ARSENIC IN FRACTURED BEDROCK AQUIFERS IN GREATER AUGUSTA, MAINE, USA

by

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ABSTRACT

ARSENIC IN FRACTURED BEDROCK AQUIFERS IN GREATER AUGUSTA, MAINE, USA

by

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Thirty one percent of private well water samples (n=790) collected in 2006 from fractured meta-sedimentary bedrock aquifers in greater Augusta, Maine were found to contain >10 μg/L of arsenic. An additional 331 samples were obtained in 2007 from 4 towns representing low to high arsenic occurrence. The spatial pattern of groundwater arsenic distribution resembled the bedrock map. Arsenic exceedance rate was highest in the Silurian pelite and sandstone/limestone (~40%), and differed significantly from those in the Silurian-Ordovician sandstone (24%), the Devonian granite (15%) and the Ordovician-Cambrian volcanic rocks (9%). This was confirmed in the 4 cluster areas with a greater sampling density. Thus, bedrock geology is associated with arsenic occurrence in fractured bedrock aquifers of the study area at scales of 10^0-10^1 km.

The elevated arsenic concentrations were associated with high pH, fluoride, molybdenum, and low dissolved oxygen, nitrate, chloride. A logistic regression model showed that bedrock geology, soil arsenic content, pH, dissolved oxygen, nitrate and sulfate played important roles on groundwater arsenic concentrations. Water geochemistry suggested a complex mobilization mechanism of oxidation of arsenic-rich

sulfide, adsorption on iron minerals, pH-dependent desorption of arsenic from iron minerals with calcite dissolution along the groundwater flow path.

Geophysical logging and water sampling from bore hole and specific fractures in two wells in Manchester, Maine found that dissolved arsenic concentrations increased when the bore hole water was replaced by the water with high dissolved arsenic coming primarily from high yielding fractures near the bottom of bore hole in response to pumping. Iron particulate precipitates were common and found to be enriched in arsenic. Laboratory experiment suggested that in the bore hole arsenic was mainly settled with iron enriched particles, probably amorphous ferric oxyhydroxides, with possibly minor adsorption on the iron minerals.

The association of arsenic distributions in groundwater, soil and stream sediment from national data sets examined by logistic regression models suggested that soil and stream sediment arsenic distributions had significant effects on groundwater arsenic occurrence at the national scale. Stronger correlations were found in Florida, New England and Nevada at regional scales and in greater Augusta, Maine at the local scale with higher sampling density.

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INTRODUCTION

Arsenic (As) is an element widely distributed in the Earth crust with an average abundance of ~3 mg/kg (CULLEN and REIMER, 1989). Chronic exposure to minute amounts of As in drinking water can increase health risks of skin cancer, bladder cancer, lung cancer and prostate cancer, and have adverse effects on various internal functions (CHEN and LIN, 1994; KARAGAS et al., 2002; TONDEL et al., 1999). Therefore, the World Health Organization (WHO) has recommended a drinking water As guideline value of 10 µg/L since 1996 (WHO, 2006) and the United States Environmental Protection Agency (EPA) has also lowered the maximum contaminant level (MCL) of As from 50 µg/L to 10 µg/L, effective January 2006 (EPA, 2001). But the drinking water standard for As is still at the higher level of 50 µg/L in many developing countries in Asia, Africa and South America. In the United States, about 10% of groundwater had As concentrations over 10 µg/L based on a nation-wide survey of approximately 30,000 wells (WELCH et al., 2000). This put about 13 million people at the risk of being exposed to high As drinking water given that 134 million people depended on groundwater for drinking (SOLLEY et al., 1998). High As concentrations were more frequently encountered in the western US (WELCH et al., 1988; WELCH et al., 2000). Recent research, however, has found that 12% of bedrock groundwater wells in New England exceeded the EPA MCL for As (AYOTTE et al., 2003).

The worrisome and frequent occurrence of As in groundwater from New England requires improved risk assessment of As exposure from drinking water drawn from domestic bedrock wells. Unlike many other contaminants with anthropogenic sources, As in groundwater from numerous countries in 5 continents are nearly always geogenic in

origin (LAHERMO and VUORINEN, 1988; SMEDLEY and KINNIBURGH, 2002; WENG et al., 2007). Therefore, the linkage between geology, water geochemistry, and the occurrence of As must be better understood to manage the risk and to reduce the exposure. Uncertainty in risk assessment and remediation design in New England includes, 1) whether the spatial distribution of As in groundwater at an intermediate scale of 10^0-10^1 km and even a local scale of less than 1 km is entirely random or systematic, 2) what are the source, controlling parameters, and mobilization mechanisms of As in fractured bedrock aquifers at the intermediate and local scales, 3) what hydrological and geochemical processes influence As evolution in individual wells, 4) are there models or methods to indicate or predict groundwater As occurrence.

I am motivated by these research questions to investigate the hydrogeochemical factors that influence groundwater As distribution at intermediate and local scales in New England to reduce the uncertainty in risk assessment that are relevant to water resources management and human health protection. I choose greater Augusta, Maine as the study area (approximately 10^3 km^2) because the geology is representative of New England and the groundwater in this area is highly contaminated by arsenic based on previous regional studies (AYOTTE et al., 2003; AYOTTE et al., 1999). The proximity to U.S. Geological Survey Maine Water Science Center and Maine Geological Survey (MGS) affords the convenience of sample collection and field work.

This thesis is composed of 4 chapters, with each chapter as or intended as a separate publishable unit. Chapter 1 explores the spatial pattern of groundwater arsenic distribution in bedrock aquifers in the greater Augusta area, Maine at intermediate and local scales, and its association with bedrock geology. Chapter 2 investigates the source,

control and mobilization mechanisms of arsenic, and develops a logistic regression model to predict arsenic occurrence at local scales. Chapter 3 conducts hydrogeophysical research to understand the reactions and processes in individual bore holes to control arsenic concentrations. Chapter 4 examines the association between groundwater arsenic and arsenic in soil and/or stream sediment on local, regional and national scales, and develops a new method to identify groundwater arsenic distribution.

The results have implications for the New Englanders who rely on groundwater pumped from their own wells for drinking. The research contributes to understanding the fate and mechanisms of arsenic mobilization in fractured bedrock aquifer systems. Such knowledge is useful for homeowner to prepare for remediation of arsenic contamination, for U.S. EPA to outreach and educate community about hazards in the environment, and for municipalities to plan for water resources and housing development.

* To protect the privacy of the homeowners, the sampling locations and tabulated arsenic concentration data are not included but available to researchers upon request for usage in accordance of IRB rules.

Chapter 1 Spatial Pattern of Groundwater Arsenic Occurrence and Association with Bedrock Geology in Greater Augusta, Maine, USA

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Abstract

In New England, groundwater arsenic occurrence has been linked to bedrock geology on regional scales. To ascertain and quantify this linkage at intermediate (10^0-10^1 km) scales, 790 groundwater samples from fractured bedrock aquifers in the greater Augusta, Maine area are analyzed. 31% of the sampled wells have arsenic >10 μg/L. The probability of [As] exceeding 10 μg/L mapped by indicator kriging is highest in Silurian pelite-sandstone and pelite-limestone units (~40%). This probability differs significantly ($p<0.001$) from those in the Silurian-Ordovician sandstone (24%), the Devonian granite (15%) and the Ordovician-Cambrian volcanic rocks (9%). The spatial pattern of groundwater arsenic distribution resembles the bedrock map. Thus, bedrock geology is associated with arsenic occurrence in fractured bedrock aquifers of the study area at intermediate scales relevant to water resources planning. The arsenic exceedance rate for each rock unit is considered robust because low, medium and high arsenic occurrences in 4 cluster areas (3-20 km^2) with a low sampling density of 1-6 wells per km^2 are comparable to those with a greater density of 5-42 wells per km^2. About 12,000 people (21% of the population) in the greater Augusta area (~1,135 km^2) are at risk of exposure to >10 μg/L arsenic in groundwater.

1.1 **Introduction**

Widespread occurrence of geogenic arsenic (As) in groundwater in the world (SMEDLEY and KINNIBURGH, 2002) is of great public health concern in the developing countries such as Bangladesh, India and China and the industrialized countries such as the United States of America. In the US, private wells, the source of drinking water for 16% of the US population mostly in rural areas (SOLLEY et al., 1998), are not subjected to the same regulation as public water supplies with a requirement to meet a recently established drinking water Maximum Contaminant Level (MCL) of 10 μg/L for As by US EPA. As a consequence, people relying on private wells are expected to be subject to a greater risk of exposure to As. Because of the geogenic nature of As in groundwater (WELCH et al., 2000), the linkage between geology and As occurrence needs to be better understood to manage the risk and to reduce exposure.

Large scale surveys of As in groundwater in the US (AYOTTE et al., 1999; WELCH et al., 2000) have shown that geology influences As occurrence in groundwater in both unconsolidated sedimentary and bedrock aquifers on the regional scales of 10^2 km or greater despite strong spatial heterogeneity at very local scales of $\leq 10^{-1}$ km. The spatial pattern has been used for risk assessment. A compilation of As concentrations in 18,850 groundwater samples in the US (RYKER, 2001) has identified high risk areas in the West (ROBERTS et al., 1985; ROBERTSON, 1989; WELCH et al., 1988) for alluvial, glacial and volcanic basin-fill sedimentary aquifers, parts of Midwest for glacial deposits, shale and sandstone aquifers (ROBERTS et al., 1985; SCHREIBER et al., 2003), and in the Northeast for fractured crystalline bedrock aquifers (AYOTTE et al., 1999; PETERS, 2008; PETERS et al., 1999). To the best of our knowledge, the population at risk of As exposure in the

West and the Midwest has not been assessed except in Michigan (MELIKER et al., 2008). Approximately 103,000 people in eastern New England were estimated to be at risk of exposure to >10 μg/L As from private water supplies based on a survey of 878 mostly public wells in the New England Coastal Basins of 59,600 km^2 (AYOTTE et al., 2003), where approximately 10% of groundwater samples had As concentrations exceeding 10 μg/L. The As problem is especially acute in New Hampshire (PETERS et al., 2006) and Maine (MARVINNEY et al., 1994) where domestic drilled wells are used for drinking in about 30% of households (U.S.BUREAU-OF-THE-CENSUS, 1999), and where the probability of finding a well exceeding MCL of As is estimated to be high (AYOTTE et al., 2006). In New Hampshire, 25% of the 474,606 households use domestic bedrock wells, and 12% of these wells are estimated to exceed the MCL using data from 2,273 wells from an area of 24,200 km^2 (PETERS et al., 2006). The analysis of several sets of groundwater As data indicated that 12%-13% of the bedrock wells had >10 μg/L As in Maine (LOISELLE et al., 2001), which could subject as many as 160,000 people to risk. Because increased health risks have been attributed to chronic exposure to As in drinking water in New Hampshire (KARAGAS et al., 2002), it is imperative that such risk be reduced in New England.

An uncertainty in risk assessment of As exposure in New England where about 877,000 housing units, 15.7% of the housing stock, rely on private wells for drinking (U.S.BUREAU-OF-THE-CENSUS, 1999) is whether the spatial distribution of As in groundwater at the intermediate scale of 10^0-10^1 km is entirely random or systematic. This is a relevant question because such knowledge is needed for outreach by government agencies, for remediation by homeowners, and for housing development

planning by municipalities. Geochemical heterogeneity in fractured bedrock aquifers can be enormous (DAY-LEWIS et al., 2000). The complexity of water flow and chemical transport in fractured bedrock aquifers may result in entirely random spatial distribution of groundwater As at the scale of 10^0-10^1 km. Indeed, at the very local scale of $\leq 10^{-1}$ km, As distribution in fractured bedrock aquifers consisting of sulfidic schist with granitic to dioritic intrusions was largely affected by fracture characteristics, hydrogeology and water chemistry (LIPFERT et al., 2006).

In order to examine to what extent the bedrock geology determines the probability of As occurrence in fractured bedrock aquifers at an intermediate scale of 10^0-10^1 km, groundwater samples from domestic bedrock wells in the greater Augusta, Maine area were collected and analyzed in 2006 and 2007. Geostatistical analyses were performed to illustrate the difference of As occurrence rates in the major bedrock units of the study area. Finally, the population at risk of high As exposure is estimated using a Geographic Information System analysis. Our results provide the basis to further investigate the source and mobilization mechanisms of As in the fractured bedrock aquifer of the greater Augusta area, and have implications on water resources management and planning in New England, and regions where drinking water are drawn from aquifers of meta-sedimentary bedrock formed under similar tectonic settings.

1.2 Materials and Methods

1.2.1 Study area

Regional studies of As occurrence in groundwater in New England have identified a number of units with calcareous and calc-silicate lithogeochemistry (AYOTTE et al., 1999) that span from central Massachusetts, southeastern New Hampshire to eastern Maine and have greater probability of encountering groundwater with > 10 μg/L As. The study area in the greater Augusta, Maine area is chosen because ~ 70% of the area is composed of bedrock units that are at least partially calcareous or calc-silicate. The bedrock units from west to east in the study area (Figure 1.1-A) are Silurian interbedded calcareous pelite and sandstone (Ss, Sangerville Formation), Silurian interbedded calcareous pelite and sandstone/limestone (Sw, Waterville Formation), and Silurian-Ordovician slightly to non-calcareous sandstone with limited cal-silicate lenses (SOv, Vassalboro Formation) (OSBERG et al., 1985). The sediment of these meta-sedimentary units was thought to be deposited in marine basins during Silurian (443-417 Ma) and contains abundant sulfide minerals (HANSON and BRADLEY, 1989). In addition to these NE-SW trending belts of meta-sedimentary rocks and several thin Silurian limestone and dolostone units, to the very eastern part of the study area lies the much older Ordovician-Cambrian mafic to felsic volcanic rocks (OZc, Cushing Formation). These formations underwent regional metamorphism from greenschist facies to amphibolites facies during the last significant tectonic event, the Acadian orogeny (420-360 Ma), and contact metamorphism by the intrusion of Devonian (417-360 Ma) plutons of granite, granodiorite, quartz monzonite and syenite (D) located in the center of the study area. These formations are nearly vertical with 80 to 89 degree dip.

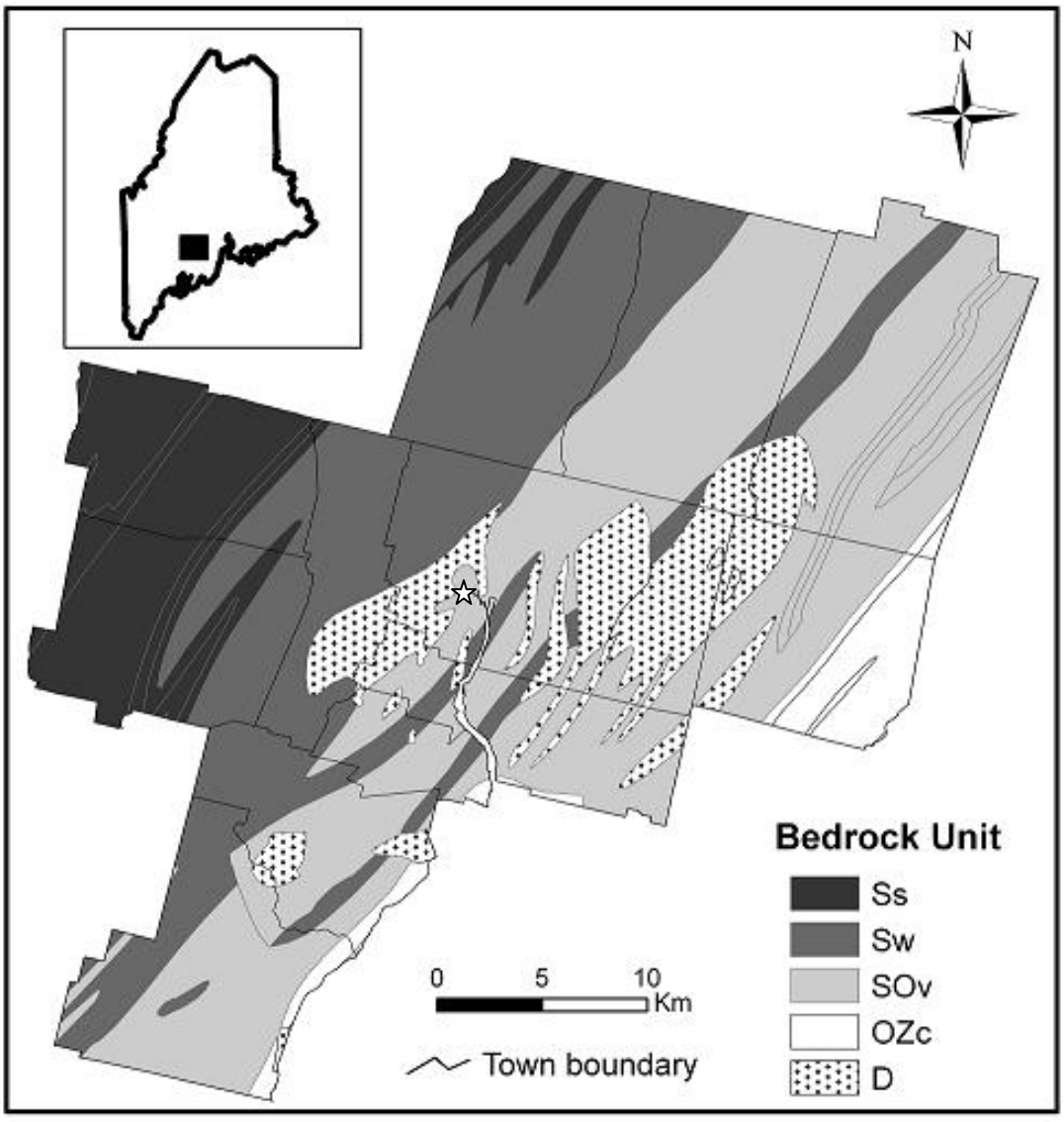
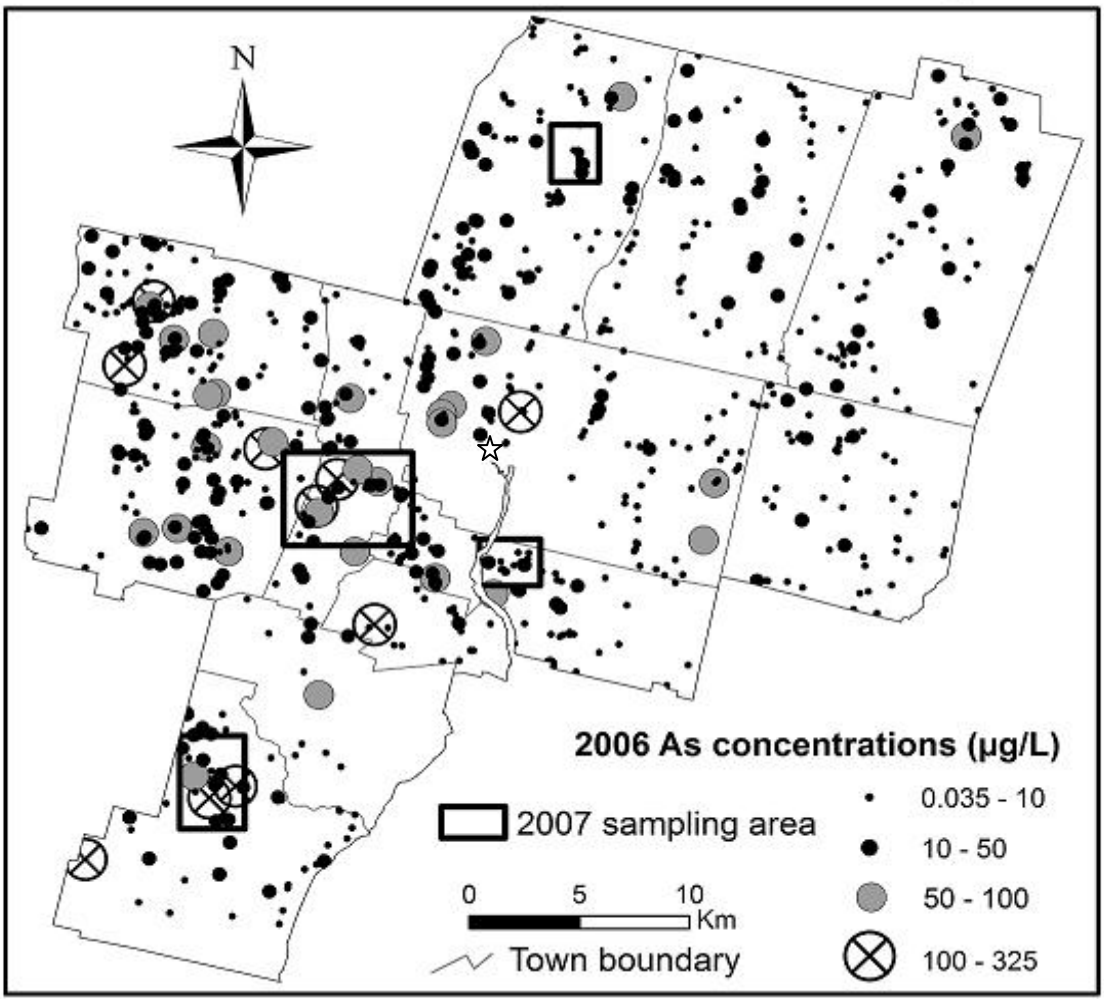


