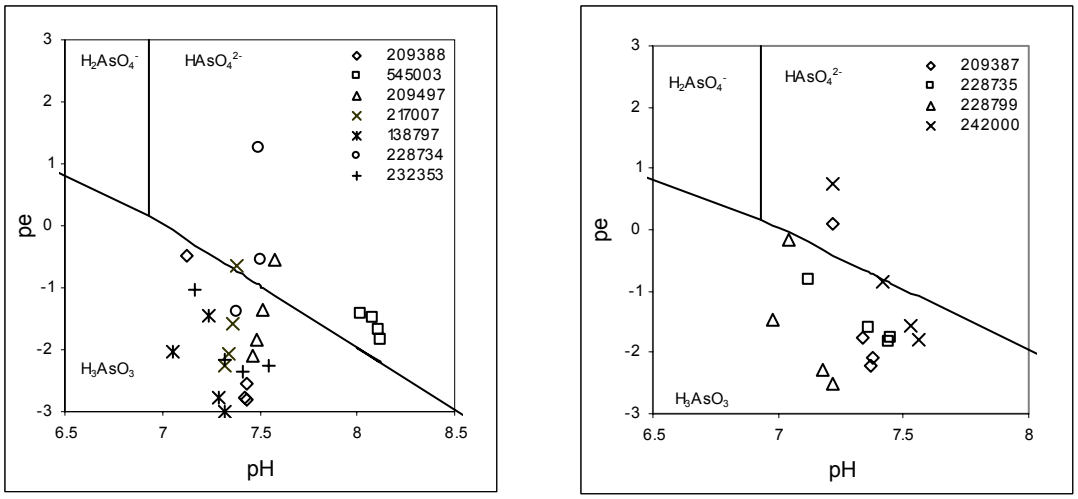
(A)



(B)

Figure 36 Short-term iron variability results

(A) Wells with no discernible arsenic concentration variability, and (B) wells with arsenic concentration variability.



(A) (B)

Figure 37 pe-pH diagrams for wells sampled for short-term arsenic variability

(A) pe-pH diagram for wells with no arsenic concentration variability; in all but one well, pe is negative when pumping begins. (B) pe-pH diagram for wells with arsenic concentration variability. In all but one well, the pe is positive or only slightly negative when the well pump starts.

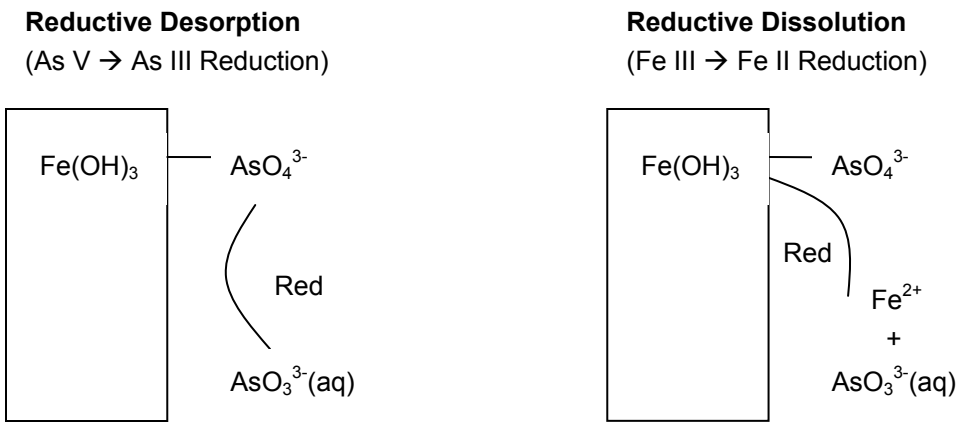


Figure 38 Schematic of reductive desorption and reductive dissolution arsenic mobilization mechanisms

12.0 References

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