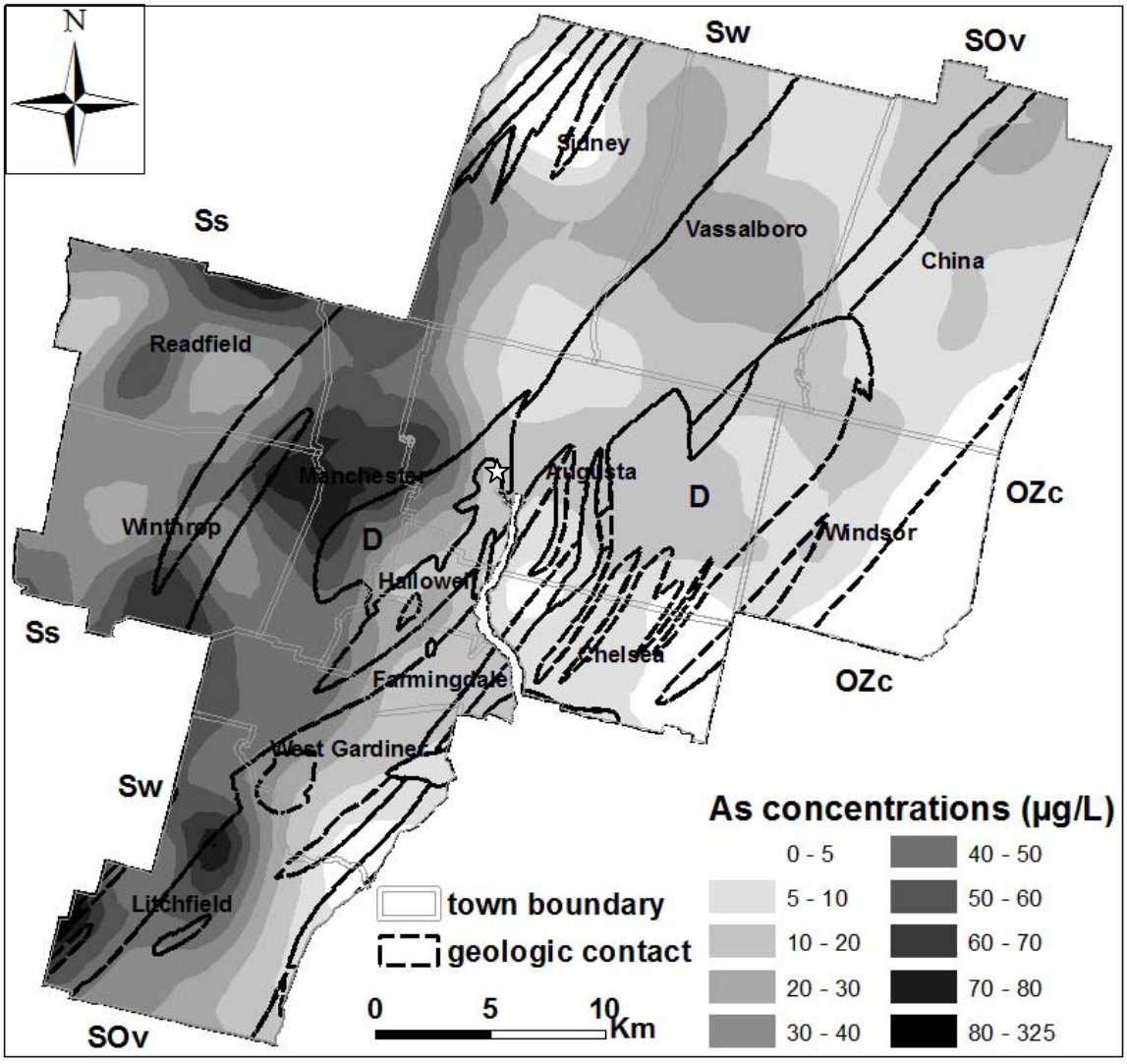
Figure 1.1 Bedrock geology and groundwater arsenic distribution in the greater Augusta area, Maine

* The star symbol in all panels indicates downtown Augusta.

A. Simplified bedrock geology. See text for description of the bedrock units. Insert is a map of Maine with rectangle representing the study area.

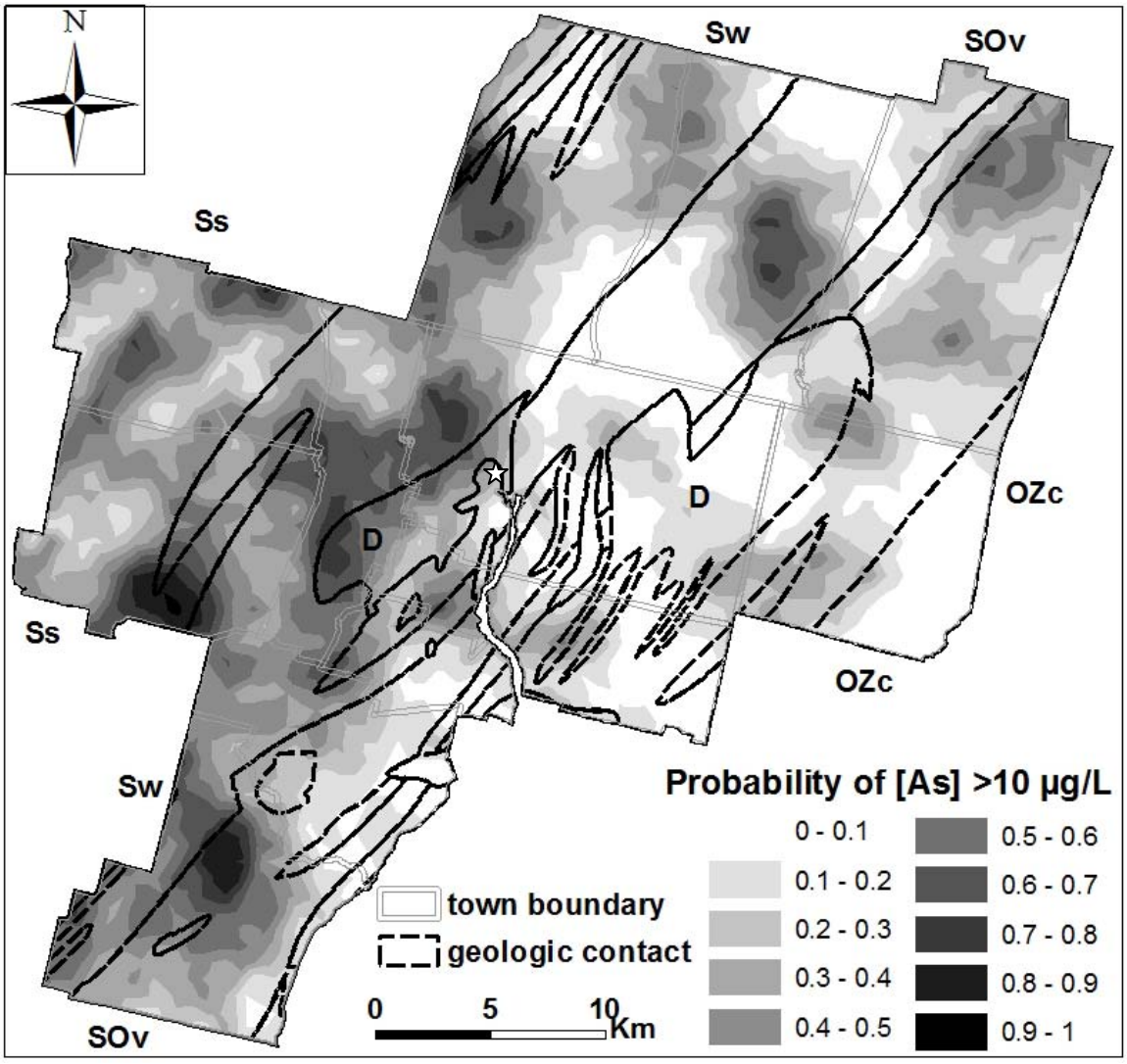


B. Discrete groundwater arsenic distribution based on 2006 sampling. The rectangles indicate the four clusters sampled at greater density in 2007.



RMS (root mean square) of predicted error =31 µg/L

C. Log-normal kriged groundwater arsenic distribution



RMS (root mean square) of predicted error = 0.43

D. Probability of groundwater arsenic >10 µg/L by indicator kriging

The study area, 1,135 km^2, encompasses thirteen towns: Sidney, Vassalboro, China, Readfield, Manchester, Augusta, Windsor, Winthrop, Hallowell, Chelsea, Farmingdale, West Gardiner and Litchfield of Kennebec County (Figure 1.1-C). The U.S. census data of 2000 reports 57,330 residents in 23,773 households. Approximately 70% of these households use private wells. Most of these wells are installed in bedrock to draw water from fractures with variable yields, with wells generally installed to greater depth to compensate for low yields. The homeowner self-reported well depth ranges from 9 to 366 meter, with a mean of 66 meter (n=539), but 72% of the wells have depth ranging from 30 to 90 meter (Figure 1.7).

1.2.2 Groundwater sampling and analysis

From May to September 2006, consent to sample wells (n=790) using an outside faucet, was obtained from the homeowners who volunteered to participate in this study. Groundwater samples were collected without filtration into an acid-cleaned HDPE vial after the temperature, conductivity and pH readings stabilized in a flow-through cell, usually after 20 minutes of pumping. The sample was acidified to 1% HNO3 (Fisher Optima) on the same day after returning to the lab. The concentrations of As and 32 other elements, were measured by High Resolution Inductively Coupled Plasma Mass Spectrometry at Lamont-Doherty Earth Observatory. NIST standard reference material 1643e "trace elements in water" with 60.45 µg/L of As was used for QA/QC standard. An average of 56.1±1.6 µg/L As from tested NIST samples (n=10) suggested the analysis was relatively accurate (7%) and precise (RSD=2.9%). Only 12 out of 790 samples (1.5%) show As concentrations between 9.3 and 10 µg/L when the concentrations could

be ≥ 10 μg/L. Homeowners completed a questionnaire about the well history, type and depth, and received a report of well water chemistry data. A brochure from the Maine Center for Disease Control was included with the report to provide information on As remediation. This dataset is used to assess the magnitude and probability of As occurrence in domestic bedrock wells.

To validate the statistical analysis and to determine sampling density appropriate to capture the spatial variability of As, from June to August in 2007, 331 additional groundwater samples were collected similarly from 4 cluster areas (Figure 1.1-B) in the towns of Chelsea (n=107), Sidney (n=62), Litchfield (n=49) and Manchester (n=113), representing low, medium to high As occurrence based on the 2006 data. The sampling density was increased from 1-6 per km^2 in 2006 to 5-42 per km^2 in 2007.

1.2.3 Geostatistical analysis

Kriging has become a standard method for spatial interpolation of limited data in environmental sciences (GAUS et al., 2003). Different kriging forms are developed to estimate environmental variables at unknown locations based on the weighted sums of neighboring samples considering the spatial pattern and other variables of interest. Kriging estimates are considered as the most accurate linear unbiased estimator (LIN et al., 2002).

Log-normal ordinary kriging (ArcGIS 9, Geostatistical Analyst) was used to estimate the As distribution in the study area. Indicator kriging was used to estimate the probability of As concentrations exceeding 10 μg/L. The kriged As distribution and exceedance rate were exported into the raster maps with cell size 150 m × 150 m (Figure

1-C, D). The variance for both ordinary and indicator kriging was not mapped because the dense and even sampling made it not very informative (GAUS et al., 2003).

The kriging theory and mathematic equations were described in details by Goovaerts and Webster et al (GOOVAERTS, 1997; WEBSTER and OLIVER, 2001). The detailed procedures of log-normal ordinary kriging and indicator kriging conducted in this research are as follows.

Log-normal Ordinary Kriging

The 2006 dataset of groundwater As concentrations (n=790) was used for the log-normal ordinary kriging. Because ordinary kriging is the realization of a stochastic process and most statistical theories are built on the normal distribution of variables, it is desirable to have a normally distributed dataset. Due to the high skewness (6.36) of As distribution in the 2006 data, a logarithmic transformation was performed to improve the efficiency of kriging. The skewness was reduced to -0.53, close to a normal distribution. The parameters were optimized to minimize the root mean square of predicted error. The high RMS of the predicted error, 31 μg/L, was the consequence of high nugget effect and poor spatial dependence at the local scale. The kriged As distribution was exported into a raster map with cell size 150 m × 150 m. When the As concentration was below the detection limit of 0.07 μg/L (93 out of 790 samples), the half detection limit, 0.035 μg/L was assigned for geostatistical analysis.

The log-normal ordinary kriging was conducted by two steps:

1) Data transformation $Z(x_i)=\ln[As]_i$,

2) Ordinary kriging $Z^*(x_0)=\sum_{i=1}^{n}\lambda_i Z(x_i)$ and $\sum_{i=1}^{n}\lambda_i=1$, where $Z^*(x_0)$ is the estimated arsenic concentration at x_0, $Z(x_i)$ is the observed arsenic concentration of neighboring

sample, λ_i is the weight assigned to the neighboring samples. The kriging weights were forced to sum to 1 to ensure an unbiased estimation.

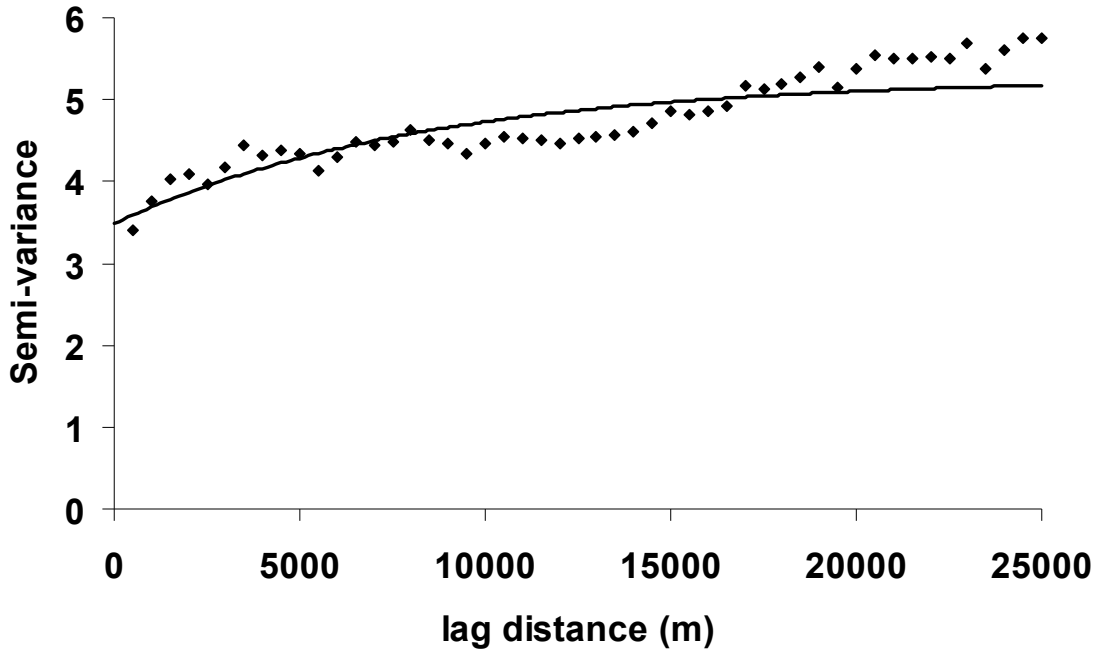


Figure 1.2 Semivariogram of log-normal ordinary kriging on 2006 dataset

The semivariances, $r(h)$, were calculated using the formula:

$$r(h) = \frac{1}{2m(h)} \sum_{i=1}^{m(h)} \{Z(x_i) - Z(x_i + h)\}^2 \quad ,$$

where $Z(x_i)$ and $Z(x_i+h)$ are the arsenic concentrations at x_i and x_i+h separated by the lag distance h, m(h) is the number of point pairs at that lag distance. Lag distance 500 meter and 50 lags are used.

An isotropic exponential model $r_{(h)} = 1.77 \times (1 - e^{-h/25000}) + 3.48$ is used to best simulate the semivariogram. Nugget effect is the degree of randomness and

represents the spatial variance of arsenic concentrations over the distance less than the minimum sampling resolution. Partial sill is the part of statistical variance besides the nugget effect. Major range indicates the spatial scale over which data are spatial correlated. In this semivariance model, nugget effect is 3.48, partial sill is 1.77. The variance is not bounded at 25 km distance.

Indicator Kriging

The probability of encountering > 10 μg/L As groundwater concentration in the study area is estimated by indicator kriging. The normality of As data is not required because indicator kriging is a robust method that applies on any forms of distribution.

The indicator kriging was also conducted by two steps:

1) Data transformation from continuous variable to binary variable using the threshold of 10 μg/L,

$$Z(x_i) = \begin{cases} 0 & [\mathrm{As}]_i < 10\,\mu g/L \\ 1 & [\mathrm{As}]_i \geq 10\,\mu g/L \end{cases},$$

2) Ordinary kriging of transformed binary variable $Z^*(x_0) = \sum_{i=1}^{n} \lambda_i Z(x_i)$ and $\sum_{i=1}^{n} \lambda_i = 1$,

where $Z^*(x_0)$ is the estimated probability of arsenic concentration greater than 10 μg/L at x_0, $Z(x_i)$ is the probability of arsenic concentration >10 μg/L of neighboring sample, λ_i is the weight assigned to the neighboring samples. The kriging weights were forced to sum to 1 to ensure an unbiased estimation.

The semivariances, $r(h)$, were also calculated using the formula:

$$r(h) = \frac{1}{2m(h)} \sum_{i=1}^{m(h)} \{Z(x_i) - Z(x_i + h)\}^2,$$

where $Z(x_i)$ and $Z(x_i+h)$ are the probabilities at x_i and x_i+h separated by the lag distance h, m(h) is the number of point pairs at that lag distance. Lag distance 300 meter and 60 lags were used.

An isotropic exponential model $r_{(h)} = 0.074 \times (1 - e^{-h/1990}) + 0.135$ is used to best simulate the semivariogram. In this semivariance model, nugget effect is 0.135, partial sill is 0.074. The variance is bounded at 1,990 meter distance.

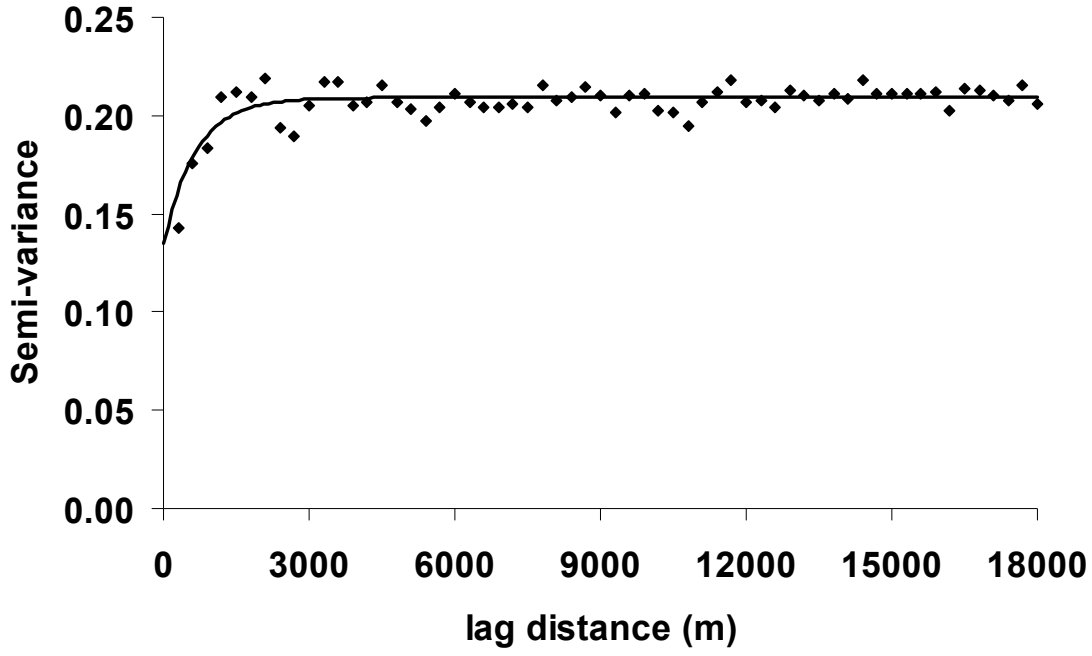


Figure 1.3 Semivariogram of indicator kriging on 2006 dataset

1.2.4 Estimation of population at risk

The population at risk of exposure to unsafe levels of As in drinking water in the greater Augusta area was estimated using the spatial pattern of the probability calculated from indicator kriging. The mean values of the probability of As exceeding 10 µg/L were

calculated for each census block. This arsenic exceedance rate for each census block was multiplied by the population using bedrock wells to arrive at the estimate of population at risk. The analysis excludes urban areas on public water supply.

1.2.5 Statistical tests

The Kruskal-Wallis test by ranks (KRUSKAL and WALLIS, 1952) was used to compare the observed As concentrations among different bedrock groups without normality assumption. The nonparametric Mann-Whitney U test (MANN and WHITNEY, 1947) was used to compare the observed As concentrations in each pair of bedrock units.

1.3 Results and Discussion

1.3.1 Groundwater arsenic concentration

In the 2006 dataset of 790 groundwater samples, the maximum As concentration was 325 µg/L, found in a well located in Litchfield (Figure 1.1-B). The dataset has a high positive skewness of 6.36, thus the median value of 3.8 µg/L is more appropriate than the mean value of 12.2 µg/L to describe the groundwater As concentrations (Table 1.1). Thirty-one percent of wells have As concentrations > 10 µg/L. The 2006 dataset also identifies clusters of wells with distinct difference in As occurrence. For example, the probability of finding a well with > 10 µg/L As was 6%, 14%, 48% and 75% for clusters located in Chelsea (n=16), Sidney (n=14), Manchester (n=21), and Litchfield (n=12), respectively (Figure 1.1-B and Table 1.2). These areas were selected for high density sampling in 2007 that increased the sampling density by a factor of about 6. The area of

the 4 clusters ranged from 2.6 km^2 for Chelsea and Sidney, to 10 km^2 for Litchfield and 20 km^2 for Manchester (Table 1.2). The probability of finding a well with > 10 µg/L As was 7%, 29%, 78% and 57% for Chelsea (n=107), Sidney (n=62), Manchester (n=113), and Litchfield (n=49), respectively for the 2007 dataset (Table 1.2). In the 2007 dataset of 331 groundwater samples, the maximum As concentration was 478 µg/L in Litchfield. The high density sampling of 2007 confirmed the order of low, medium to high As median values from Chelsea, Sidney, Litchfield to Manchester, as in 2006, although the median As concentrations for each cluster differ between two datasets. The probability of As exceedance gave the same order of ranking as the As median values in 2007 dataset. The only exception from the probability in Litchfield may be due to the large variance of As concentration in Litchfield, reflected in the inter-quartile range (0.75 quartile - 0.25 quartile) in 2006 and 2007 datasets (Table 1.2).

Table 1.1 Summary statistics of groundwater arsenic from the greater Augusta area, Maine in 2006

			As in simplified bedrock unit				
	As	**Ln(As)**	**Ss**	**Sw**	**SOv**	**D**	**OZc**
number of observations (n)	790	790	163	259	249	87	32
mean (µg/L)	12.2	0.9	16.3	14.4	10	7.7	3
standard deviation (µg/L)	25.9	2.2	27.5	22.7	31.1	15.6	8.6
median (µg/L)	3.8	1.3	6.8	6.1	2.0	2.5	0.2
Maximum (µg/L)	325	5.8	200	199	325	95	41
skewness	6.4	-0.5					
observed probability of >10µg/L	31%		42%	39%	24%	15%	9%
kriged probability of >10µg/L			40(±3)%	38(±2)%	25(±2)%	21(±4)%	7(±3)%

[a] Values in the parenthesis indicate 95% confidence interval.
[b] The well depth analysis shows no significant difference in the 5 bedrock units (see Table 1.5)

Table 1.2 Summary statistics of groundwater arsenic in four clusters in greater Augusta area, Maine

	clusters	Manchester	Litchfield	Sidney	Chelsea
	sampling area (km^2)	20	10	2.6	2.6
	sample size (n)	113	49	62	107
	sampling density (n/km^2)	6	5	24	42
2007	*median As (µg/L)*	22.2	14.6	4.1	0.9
	inter-quartile range (µg/L)	31.4	37.5	10.2	4.3
	probability of As >10 µg/L	78%	57%	29%	7%
	sample size (n)	21	12	14	16
	sampling density (n/km^2)	1	1	5	6
2006	*median As (µg/L)*	31.1	22.7	0.2	ND
	probability of As >10 µg/L	48%	75%	14%	6%
	kriged probability of As >10 µg/L	53%	70%	17%	13%

1.3.2 Spatial distribution of groundwater arsenic

Towns in the western part of the study area, and in particular, Manchester, Litchfield, Readfield, and Winthrop, display higher median As concentrations as well as higher probability of encountering a well with >10µg/L As than towns in the eastern part (Table 1.3). When As concentrations of individual wells were plotted (Figure 1.1-B), a heterogeneous distribution can be observed. This large spatial variability is reflected by high nugget effects in semi-variograms (Figure 1.2 and 1.3). The nugget effect for As concentration is 3.48, which is 66% of the total variance of 5.26. The nugget effect for probability of As exceeding MCL is 0.135, which is 65% of the total variance of 0.209. These suggest that ordinary kriging and indicator kriging models capture only one third of As variability in bedrock aquifers at 10^0-10^1 km scales. The Root Mean Square values of predicted error of As concentration (31 µg/L) and probability (0.43) were also high due to this heterogeneity. Despite these errors, the west to east spatial pattern of groundwater As distribution in the study area is evident in the As concentration map

(Figure 1.1-C) and the probability map (Figure 1.1-D). The spatial distribution of groundwater arsenic in the study area is more systematic than random.

Table 1.3 Population at risk in 13 towns in the greater Augusta area, Maine

town	bedrock unit	median As (µg/L)	total population (n)	population at risk (n)	probability of As >10 µg/L
Augusta	D, SOv, Sw	3.01	18,560	1,017	5.5%
Chelsea	SOv, D	0.51	2,559	398	15.5%
China	SOv, D, Sw, OZc	1.88	4,106	1,012	24.6%
Farmingdale	SOv, Sw	3.13	2,804	181	6.5%
Hallowell	SOv, D, Sw	2.62	2,467	154	6.2%
Litchfield	SOv, Sw, D	4.28	3,110	1,367	44.0%
Manchester	Sw, D	9.16	2,465	1,346	54.6%
Readfield	Ss, Sw	8.51	2,360	914	38.7%
Sidney	Sw, Ss, SOv	3.40	3,514	1,078	30.7%
Vassalboro	SOv, Sw, D	3.87	4,047	854	21.1%
West Gardiner	SOv, Sw, D, OZc	3.42	2,902	773	26.6%
Windsor	OZc, SOv, D	0.60	2,204	296	13.4%
Winthrop	Ss, Sw	8.80	6,232	2,658	42.7%
		total	**57,330**	**12,047**	**21.0%**

[a] Only population in rural area using private bedrock wells as water supply is used for calculation.

1.3.3 Population at risk

A total of 12,047 people in the study area, or 21.0% of the total population of 57,330 (UNITED-STATES-CENSUS-2000), are estimated to be at risk of exposure to > 10 µg/L As in groundwater. Due to the spatial heterogeneity of As occurrence and population distribution, the percentages of population at risk in 13 towns varied from as low as 6% in Augusta, Farmingdale and Hallowell to as high as 55% in Manchester (Table 1.3). The actual population at risk might be lower due to the use of bottled water and water treatment systems (AYOTTE et al., 2003). This estimate does not account for the increase of population since 2000.

Table 1.4 Chi-square values of Mann-Whitney U test

bedrock unit	Ss	Sw	SOv	OZc	D
Ss					
Sw	0.54*				
SOv	27.19	27.64			
OZc	34.77	36.71	19.29		
D	15.82	13.45	0.43#	22.58	

[a] Null hypothesis is that each pair of bedrock units have the same As distribution.
[b] All the p values are less than 0.0001 except * and #.
* p value 0.4623
# p value 0.5097

1.3.4 Association with bedrock

The 2006 dataset allows for quantitative assessment of As occurrence in each bedrock unit in the greater Augusta area. It is important to note that the source for the bedrock units is a highly generalized map at the scale of 1:500,000 (OSBERG et al., 1985). The spatial accuracy of unit contacts on this map may be on the order of 1 km and introduces considerable uncertainty to the designation of the bedrock unit for each well in the dataset. However, this uncertainty does not affect the spatial analysis of arsenic distribution at the 10 km scale in the study area. Both median values of As and the probability of [As] > 10 µg/L give consistent ranking of As occurrence from low, medium to high in the order of OZc, D/SOv, and Ss/Sw (Figure 1.4 and Table 1.1). The Ss and Sw units have the highest median [As] and also the highest percentage (~ 40%) of wells with [As] > 10µg/L. The much older OZc unit has the lowest median [As] and the lowest percentage (~ 10%) of wells with [As] >10µg/L. The ranking of As occurrence based on observed [As] among different bedrock groups was statistically significant based on Kruskal-Wallis test (Chi-square value = 75.32, p-value < 0.0001). Statistical

values of the Mann-Whitney U test showed that there was no significant difference between the Ss and Sw units, neither between D and SOv unit. Except these two pairs, all other pairs of bedrock units showed significantly different As concentrations (Table 1.4).

The bedrock of the study area is currently being mapped by the Maine Geological Survey at the 1: 24,000 scale so that the spatial As pattern recognizable in the 4 cluster areas and their association with lithogeochemistry can be compared in the future. This will also help assess the uncertainty introduced by using regional scale maps for these analyses.

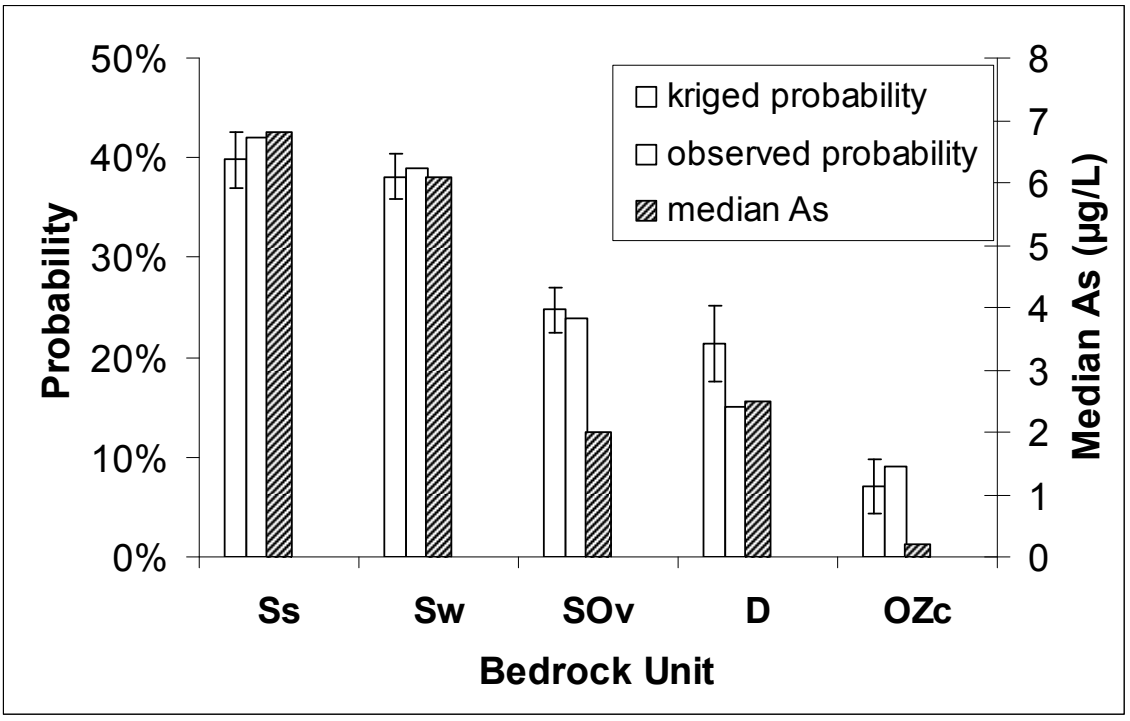


Figure 1.4 Groundwater arsenic occurrence in simplified bedrock units
The Error bars stand for 95% confidence interval.

1.3.5 Association between bedrock and groundwater As: regional vs. intermediate scale

On a regional scale of 10^2-10^3 km in New England, Ayotte et al (AYOTTE et al., 2006) applied a logistic regression model to data including 2,470 bedrock wells at a sampling density of 1 per 70 km^2 and showed that groundwater As distribution was controlled primarily by bedrock lithogeochemistry, with the highest occurrence rate found in units of calcareous and calc-silicate lithogeochemsitry (AYOTTE et al., 1999; ROBINSON and AYOTTE, 2006). In New Hampshire, no apparent geographic relationship between bedrock As concentrations (n=307) and groundwater As concentrations from bedrock wells (n=2,273) can be identified (PETERS et al., 2006). This suggests that aqueous geochemistry and groundwater flow path other than As concentrations in bedrocks play significant roles on groundwater As distribution.

Studies conducted at the intermediate scale of 10^0-10^1 km appear to suggest a linkage between bedrock type and groundwater As occurrence. In Hillsborough, Rockingham, and Strafford Counties of southeastern New Hampshire, Montgomery et al (MONTGOMERY et al., 2003) found that high groundwater As concentrations were related to geologic units such as the Ayer granodiorite, Eliot Formation, Rangeley Formation and Berwick Formation, the last three units showing calcareous to calc-silicate lithogeochemistry. In Maine, Marvinney et al (MARVINNEY et al., 1994) found a mean value of 2.7 µg/L As in 1,111 domestic bedrock wells from the Buxton and Hollis area of 192 km^2 in Southwestern Maine Plain, with 42% containing > 10 µg/L of As. As occurrence in bedrock wells in the granites in the southern Buxton-Hollis area was apparently lower than in the meta-sedimentary rock units composed of sandstone, shale, and limestone with weathered rusty sulfide-bearing rocks.

How do the distinctly different groundwater As occurrence rates among bedrock units in the study area compare to those found in regional studies of New England? In the decreasing rank of order, the percentages of groundwater [As] > 10 μg/L were the calcareous and calc-silicate units (21%), the noncalcareous and nonsulfidic units (15%), the mafic/felsic igneous units (6-9%) to the sulfidic units (3%) in the entire New England region (AYOTTE et al., 1999). At the intermediate scale (10^0-10^1km), the present study identified two bedrock units, the Ss and Sw (both calcareous and calc-silicate units), that have higher percentage of wells with As exceedance than that in the regional study (Table 1.1). The Ss and Sw units rank the highest in groundwater As occurrence, with 42% and 39% of wells in exceedance of MCL, respectively. Future surveys at sufficient spatial sampling density should target bedrock units similar to Ss and Sw first. The As exceedance rate of 24% in the SOv unit is comparable to its regional counterpart, but it is unclear whether this is a coincidence or whether this group in the regional study included more samples from other rock units similar to SOv. Highly heterogeneous OZc unit has an As exceedance rate of 9%, which is slightly higher than the percentage in regional study. Again, more studies at the local scale are needed to confirm the significance of the similarity of the two estimates.

The higher As exceedance in the Devonian granite unit (D, 15%) compared to the corresponding regional group of felsic igneous rocks (6%) may be related to pegmatite formation during granitic intrusion. In central New Hampshire, the Concord granite and pegmatite (felsic igneous rock in regional scale) showed a higher percentage of groundwater As >10 μg/L than Rangeley Formation and Smalls Falls Formation (as sulfidic unit in regional study) (PETERS and BLUM, 2003). Especially noteworthy is the

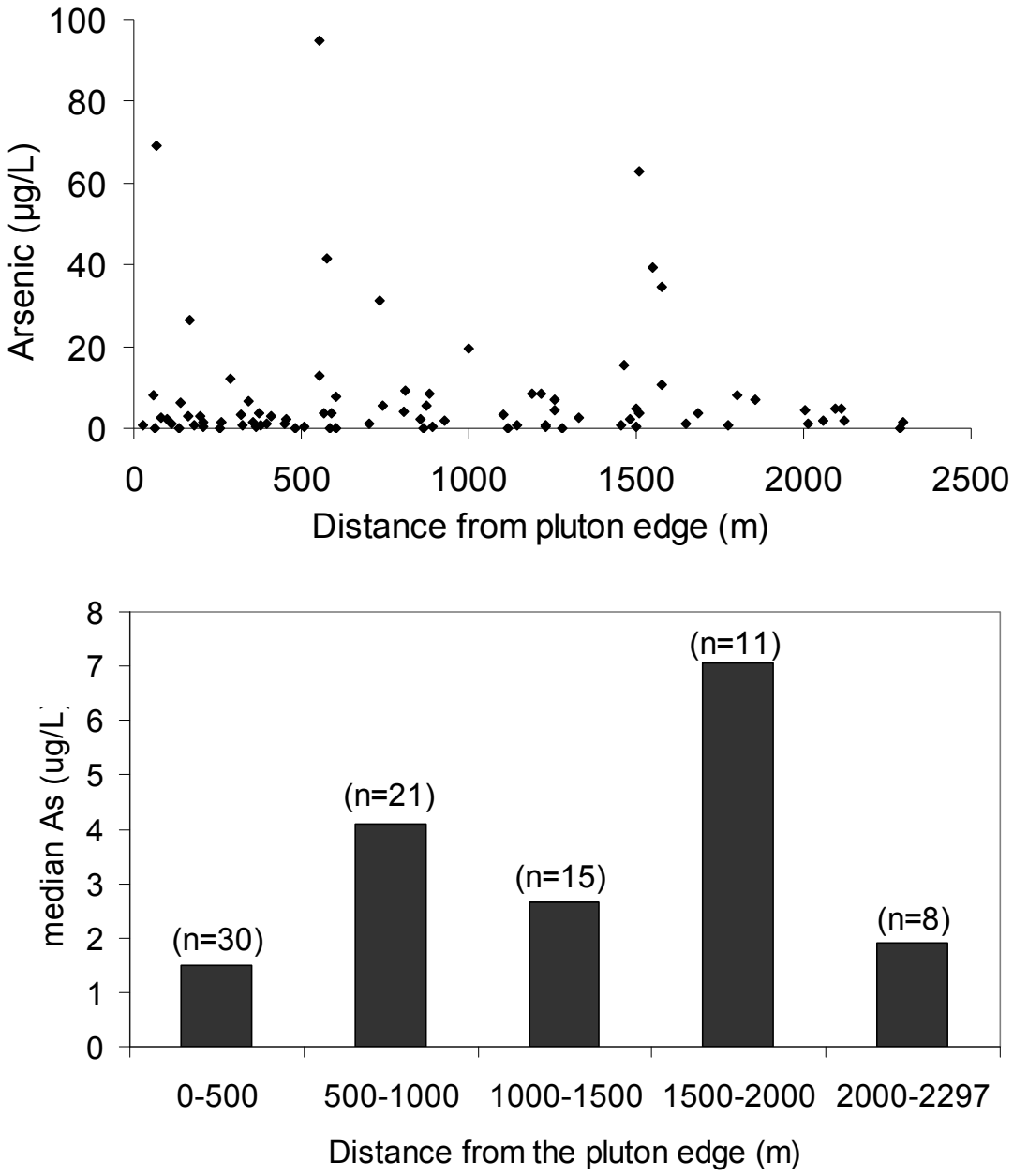


Figure 1.5 Relation of groundwater arsenic concentrations within the granite intrusion (D unit) to the pluton boundary

[a] All the samples within 3 plutons are plotted together in the top graph.
[b] Numbers above the bars (n) in the bottom graph represent the amount of samples falling in that distance range.
[c] The distances are based on the geological map.

observation that the wells with elevated As tended to be within 5 km of the boundary where the granite plutons intrude to the metasedimentary rocks. In our study area, the Devonian granite intrudes the metasedimentary units where groundwater As exceedance rates are high. However, probably due to the small size of granite plutons (short axis <3 km) and that shallow plutons are closer to water sample points vertically than horizontally, this relationship was not evident (Figure 1.5).

The different groundwater As occurrence rates found in bedrock units at intermediate scale in the greater Augusta, Maine area, likely reflect in part bedrock geochemical composition differences. At the regional scale of 10^2-10^3 km, geochemical composition of bedrock plays a dominant role on bedrock well water As distribution in New England, among many other factors (AYOTTE et al., 2006). Further work to characterize the composition of the bedrock samples at the intermediate scale (10^0-10^1 km) is much needed.

1.3.6 Consideration of sampling density

Our results suggest that a sampling density of 1-5 per km^2 is sufficient to capture the spatial pattern of groundwater As distribution in fractured bedrock aquifers of New England at the intermediate scale (10^0-10^1 km) using interpolation methods. In addition to the statistically meaningful differences of As occurrence in each bedrock unit, a 6 times higher sampling density in four representative cluster areas did not change the ranking of the As occurrence significantly (Table 1.2). Furthermore, the kriged probability is consistent with the observed As occurrence from low, median to high in these clusters at km scales.

At local scales ($\leq 10^{-1}$ km), the spatial variance of groundwater As distribution is very large, and generally increases with increasing median As concentrations (Table 1.1). The inter-quartile range of As distribution based on high density sampling in 2007 was 31 and 38 μg/L for Manchester and Litchfield, respectively, while median [As] was 22 μg/L and 15 μg/L, respectively. The inter-quartile range was 10 μg/L in Sidney with a median [As] of 4.1 μg/L. and is only 4.3 μg/L in Chelsea with a median [As] of 0.9 μg/L. The higher sampling density of 24-42 per km^2 in Sidney and Chelsea may result in the smaller inter-quartile range compared to Manchester and Litchfield with lower sampling density of 5-6 per km^2. This possibility can only be tested if the sampling density in Manchester or Litchfield is further increased. This is presently not possible because of the absence of wells (also housing) in this area. Nevertheless, our results suggest that to identify the As spatial pattern at local scales of $\leq 10^{-1}$ km, higher sampling density of tens of wells per km^2 is desirable.

This large As variability at local scales was also seen in unconsolidated sedimentary aquifers because of the heterogeneity of aquifer media and complicated geochemical mechanisms controlling As mobilization. In fractured bedrock aquifers, this variance could be further enlarged by the anomalous flow paths of ground water as well as the poor connectivity and magnitude of fractures that water flows through at scales of 100 meters. Considering this, the spatial dependence of As concentrations in fractured bedrock aquifers at scales of $\leq 10^{-1}$ km should not be used to interpolate As distribution at intermediate scales.

1.3.7 Arsenic distribution with depth

The median depth of wells in each bedrock unit (Table 1.5) is not significantly different. The p value of Kruskal-Wallis rank sum test for all the bedrock units is 0.32. The p values of Mann-Whitney U test between each pair of the bedrock units are all greater than 0.07.

Table 1.5 Median depth of wells in each bedrock unit of Greater Augusta

Bedrock unit	Number of samples	Median depth (meter)
Ss	131	62
Sw	158	60
SOv	168	55
D	59	61
OZc	23	49

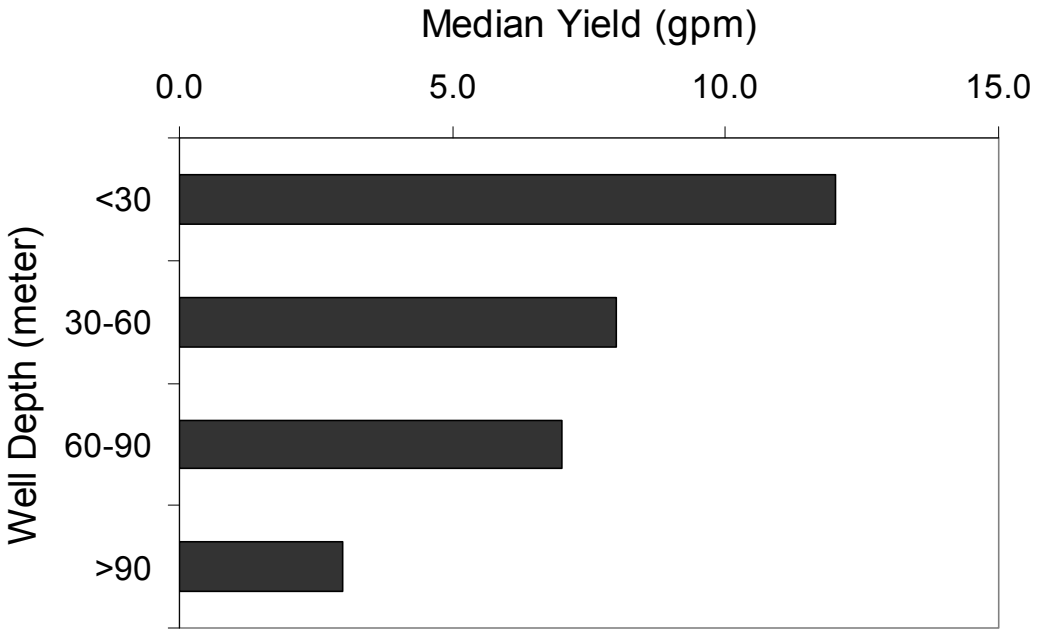


Figure 1.6 Yield vs. well depth in fractured bedrock aquifers of Greater Augusta

Well yield decreased from shallow to deep (Figure 1.6). This suggests that the transmissivity or density of fractures at depth are not as high as shallow ones in bedrock

aquifers, so the supply to meet instantaneous demand is maintained by the storage of water in the bore hole.

The depth pattern of groundwater As is analyzed for 539 drilled bedrock wells (Figure 1.7). This analysis excluded 26 dug wells that were either indicated by homeowners or were <9 meter in depth. The wells are classified into four groups according to the well depth. Well water [As] were found to increase with depth, both in terms of median [As] and percentage exceeding 10 μg/L. Statistical analysis shows that the increasing trend of the median [As] and percent of [As] >10 μg/L with depth is significant, except between the two deepest groups of 60-90 meter and > 90 meter. For the median [As], the chi-squared value of Kruskal-Wallis rank sum test for all the groups is 19.69 with the p value of 0.0002. The p values of Mann-Whitney U test between the group <30 meter and the group 30-60 meter, between the group 30-60 meter and the group 60-90 meter are <0.02, except the p value between the group 60-90 meter and the group >90 meter is 0.37. For the percent of [As] >10 μg/L, the chi-squared value of Kruskal-Wallis rank sum test for all the groups is 15.10 with the p value of 0.002. The p values of Mann-Whitney U test between the group <30 meter and the group 30-60 meter, between the group 30-60 meter and the group 60-90 meter are < 0.03, except the p value between the group 60-90 meter and the group >90 meter is 0.15.

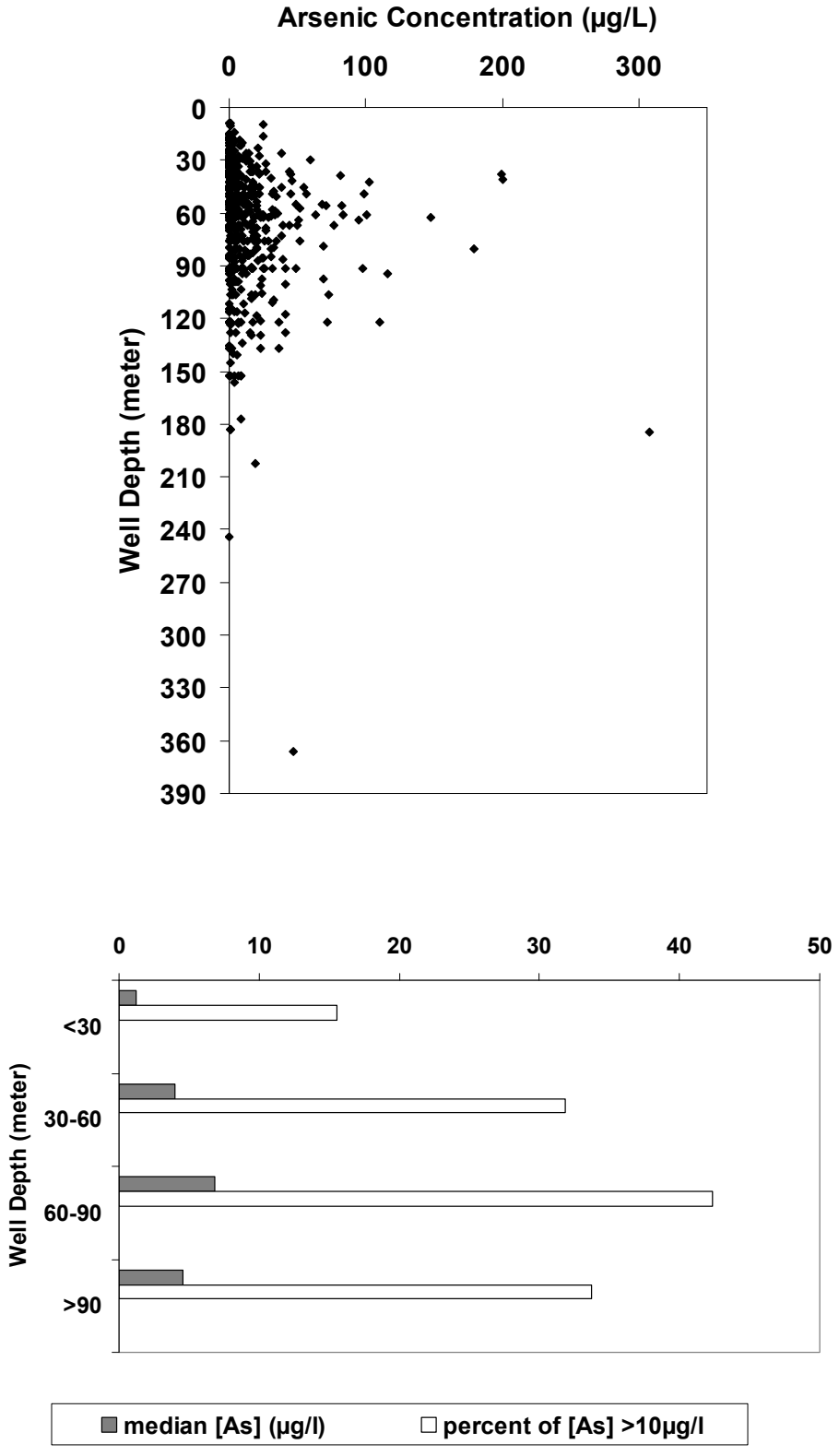


Figure 1.7 Relation of arsenic occurrence to well depth in 2006 sampling

1.3.8 Limitations

Temporal variation of groundwater arsenic concentrations was evaluated in limited samples (Chapter 2). Nevertheless, the temporal change of As concentrations have previously been found to be insignificant or at least much lower than the spatial variation (AYOTTE et al., 2003; COLT et al., 2002; KARAGAS et al., 2002).

Chapter 2 Geochemical Characteristics of High Arsenic Groundwater in Fractured Bedrock Aquifers in Greater Augusta, Maine, USA

Abstract

Thirty one percent of private well water samples (n=790) collected in 2006 from fractured bedrock aquifers in the greater Augusta area, Maine were found to contain more than 10 μg/L of arsenic, with the highest occurrence rate in the Silurian calcareous pelite and sandstone bedrock units. In 2007, an additional 331 samples were obtained from four towns representing low to high arsenic occurrence, and a subset of those (n=36) that were re-visits of 2006 samples showed little temporal change. The elevated arsenic concentrations were more frequently found in samples with high pH (>7), low dissolved oxygen (< 1 mg/L), low nitrate, and low chloride (<30 mg/L). A logistic regression model showed that bedrock geology, soil arsenic content, pH, dissolved oxygen, nitrate and sulfate played important roles on groundwater arsenic concentrations in the study area. The strong association of groundwater arsenic with fluoride and molybdenum, and the correlation with bedrock geology and soil arsenic distribution suggested a sulfidic source of groundwater arsenic, and a complex mobilization mechanism of oxidation of arsenic-rich sulfide, adsorption on iron minerals, pH dependent desorption and neutralization by calcite along the groundwater flow path. This research contributes to the understanding of trace metal source and mobilization mechanisms in fractured bedrock aquifer systems, and assists remediation of arsenic contamination in drinking water.

2.1 Introduction

Elevated arsenic in groundwater (greater than 10 μg/L, World Health Organization guideline value for drinking water) has been recognized as a worldwide public health problem. In the United States, millions of people are subjected to risks of skin, bladder, lung and other cancers or diseases from arsenic in drinking water from private wells (KARAGAS et al., 2002). In New England, especially the states of Maine and New Hampshire, the arsenic problem in groundwater is severe not only because of the high arsenic occurrence rate but also the fact that most rural residents rely solely on fractured bedrock aquifers for drinking water. In New Hampshire, approximately 120,000 (or 25%) of the total 474,606 households used domestic bedrock wells. About 12% of these wells were estimated to have more than 10 μg/L of arsenic (PETERS et al., 2006), which is also the U.S. Environmental Protection Agency (EPA) Maximum Contaminant Level (MCL) for arsenic. In Maine, approximately 549,000 (or 43%) of the total 1,270,000 population used domestic bedrock wells (HUTSON et al., 2004), and 44.7 % of these wells were estimated to exceed 5 μg/L of arsenic (AYOTTE et al., 2006).

While most arsenic affected aquifers around the world are sedimentary, more attentions have been recently turned to arsenic contamination in bedrock aquifers, such as in New England (AYOTTE et al., 2003; LIPFERT et al., 2006; MARVINNEY et al., 1994; PETERS, 2008; PETERS and BLUM, 2003; SIDLE et al., 2001), North Carolina (PIPPIN et al., 2006), British Columbia, Canada (BOYLE et al., 1998), Bavaria, Germany (HEINRICHS and UDLUFT, 1999), Ankobra Basin, Ghana (KORTATSI, 2007), and Central Lesvos, Greece (ALOUPI et al., 2009). The elevated arsenic in these aquifers has been attributed to

the release of arsenic-rich sulfide minerals, such as arsenopyrite and arsenian pyrite in meta-sedimentary or volcanic/volcaniclastic bedrocks via oxidation.

In New England, arsenic occurrence on the regional scale has been shown to depend on many factors, including bedrock geology, arsenic levels in stream sediments, geochemical factors, proximity to granitic intrusions, and hydrologic and landscape variables related to groundwater residence time (AYOTTE et al., 2006). At the very local scale of $\leq 10^0$ km, arsenic distribution in fractured bedrock aquifers consisted of sulfidic schist with granitic to dioritic intrusions was largely affected by fracture characteristics, hydrogeology and water chemistry (LIPFERT et al., 2006), although no quantitative relationship with any of these factors could be established in part due to the well known complexity of water flow and chemical transport in bedrock aquifer systems (DAY-LEWIS et al., 2000).

This study is motivated to understand the hydrogechemical factors that are related with groundwater arsenic occurrence at local scales of 10^0 to 10^2 km. Our recent study in the greater Augusta area, Maine has shown that arsenic occurrence rate is different among the major bedrock formations and is the highest in the meta-sedimentary sequences (YANG et al., 2009). This research builds on the findings and further reports on the geochemical characteristics of high arsenic groundwater. The correlation between groundwater arsenic and hydrogeochemical parameters is examined by statistical analyses and a step-wise logistic regression model to understand the source and mobilization mechanisms of groundwater arsenic in fractured bedrock aquifers. Because the bedrock geology of greater Augusta, Maine is representative of that of New England, the findings have implications for U.S. EPA to outreach and educate communities about

hazards in New England, for municipalities to plan for water resources and housing development, and for homeowners to select remediation methods to lower arsenic exposure.

2.2 Materials and Methods

2.2.1 Study area

The greater Augusta area in Kennebec County, Maine encompasses thirteen towns and an area of 1,135 km^2. Approximately 70% of the 23,773 households used private wells as their only water source (UNITED-STATES-CENSUS-2000).

There are five major geologic formations (OSBERG et al., 1985) from west to east in the study area (Figure 2.1), with high to low arsenic occurrence rates in the order of Ss, Sw, SOv, D and OZc (YANG et al., 2009). It was thought that the sediment of three meta-sedimentary formations (Ss, Sangerville Formation; Sw, Waterville Formation; SOv, Vassalboro Formation) was deposited in anoxic marine basins during Silurian (443-417 Ma BP) and contained abundant sulfide minerals (HANSON and BRADLEY, 1989).

2.2.2 Groundwater sample collection and analysis

Unfiltered groundwater samples (n=790) were collected from private wells from June to September in 2006. An additional 331 well samples were collected from June to August in 2007 from four clusters (Figure 2.2) in the towns of Chelsea, Sidney, Litchfield and Manchester representative of low to high arsenic occurrence, with 36 well samples being re-visited to assess temporal variability of groundwater arsenic concentrations.

Arsenic and other 32 elements were analyzed by High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS) (YANG et al., 2009). Anions including fluoride, bromide, chloride, nitrate, nitrite, phosphate and sulfate were measured by Ion-exchange Chromatography (IC) following EPA method 300. A subset of groundwater samples (n=105) from 2006 sampling throughout the study area, and all the water samples (n=331) from 2007 sampled clusters were analyzed for alkalinity using the Gran titration method.

2.2.3 Soil sample collection and analysis

Soil samples (n=58) were collected throughout the study area with a sampling density of 1 per 20 km^2 in 2007 and 2008 summers. Most samples were collected from the thin soil layer immediately above bedrock outcrops, which were considered to represent the weathered products of bedrock. Two series of soil cores (n=9) from the land surface to approximately 70 cm depth were collected using hand auger from the towns of Chelsea and Manchester, with horizon C sections separated out to represent the sampled core sites.

Reductive leaching (1 M hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) in 25% acetic acid (CH_3COOH)) (CHESTER and HUGHES, 1967) and oxidative leaching (concentrated nitric acid (HNO_3) and 30% hydrogen peroxide (H_2O_2)) (EPA, 1996) were performed to estimate the fraction of labile arsenic that can be released into groundwater under favorable conditions. Approximately 100-200 mg of the samples were digested in a microwave digestion system using mixed concentrated perchloric acid, hydrofluoric acid and nitric acid ($HClO_4$-HF-HNO_3) (ZHENG et al., 2003) to determine the arsenic

concentrations in bulk soils. The leachates and digests were analyzed for arsenic by HR ICP-MS (Table 2.1).

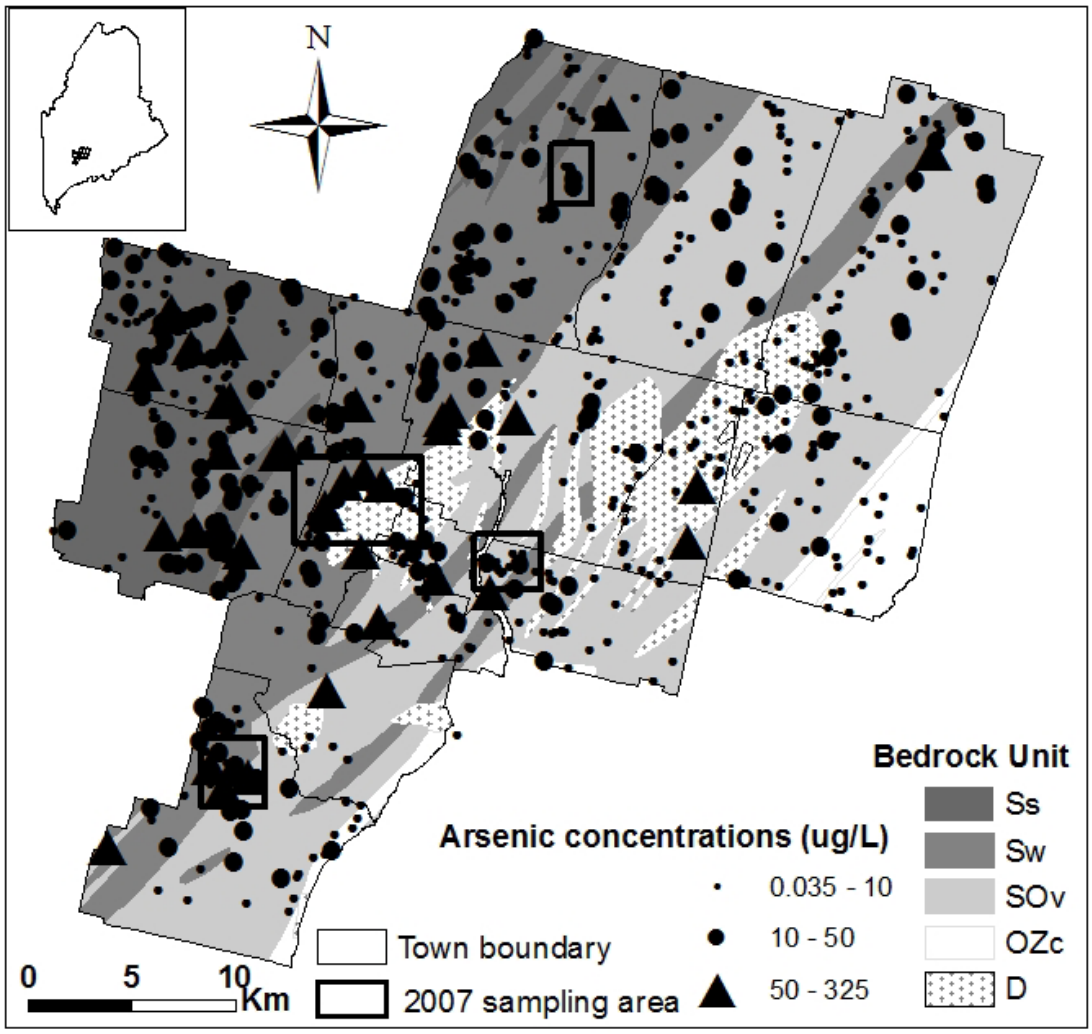
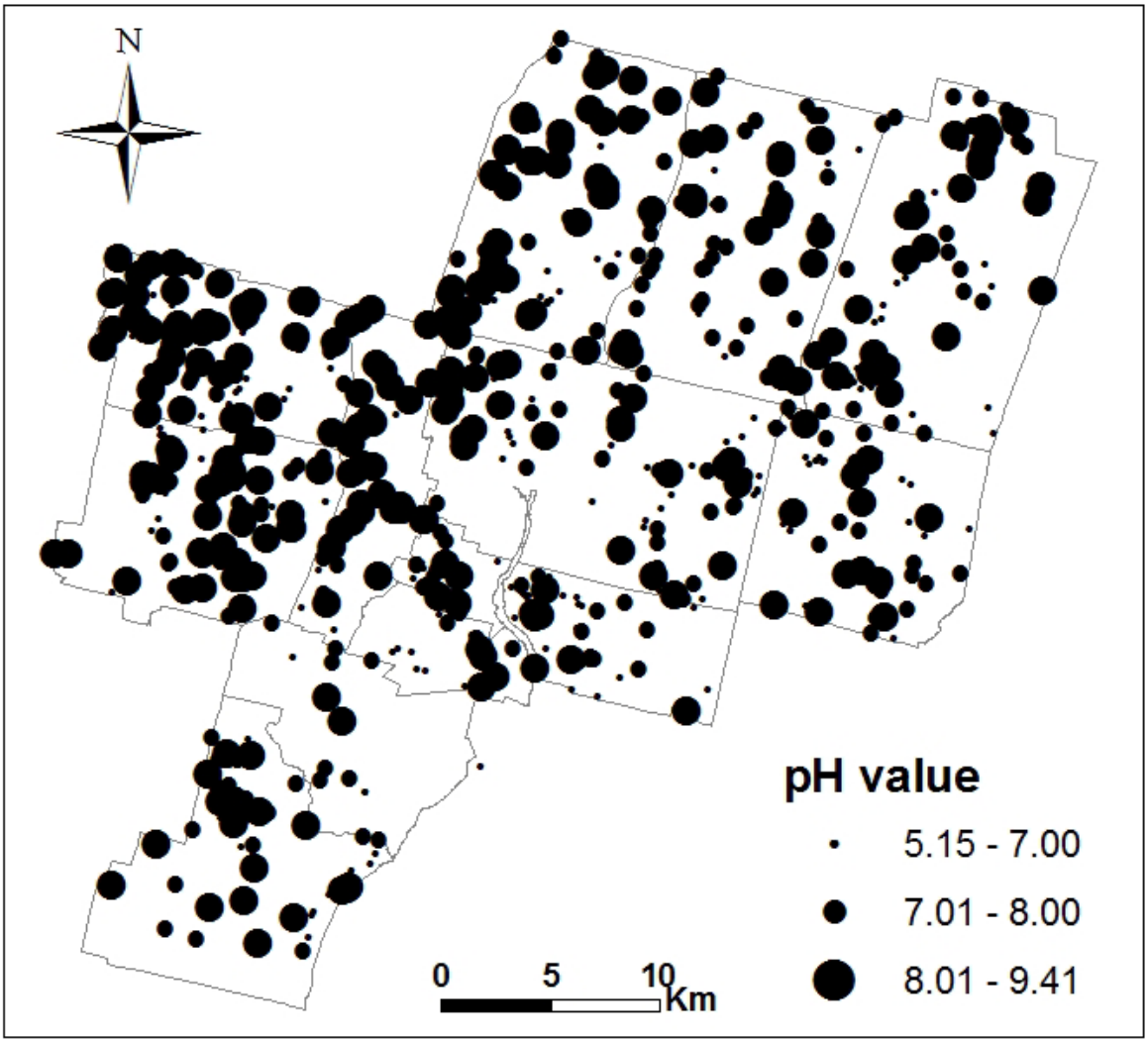
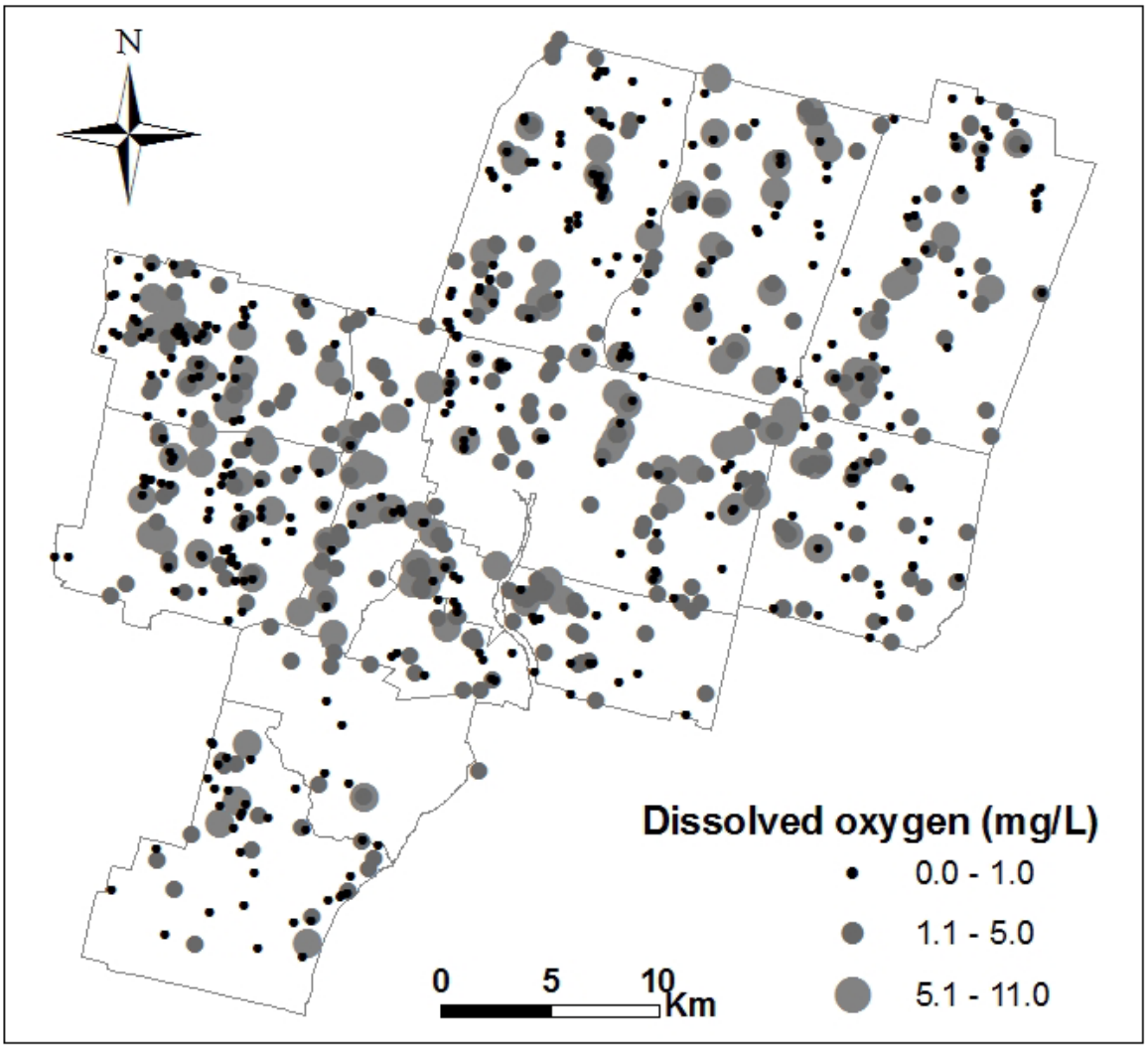


Figure 2.1 Groundwater arsenic distribution plotted on simplified bedrock geology map, and distributions of pH, dissolved oxygen, nitrate, fluoride, and molybdenum in the greater Augusta area, Maine in 2006 sampling

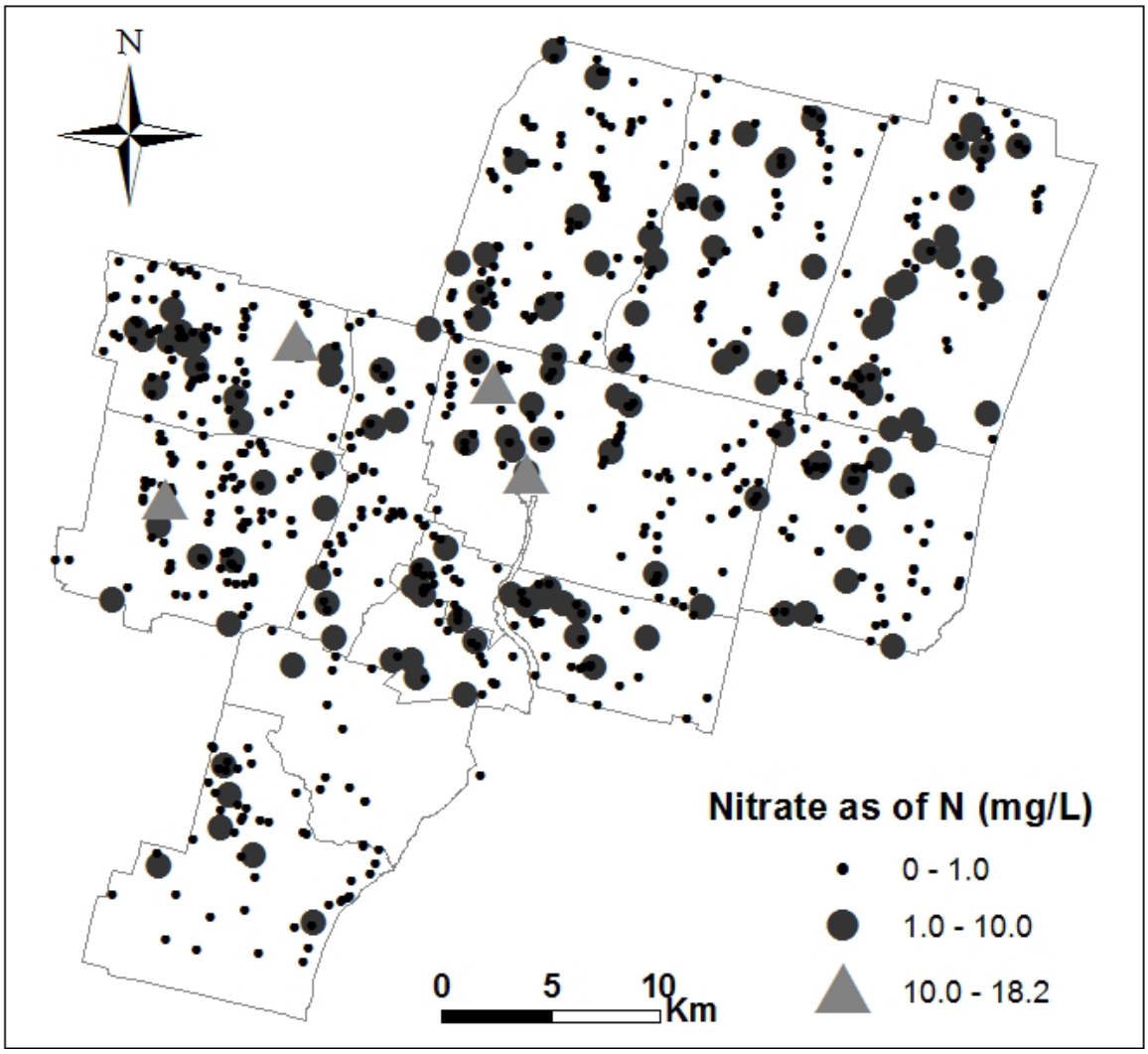
A. Groundwater arsenic distribution plotted on simplified bedrock geology map



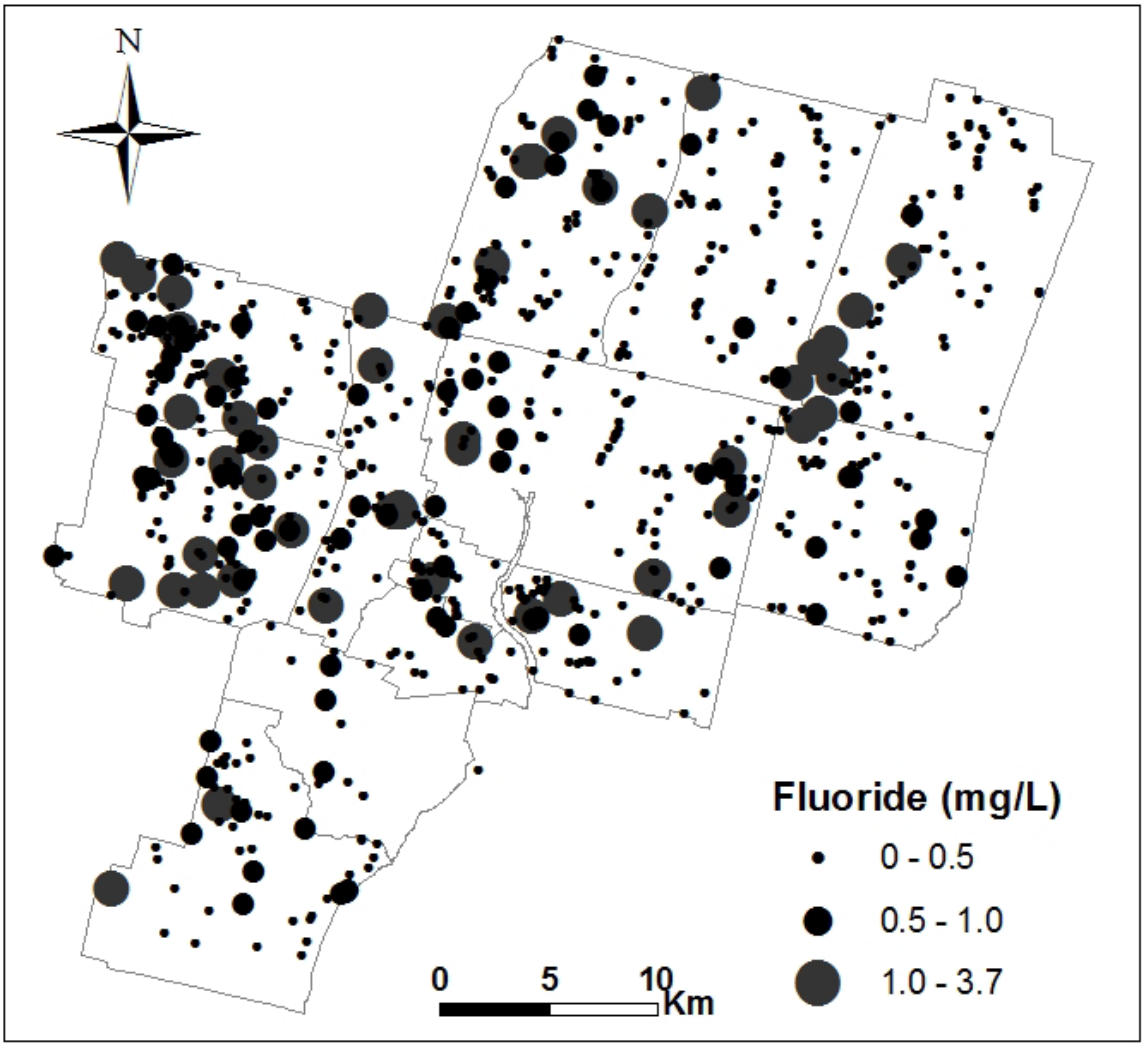
B. Distributions of groundwater pH in the greater Augusta area, Maine in 2006 sampling



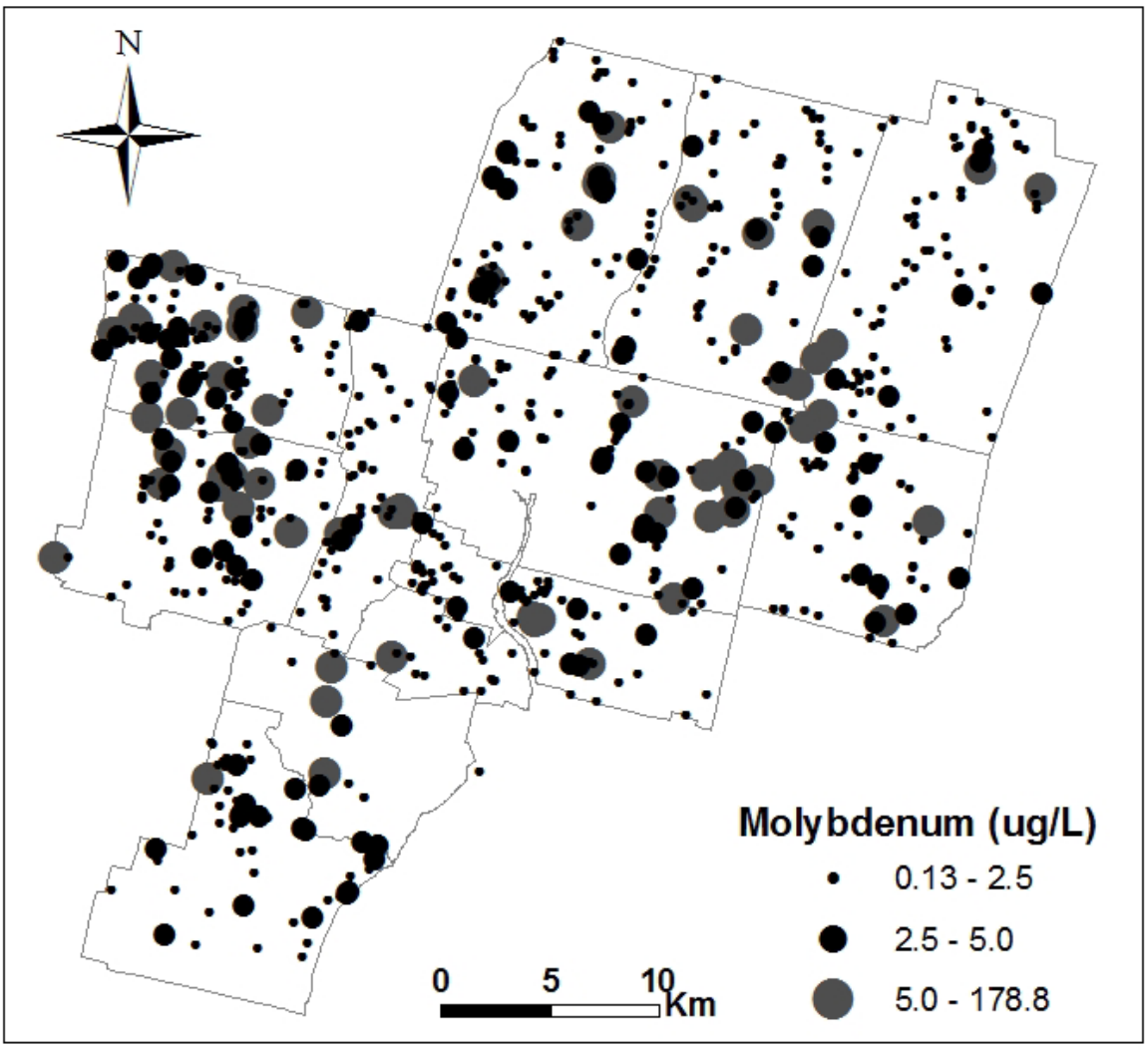
C. Distributions of groundwater dissolved oxygen in the greater Augusta area, Maine in 2006 sampling



D. Distributions of groundwater nitrate (as of nitrogen) in the greater Augusta area, Maine in 2006 sampling

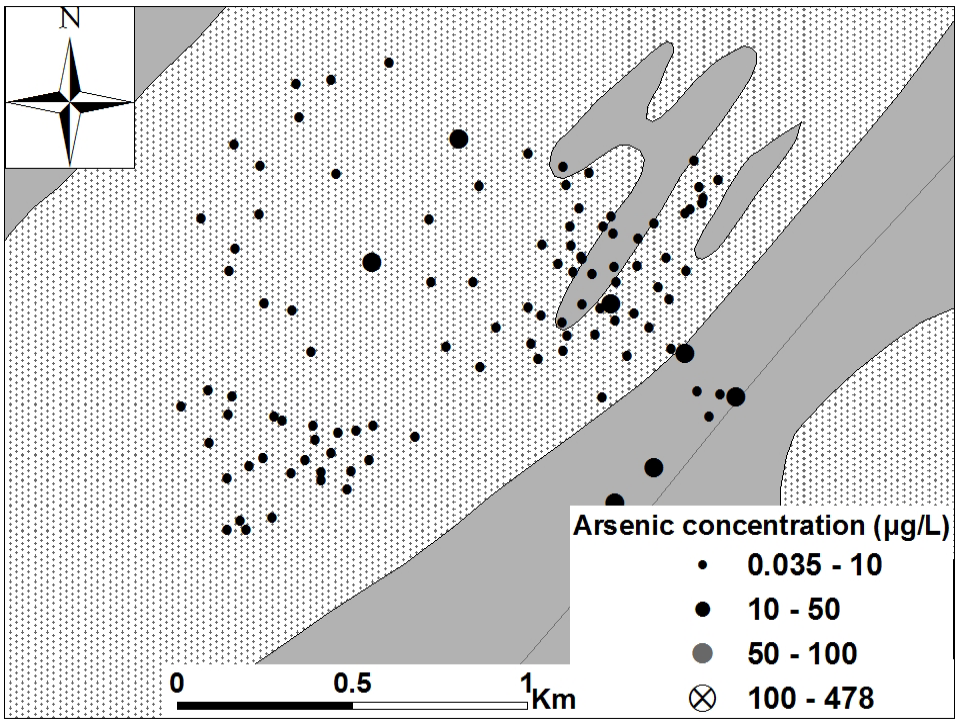


E. Distributions of groundwater fluoride in the greater Augusta area, Maine in 2006 sampling

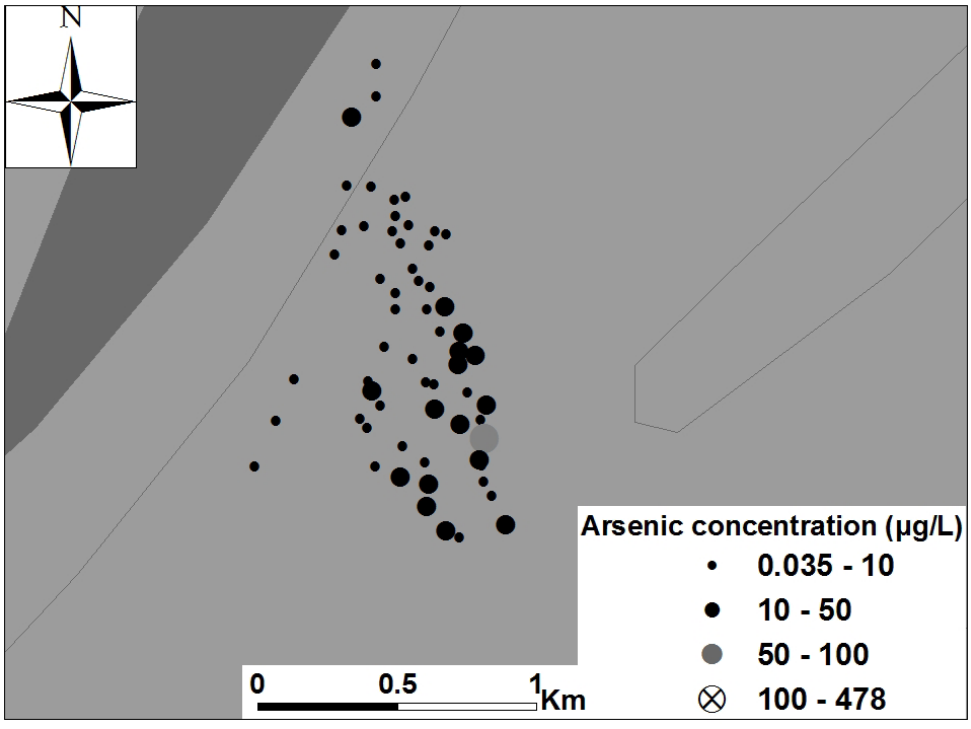


F. Distributions of groundwater molybdenum in the greater Augusta area, Maine in 2006 sampling

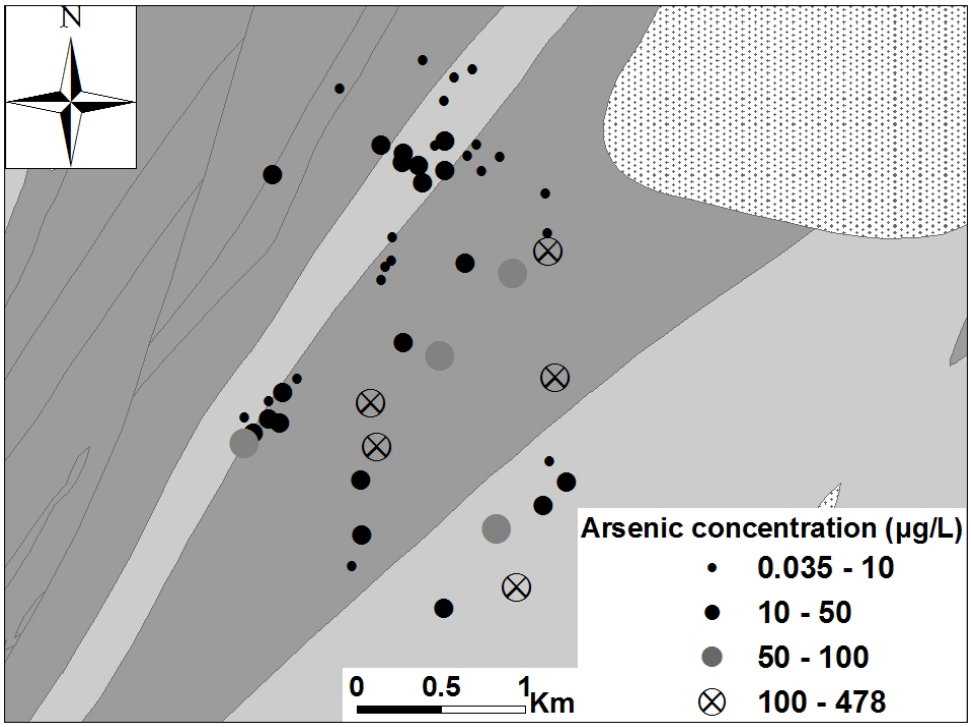
A


N
Arsenic concentration (µg/L)
0.035 - 10
10 - 50
50 - 100
100 - 478
0
0.5
1
Km

B


N
Arsenic concentration (µg/L)
0.035 - 10
10 - 50
50 - 100
100 - 478
0
0.5
1
Km

C



D

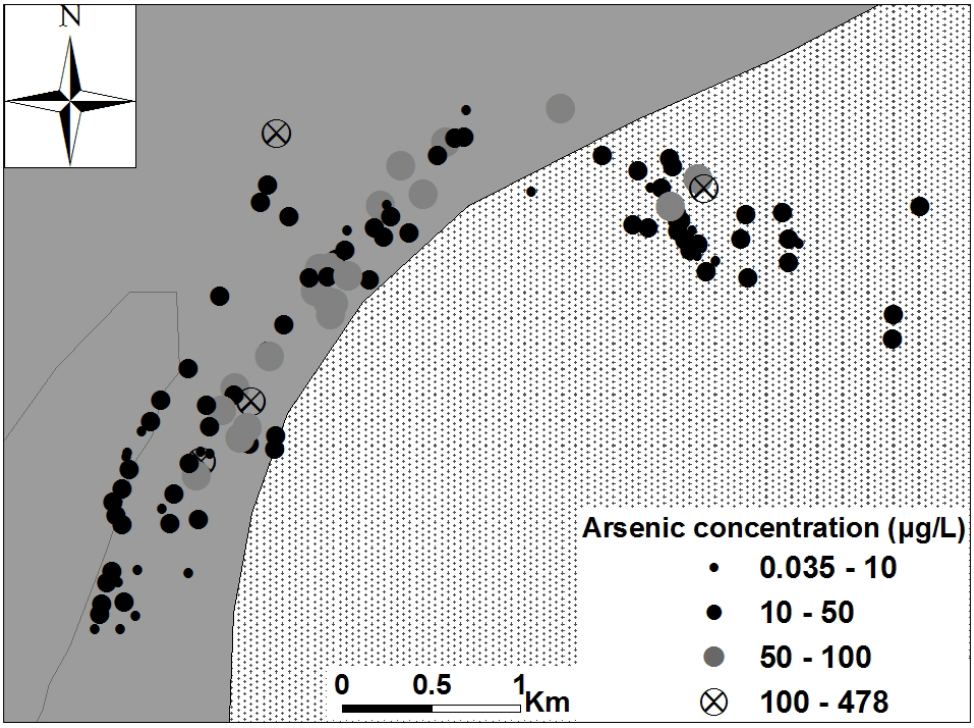


Figure 2.2 Groundwater arsenic distributions in 2007 sampled clusters plotted on simplified bedrock geology map

* Bedrock units refer to Figure 2.1-A

A – Chelsea; B – Sidney; C – Litchfield; D- Manchester

Table 2.1 Leachable and digested arsenic concentrations (mg/kg) in soil samples

Sample	reductive leachable As	oxidative leachable As	total digested As
M1-C	2.1	5.0	ND
M2-C	4.2	11.6	ND
M3-C	4.4	11.7	ND
M4-C	5.6	29.4	ND
M5-C	3.1	6.9	ND
C1-C	0.6	9.8	ND
C2-C	1.2	12.5	ND
C3-C	1.2	15.3	ND
C4-C	0.7	8.8	ND
7S001	22.0	92.5	79.2
7S002	2.4	19.5	17.3
7S003	1.7	27.5	28.3
7S007.5	0.7	8.0	8.9
7S018	6.4	113.2	144.4
7S019	1.4	5.9	6.0
7S020	2.3	4.6	10.2
7S021	3.2	12.0	12.7
7S022	4.1	36.8	36.1
7S023	2.6	5.6	14.7
7S024	0.9	7.6	9.6
7S025	2.2	13.0	18.2
7S026	2.0	34.4	41.3
7S027	1.7	95.9	81.9
7S029	0.4	8.4	12.4
7S032	0.5	9.5	18.5
7S035	0.5	8.7	18.3
7S042	0.4	10.5	18.2
7S043	0.4	8.9	14.0
7S050	6.1	193.4	176.5
S8001	10.5	25.3	23.0
S8002	10.8	24.6	36.9
S8003	1.5	13.2	23.8
S8004	4.4	11.0	16.7
S8005	2.0	12.4	19.5
S8006	0.9	14.4	13.3
S8007	1.0	8.5	16.5
S8008	4.4	8.5	10.5
S8009	2.1	14.4	9.7
S8010	1.9	54.2	39.1
S8011	0.4	11.4	13.6
S8012	6.2	13.4	22.2
S8013	2.0	13.9	22.3
S8014	7.0	15.5	27.1
S8015	2.2	9.8	13.8
S8016	12.9	16.9	25.3
S8017	1.1	13.4	21.2
S8018	4.7	25.5	24.5
S8019	1.6	16.3	25.0
S8020	4.1	19.5	38.0
S8021	9.6	82.0	88.8
S8022	3.4	38.6	34.5
S8023	1.6	17.9	17.7
S8024	5.0	11.4	17.6
S8025	3.7	14.9	14.8
S8026	6.3	31.3	30.4
S8027	24.4	58.6	33.4
S8028	8.0	72.7	63.0
S8029	1.3	39.6	35.4
S8030	0.6	20.5	23.7
S8031	0.5	9.3	15.8
S8041	0.6	13.7	17.0
S8042	0.3	4.9	11.3
S8043	0.3	2.3	9.8
S8044	0.3	1.3	9.4
S8045	0.2	2.8	10.7
S8046	0.3	7.3	9.9
S8047	1.2	8.7	16.0

2.2.4 Spearman's correlation

Non-parametric Spearman's rank correlation coefficient (ρ) between groundwater arsenic and other hydrogeochemical parameters was calculated because the data did not follow normal distributions. The test significance (p value) was determined using two tailed student's *t* test with n-2 degrees of freedom.

2.2.5 Logistic regression model

A stepwise logistic regression method was conducted to examine the controlling parameters of groundwater arsenic using the 2006 date set. The groundwater arsenic concentrations were converted into binary data using a threshold of 10 μg/L and then used as the response variable. All the available hydrogeochemical factors were used as explanatory variables, including well type (dug well or drilled well), well depth, elevation, water temperature, pH, dissolved oxygen, bedrock unit, major cations and anions, alkalinity, Fe, Mn and other trace elements, and soil arsenic content. First, each factor was tested if it could be used as an indicator of elevated groundwater arsenic concentrations using a univariable logistic regression. Those factors with higher statistical significance (p value <0.05) and geochemical meaning were included in a multivariable logistic regression model, the Hosmer and Lemeshow goodness-of-fit test was used to verify the model. Only significant parameters from the multivariable model were retained in the final model to predict arsenic exceedance rate, with the model verified by the Hosmer and Lemeshow goodness-of-fit test again. The regression models

and tests were performed in R program. The model results were calibrated using the 2007 data set of four clustered samplings.

2.3 Results and Discussions

2.3.1 Correlation between arsenic and geochemical parameters

Groundwater arsenic shows a positive correlation with pH (ρ = 0.54) and a negative correlation with dissolved oxygen (ρ = -0.35) (Table 2.3 and Figure 2.3). This is consistent with the regional study where the elevated arsenic concentrations were more frequently found in samples with high pH (AYOTTE et al., 2003).

There is no apparent correlation between arsenic and major cations in 2006 sampling. There is only a very weak negative correlation between arsenic and Mg, K and Ca in the Litchfield cluster of 2007 sampling. Elevated arsenic levels are more often detected in water samples with lower chloride (Figure 2.3), which is also reflected by the negative correlation between arsenic and chloride (ρ = -0.23) (Table 2.3). Neither alkalinity nor sulfate shows correlation with arsenic.

Positive correlations are found between arsenic and fluoride in both 2006 sampling (ρ = 0.39) and in all the 4 clusters sampled in 2007 (ρ= 0.33 ~ 0.64). There are negative correlations between arsenic and nitrate in 2006 and 2007 samplings (ρ = -0.31 ~ -0.66) (Table 2.3 and Figure 2.3). Molybdenum displays highly significant (p value < 0.001) and positive correlations with arsenic in 2006 and 2007 samplings (ρ = 0.38 ~ 0.67) (Table 2.3 and Figure 2.3). No correlation between arsenic and iron, manganese, or other trace elements is observed.

Table 2.2 Summary of physic-chemical parameters of groundwater in 2006 and 2007 sampling in the greater Augusta area, Maine

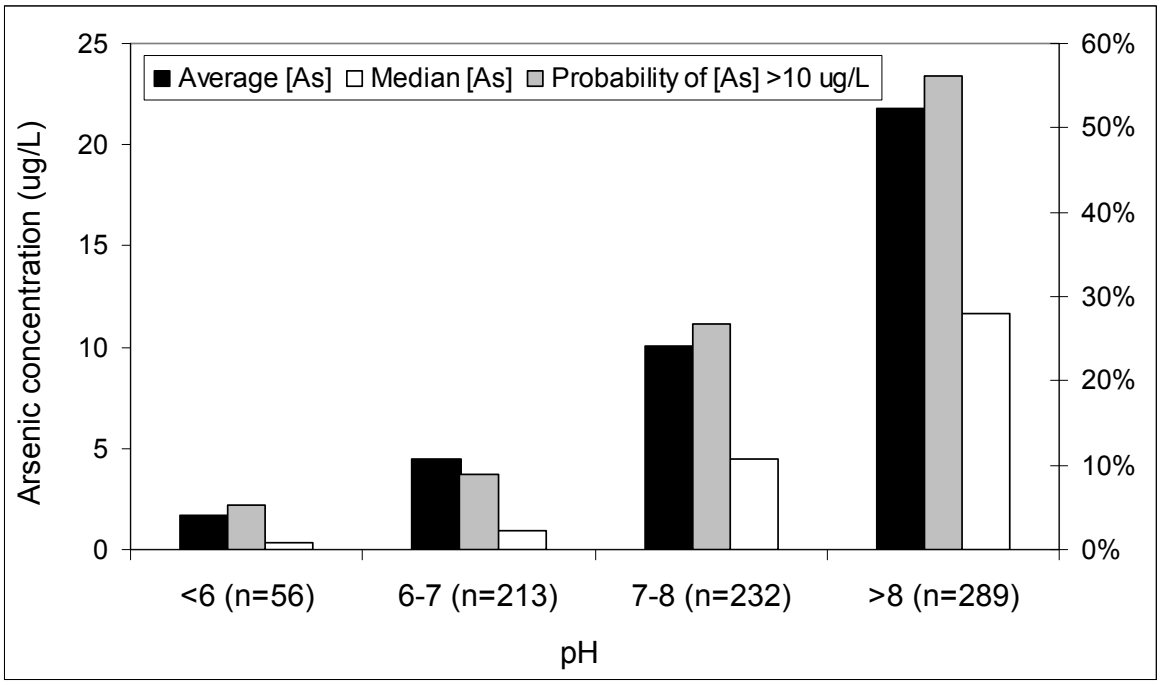
Parameter	Unit	2006 Greater Augusta		2007 Chelsea		2007 Sidney		2007 Litchfield		2007 Manchester	
		n	median	n	median	n	median	n	median	n	median
well depth	foot	565	192	51	184	27	200	26	212	55	185
yield	gpm	393	7.0	33	6.0	17	7.0	21	10.0	29	8.0
temperature	deg. C	790	10.5	107	10.7	62	10.6	49	10.6	113	10.4
pH		790	7.59	107	6.80	62	8.17	49	7.78	113	8.27
DO	mg/L	781	1.5	107	2.0	62	0.6	49	1.0	113	1.0
Na	mg/L	789	10.9	107	13.2	62	8.4	49	8.3	113	8.3
Mg	mg/L	789	3.2	107	4.3	62	2.0	49	1.4	113	1.6
Si	mg/L	789	8.7	97	7.4	17	6.8	43	6.4	108	5.7
K	mg/L	789	2.3	107	3.0	62	1.5	49	2.1	113	1.9
Ca	mg/L	789	30.8	107	36.9	62	18.2	49	25.8	113	17.6
alkalinity	mmol/L	105	1.28	107	1.45	62	1.17	49	1.27	113	1.28
Cl	mg/L	788	9.67	107	43.96	62	8.09	49	11.79	113	3.57
SO4	mg/L	788	14.62	107	17.51	62	19.41	49	15.36	113	8.62
F	mg/L	788	0.10	107	0.04	62	0.39	49	0.09	113	0.36
NO3	mg/L	788	0.91	107	4.54	62	0.00	49	0.00	113	0.15
TDS	mg/L	790	105.1	107	241.2	62	148.6	49	172.3	113	136.1
As	ug/L	789	3.82	107	0.93	62	4.12	49	14.55	113	22.23
Fe	ug/L	789	113.2	107	47.2	62	125.9	49	92.0	113	90.6
Li	ug/L		ND	107	11.4	62	3.3	49	7.0	113	8.3
Be	ug/L		ND	107	0.0	62	0.0	49	0.0	113	0.0
V	ug/L	789	0.3	107	0.6	62	0.3	49	0.4	113	0.6
Cr	ug/L	789	0.6	98	1.4	62	0.2	49	0.3	32	7.6
Mn	ug/L	789	10.4	107	2.9	62	23.5	49	12.5	113	4.6
Co	ug/L	789	0.1	107	0.2	62	0.1	49	0.1	113	0.1
Ni	ug/L	789	3.8	107	7.3	62	2.3	49	2.1	113	11.8
Cu	ug/L	789	9.5	107	26.1	62	4.0	49	6.1	113	13.7
Zn	ug/L	789	10.6	107	15.8	62	11.0	49	11.7	113	10.8
Sr	ug/L	789	101.2	107	121.3	62	145.9	49	84.2	113	78.1
Rb	ug/L		ND	107	6.4	62	2.6	49	6.1	113	2.7
Mo	ug/L	789	1.2	107	0.5	62	2.5	49	0.5	113	2.0
Cd	ug/L		ND	107	0.1	62	0.0	49	0.0	113	0.0
In	ug/L	789	0.0	107	0.0	62	0.0	49	0.1	113	0.0
Sn	ug/L	789	0.2	107	0.3	62	0.2	49	0.2	113	0.2
Sb	ug/L	789	0.1	107	0.1	62	0.1	49	0.1	113	0.1
Cs	ug/L	789	0.2	107	0.4	62	0.3	49	0.4	113	0.2
Ba	ug/L	789	3.6	107	4.5	62	1.9	49	5.0	113	0.9
Re	ug/L	789	0.3	107	0.0	62	0.0	49	0.0	113	0.0
Hg	ug/L	789	0.9	46	0.4		ND		ND	83	0.3
Tl	ug/L	789	0.2		ND		ND		ND		ND
Pb	ug/L	789	0.8	107	1.2	62	0.5	49	0.6	113	0.6
U	ug/L	789	1.1	107	7.7	62	0.5	49	2.0	113	7.0
Rn	pCi/L	786	2394	106	7478	62	1229	48	3416	113	6077
NO2	mg/L	788	<DL	107	<DL	62	<DL	49	<DL	113	<DL
Br	mg/L	788	<DL	107	<DL	62	<DL	49	<DL	113	<DL
PO4	mg/L	788	<DL	107	<DL	62	<DL	49	<DL	113	<DL

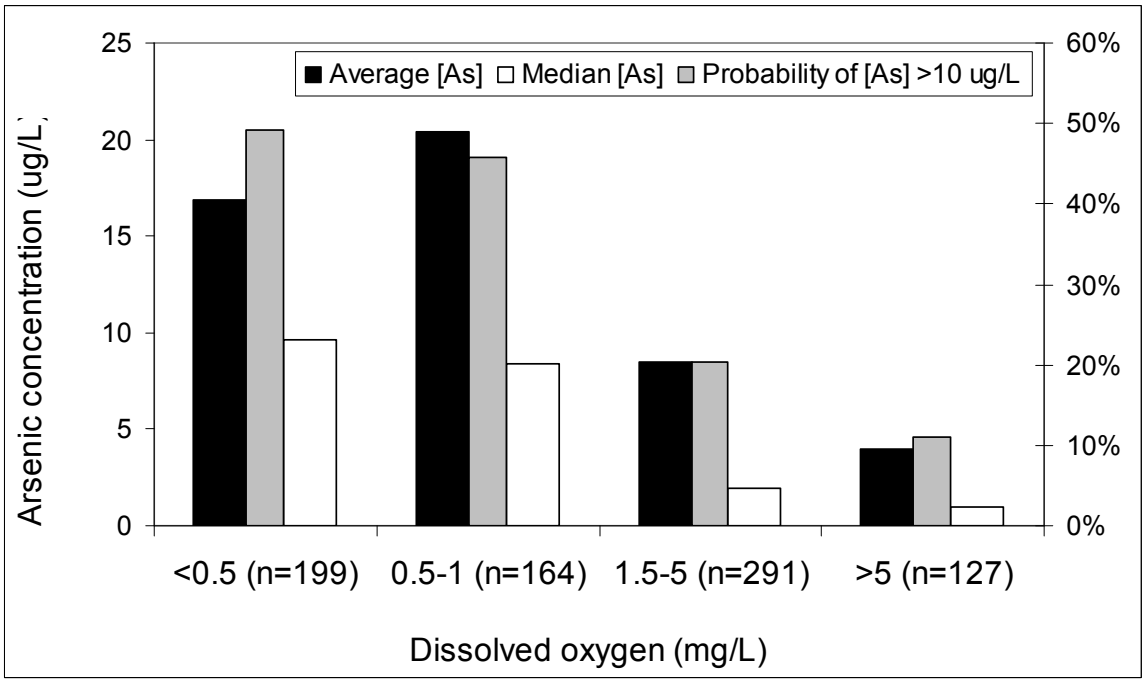
* ND – no data; <DL – below detection limit

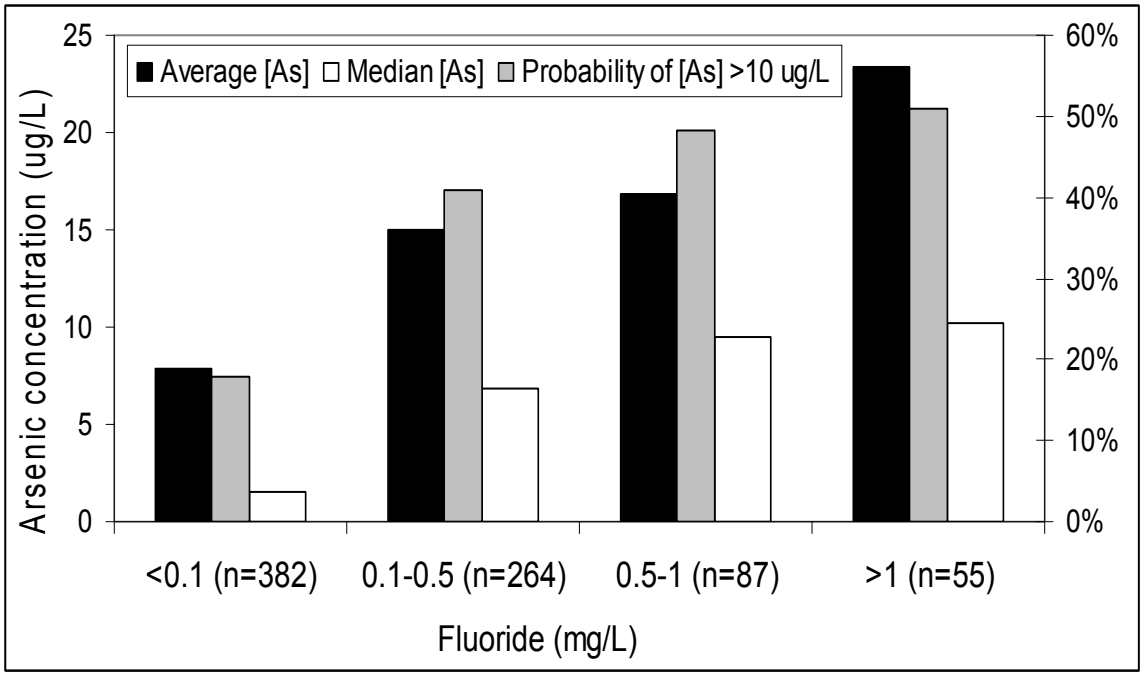
Table 2.3 Spearman's ρ values between arsenic and various parameters in groundwater samples from the greater Augusta aquifers

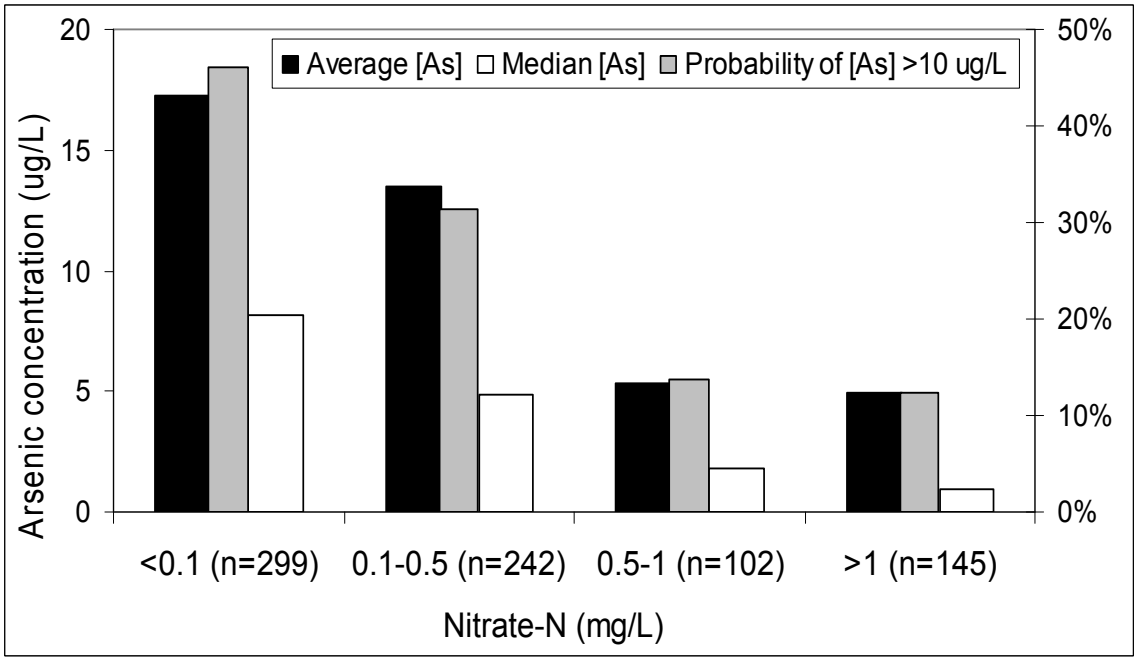
Parameter	2006	2007			
	Greater Augusta	Chelsea	Sidney	Litchfield	Manchester
well depth	0.21				
yield					
elevation		-0.26	-0.59		
temperature	0.09				
pH	0.54	0.48	0.50	0.64	0.43
dissolved oxygen	-0.35	-0.29	-0.43	-0.41	-0.36
Na					0.24
Mg	-0.11			-0.35	
Si	-0.14				
K	-0.12			-0.56	
Ca	-0.08			-0.64	-0.23
alkalinity					
chloride	-0.23	-0.42		-0.48	-0.23
sulfate		-0.24			
nitrate	-0.31	-0.41	-0.45	-0.66	-0.48
TDS	-0.18			-0.57	
cation-chloride	0.10	0.22	0.34		0.22
Fluoride	0.39	0.51	0.33	0.64	0.60
Nitrite					
Br					
P	0.22	0.26		0.55	
Li					
Be			-0.44		0.25
V	0.16				
Cr		-0.27			
Mn	0.08	0.24			0.30
Fe		0.27			
Co	-0.20			-0.39	
Ni	-0.10		-0.42		
Cu	-0.24	-0.27			
Zn					
Rb			-0.33		
Sr				-0.45	-0.23
Mo	0.38	0.46	0.67	0.61	0.61
Cd			0.39		0.27
In					
Sn					
Sb	0.14				0.23
Cs	0.20				0.26
Ba	-0.28	-0.23		-0.52	-0.30
Re	-0.07		0.36		
Hg					
Tl	0.15				
Pb	-0.22				
U	0.23	0.28	0.59		
Rn			-0.41		
cation-chloride vs. pH	0.17	0.49	0.30	0.33	

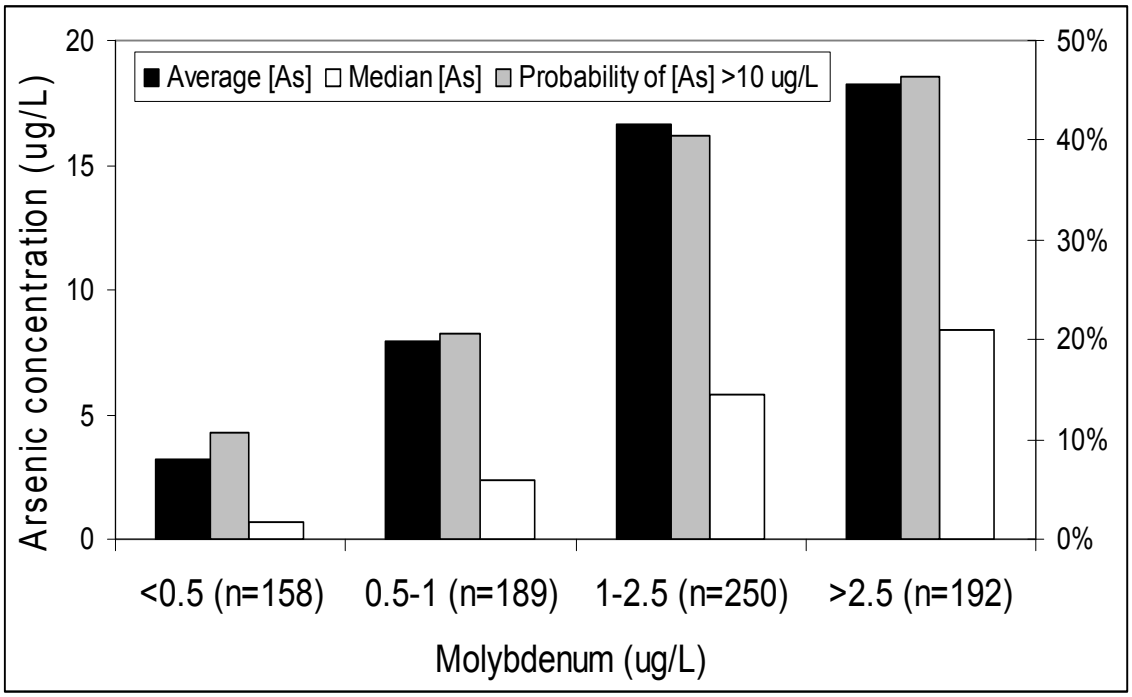
* Only values significant at $p < 0.05$ are shown.


Average [As]
Median [As]
Probability of [As] >10 ug/L
Arsenic concentration (ug/L)
25
20
15
10
5
0
60%
50%
40%
30%
20%
10%
0%
<6 (n=56)
6-7 (n=213)
7-8 (n=232)
>8 (n=289)
pH


Average [As]
Median [As]
Probability of [As] >10 ug/L
Arsenic concentration (ug/L)
25
20
15
10
5
0
60%
50%
40%
30%
20%
10%
0%
<0.5 (n=199)
0.5-1 (n=164)
1.5-5 (n=291)
>5 (n=127)
Dissolved oxygen (mg/L)


Average [As]
Median [As]
Probability of [As] >10 ug/L
Arsenic concentration (ug/L)
25
20
15
10
5
0
60%
50%
40%
30%
20%
10%
0%
<0.1 (n=382)
0.1-0.5 (n=264)
0.5-1 (n=87)
>1 (n=55)
Fluoride (mg/L)


Average [As]
Median [As]
Probability of [As] >10 ug/L
Arsenic concentration (ug/L)
20
15
10
5
0
50%
40%
30%
20%
10%
0%
<0.1 (n=299)
0.1-0.5 (n=242)
0.5-1 (n=102)
>1 (n=145)
Nitrate-N (mg/L)



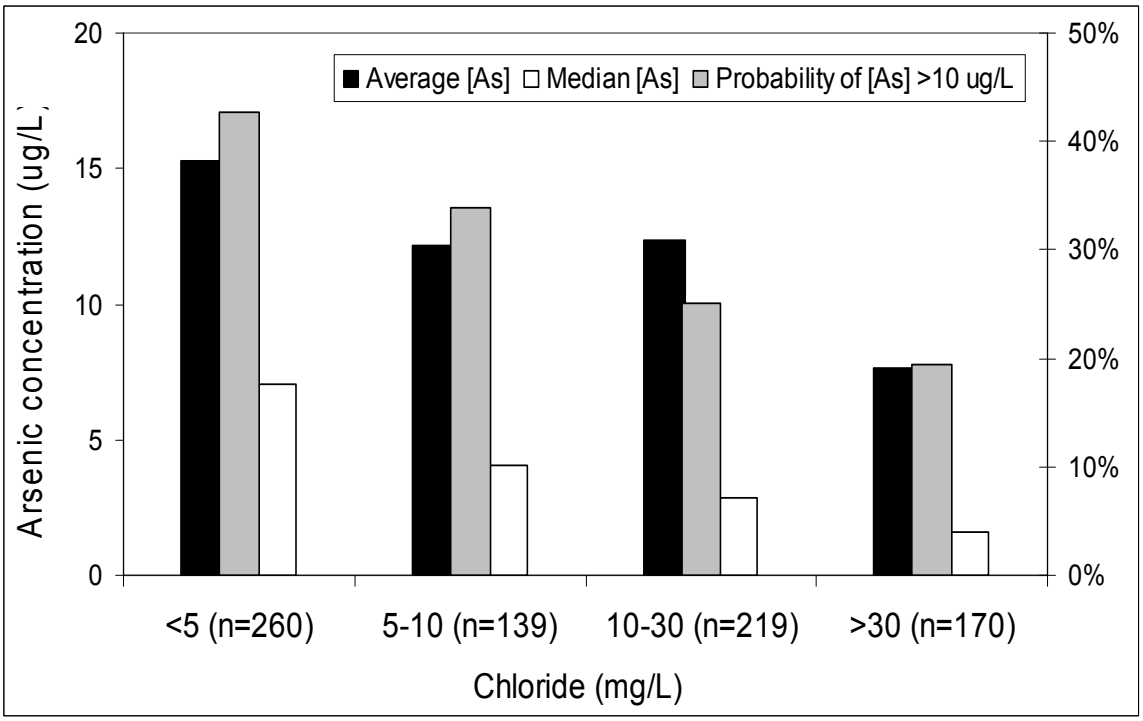


Figure 2.3 Arsenic concentrations and exceedance rates vs. pH, dissolved oxygen, fluoride, nitrate, molybdenum, and chloride

Table 2.4 Summary statistics of key parameters of groundwater from the greater Augusta area, Maine in 2006 sampling

bedrock unit	Ss (n=161)		Sw (n=259)		SOv (n=248)		D (n=86)		OZc (n=30)	
	median	mean	median	mean	median	mean	median	mean	median	mean
arsenic(µg/L)	6.8	16.4	6.1	14.4	2.0	10.1	2.5	7.8	0.2	2.5
pH	8.0	7.6	7.9	7.7	7.3	7.3	6.9	7.1	7.3	7.2
dissolved oxygen(mg/L)	1.0	2.1	1.5	2.5	2.0	2.7	4.0	3.8	1.3	1.7
chloride(mg/L)	6.2	26.3	8.9	33.2	14.5	28.7	12.1	28.2	6.3	14.9
fluoride(mg/L)	0.2	0.4	0.1	0.3	0.0	0.2	0.1	0.4	0.1	0.2
nitrate as N(mg/L)	0.1	0.6	0.1	0.6	0.3	0.8	0.2	0.6	0.1	0.4
molybdenum(µg/L)	2.1	2.5	1.2	2.6	0.9	1.4	1.8	3.5	1.3	3.0
uranium(µg/L)	0.6	1.9	0.7	9.2	1.3	5.4	4.9	18.1	1.0	3.0

2.3.2 Spatial distribution of groundwater parameters

In the 2006 data set, the pH values ranged from 5.2 to 9.4, with a median value of 7.6 (Table 2.2). Higher pH values are more frequently found in the western part of study area where arsenic occurrence was also high (Figure 2.1). Mean and median pH values are significantly higher in Ss and Sw rock units than in the others (Table 2.4). In the 2007 data set, the median pH value (6.8) of groundwater from the Chelsea cluster within the granite intrusions (D) according to most updated bedrock geology map (MAINE_GEOLOGICAL_SURVEY, 2008) and also with the lowest arsenic occurrence, is significantly lower than the median pH values of water samples in other three clusters (8.2, 7.8, 8.3, respectively) that are mostly in Waterville formation (Table 2.2).

The dissolved oxygen concentrations in 2006 sampling were between 0.1 and 11 mg/L, with a median value of 1.5 mg/L (Table 2.2). There is a slightly higher percentage of low dissolved oxygen groundwater (<1 mg/L) in the western part than in the eastern part (Figure 2.1). The mean and median dissolved oxygen concentrations increase from west to east in Ss, Sw, SOv and D units, but is low in the OZc unit (Table 2.4). The

median dissolved oxygen level (2.0 mg/L) of groundwater in Chelsea cluster is higher than those in other areas (0.6, 1.0, 1.0 mg/L, respectively) (Table 2.2).

The nitrate concentrations were generally low with a median value of 0.9 mg/L in 2006 sampling (Table 2.2). Nitrite concentrations were below the detection limit (0.02 mg/L) in most samples. Low nitrate groundwater occurs more frequently in the western part than that in the eastern part (Figure 2.1), consistent with lower mean and median nitrate concentrations in Ss and Sw units than in the others (Table 2.4). The Chelsea cluster with the lowest arsenic occurrence has a much higher median nitrate value (4.5 mg/L) than those in the other clusters (0, 0, 0.2 mg/L, respectively) (Table 2.2).

Like arsenic, high fluoride and molybdenum concentrations are more frequently found in groundwater samples from Ss and Sw units (Figure 2.1 and Table 2.4) and granite intrusions.

Most groundwater samples from 2006 sampling were Ca^{2+} rich, with a few being Na^{+}+K^{+} rich. Mg was negligible in all the samples. HCO_3^{-} dominated the anions in most samples, with some samples having high levels of Cl^{-} from Devonian granite intrusions and Sangerville/Waterville formations (Figure 2.4). The major water types of well samples in the four clusters sampled in 2007 were similar to that in 2006, except in Chelsea where more groundwater samples showed high concentrations of Cl^{-} (Figure 2.5).

Arsenic distribution in soil follows a similar spatial pattern as that of groundwater arsenic distribution in the study area. It has been suggested that soil arsenic can be used as an indicator of arsenic distribution in groundwater at local, regional and national scales (Chapter 4) (YANG and ZHENG, In preparation).

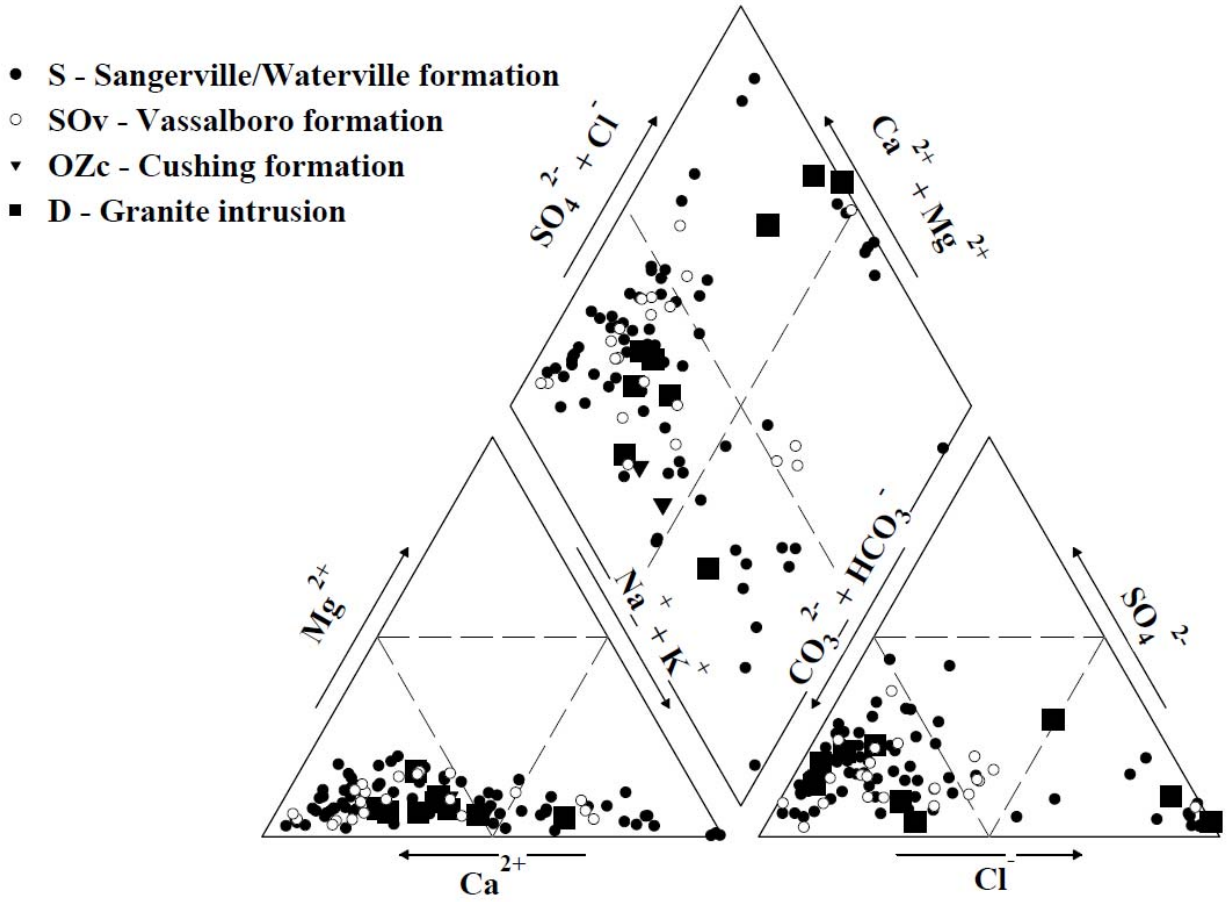


Figure 2.4 Piper diagram of selected groundwater samples (n=105) in the greater Augusta area, Maine in 2006 sampling

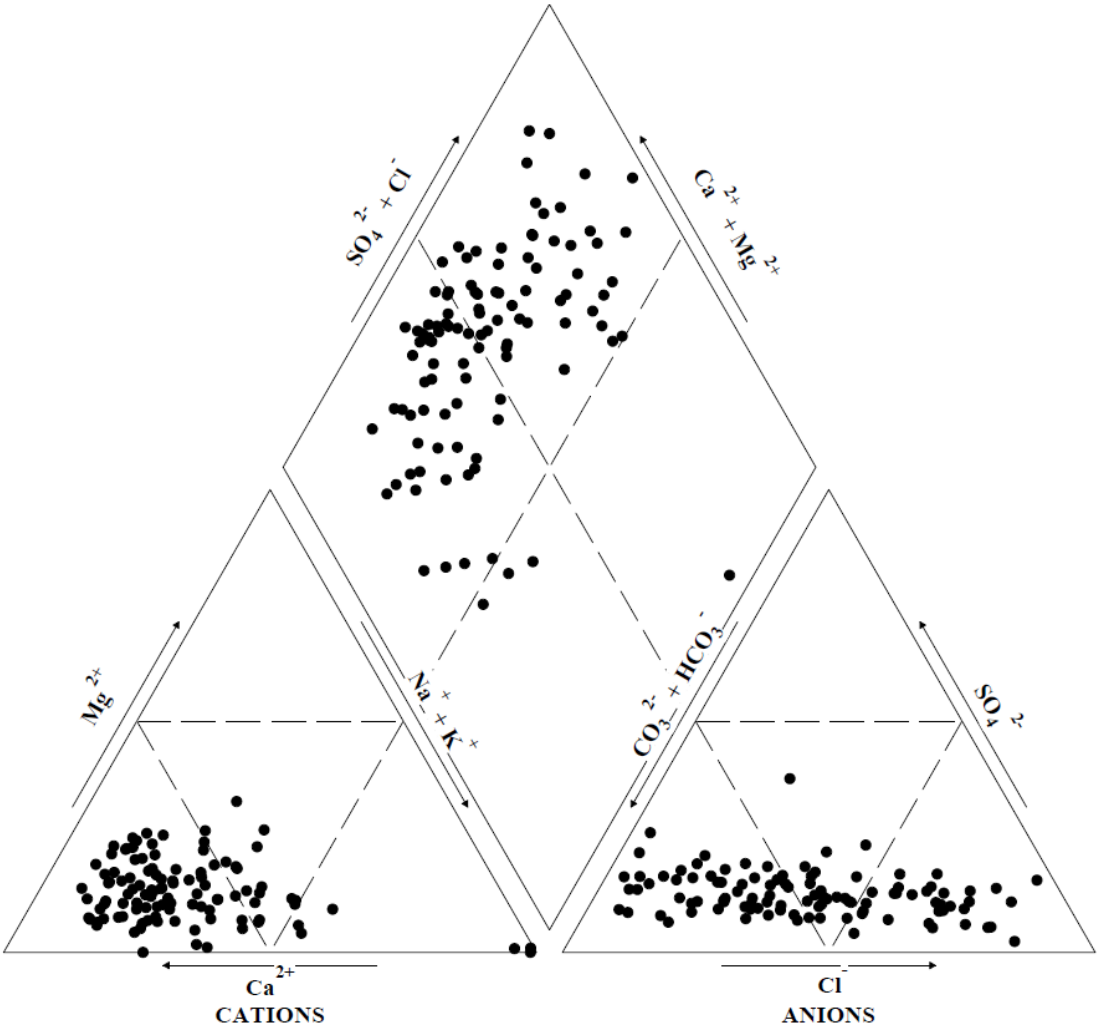
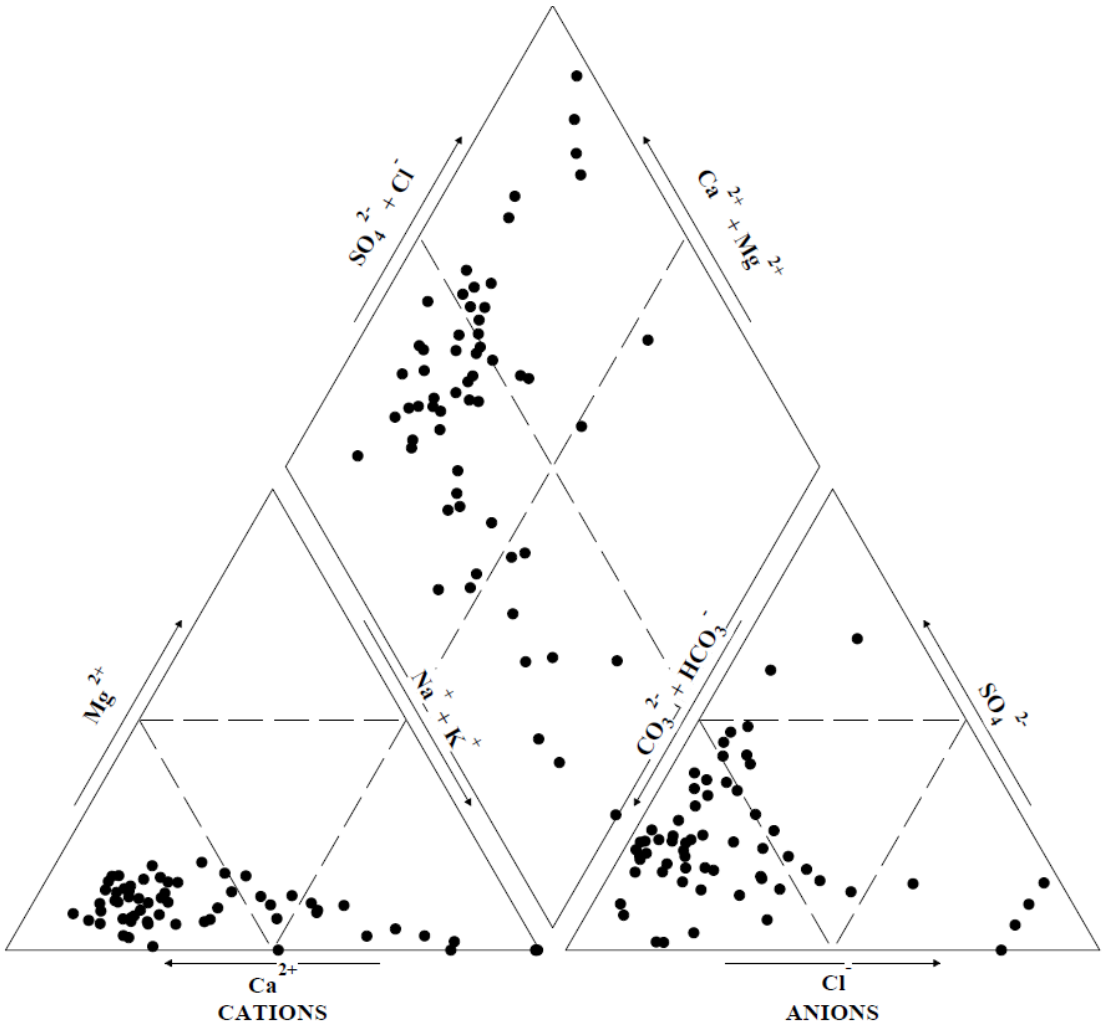
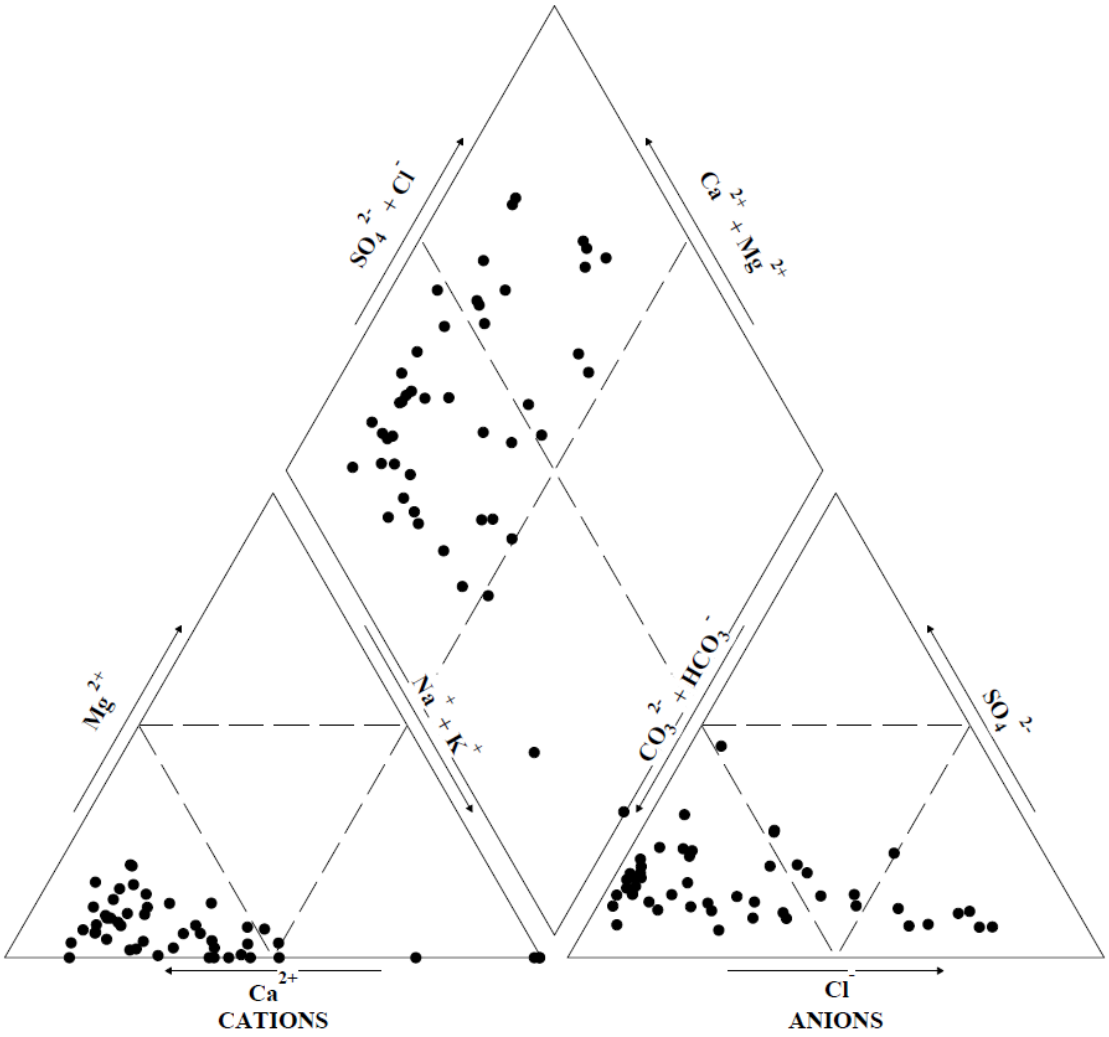


Figure 2.5 Piper diagrams of groundwater samples in 4 clusters of 2007 sampling

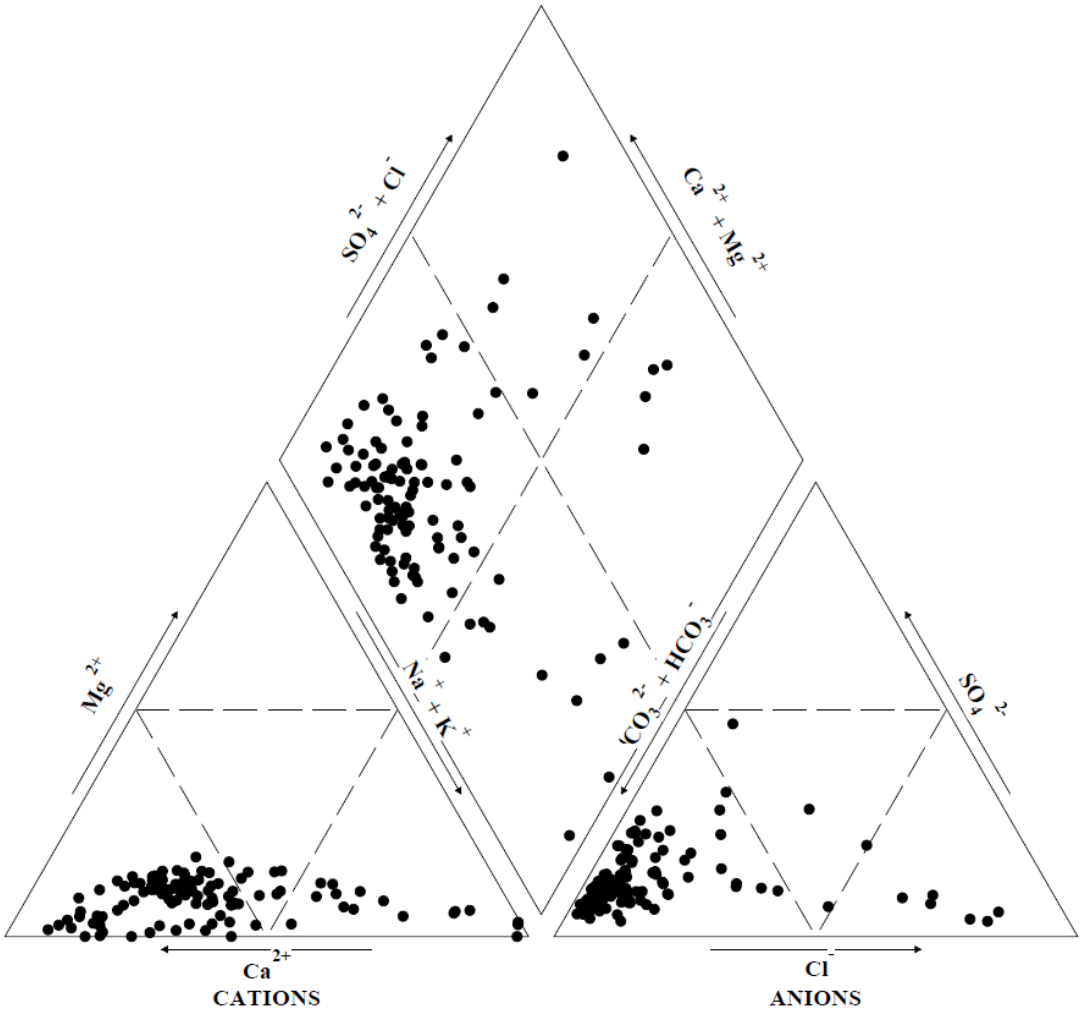
A – Chelsea



B – Sidney



C – Litchfield



D – Manchester

2.3.3 Logistic regression model

Twenty hydrogeological and geochemical factors, including bedrock geology, well depth, pH, dissolved oxygen, fluoride, chloride, nitrate, sulfate, alkalinity, Mg, Ca, Si, V, Ni, Sb, Cs, Ba, Re, Tl, and soil arsenic content, showed significant association with the probability of groundwater arsenic > 10 μg/L based on the univariable regressions.

In the multivariable logistic regression model, alkalinity was excluded because of too few alkalinity data available which made the model unable to converge otherwise. Trace elements (V, Ni, Sb, Cs, Ba, Re, Tl) were also excluded because they are normally not the controlling factors in groundwater systems. The Hosmer and Lemeshow goodness-of-fit test had a p value of 0.62, much higher than the critical value of 0.05, which indicated the robustness of the model. The model results showed that six parameters were significant. They were pH, dissolved oxygen, bedrock geology, nitrate, sulfate, and soil arsenic content. The results of step-wise logistic regression models are as follows.

The final regression model including the above six parameters (Table 2.5) had a Hosmer and Lemeshow goodness-of-fit test p value of 0.38. The model results show that Sangerville/Waterville formations and Vassalboro formation have 2-3 folds higher odds of containing elevated groundwater arsenic than granite intrusions, and that Cushing formation has the lowest odds, which is consistent with the spatial analysis of groundwater arsenic distribution (YANG et al., 2009). Soil arsenic distribution shows a weak positive effect. Among water geochemistry parameters, pH is the most important, with the greatest odds ratio of 2.8, while dissolved oxygen and nitrate are negatively

Model results of step-wise logistic regression method

The form of logistic regression model is $\frac{P[y=1|x]}{1-P[y=1|x]} = e^{(\beta_0+\beta_1x_1+\beta_2x_2+\ldots+\beta_nx_n)}$. In this research, P[y=1|x] represents the response variable, probability of groundwater [As] >10 μg/L; x1, x2, … xn represent explanatory variables or coefficientss; β0 represents intercept, β1, β2, … βn represent estimate; standard error is the prediction error of each estimate; z value is estimate divided by standard error; Pr(>|z|) is the two-tailed p value, coefficients having p-values less than alpha (usually 0.05) are statistically significant.

The multivariable logistic regression model

Coefficients	Estimate(β)	Std. Error	z value	Pr(>|z|)
(Intercept)	-8.999e+00	1.656e+00	-5.435	5.5e-08
Well Depth	-2.390e-06	9.525e-04	-0.003	0.99800
pH	9.698e-01	1.900e-01	5.106	3.3e-07
DO	-1.364e-01	6.448e-02	-2.115	0.03444
AGE-OZ	1.545e-01	8.049e-01	0.192	0.84775
AGE-S	1.464e+00	5.087e-01	2.879	0.00399
AGE-SO	1.195e+00	5.223e-01	2.287	0.02217
Mg	5.342e-02	5.327e-02	1.003	0.31597
Si	1.838e-02	2.826e-02	0.650	0.51552
Ca	-5.374e-03	6.344e-03	-0.847	0.39699
F	-2.131e-01	2.816e-01	-0.757	0.44922
Cl	-1.270e-03	3.598e-03	-0.353	0.72397
NO3-N	-3.883e-01	1.820e-01	-2.133	0.03291
SO4	-2.646e-02	1.298e-02	-2.038	0.04154
Soil [As]	2.089e-02	1.355e-02	1.542	0.12316

* Hosmer-Lemeshow goodness of fit test p value = 0.6208

The final logistic regression model

Coefficients	Estimate	Std. Error	z value	Pr(>|z|)
(Intercept)	-9.223968	1.289130	-7.155	8.36e-13
pH	1.017732	0.149663	6.800	1.04e-11
DO	-0.103781	0.051886	-2.000	0.04548
AGE-OZ	-0.209356	0.730170	-0.287	0.77432
AGE-S	1.057876	0.397591	2.661	0.00780
AGE-SO	0.938122	0.407257	2.304	0.02125
NO3_N	-0.252216	0.131305	-1.921	0.05475
SO4	-0.029622	0.009595	-3.087	0.00202
Soil [As]	0.026012	0.011502	2.262	0.02373

* Hosmer-Lemeshow goodness of fit test p value = 0.3820

correlated with groundwater arsenic. Sulfate shows a very weak negative correlation to arsenic in groundwater.

Table 2.5 Explanatory variables used in the final logistic regression model of bedrock aquifers in the greater Augusta area, Maine

Variable	Type	exp(β)	p-value
Intercept		0.000	<0.0001
Bedrock geology			
Sangerville/Waterville formation	categorical	2.880	0.0078
Vassalboro formation	categorical	2.555	0.0213
Cushing formation	categorical	0.811	0.7743
Granite intrusion (comparison varibale)	categorical	1.000	
Overburden material			
Soil As content	continuous	1.026	0.0237
Water geochemistry			
pH	continuous	2.767	<0.0001
Dissolved Oxygen	continuous	0.901	0.0455
Nitrate	continuous	0.777	0.0548
Sulfate	continuous	0.971	0.0020

The final formula to predict the groundwater arsenic exceedance rate in the Augusta aquifers is as follows.

$$\frac{\Pr obability([As]>10ug/L)}{1-\Pr obability([As]>10ug/L)} = \exp(-9.22+1.06S+0.94SOv-0.21OZc+0.03Soil+1.02pH-0.10DO-0.25NO_3-0.03SO_4)$$

where S is Sangerville or Waterville formation, SOv is Vassalboro formation, OZc is Cushing formation, Soil is arsenic concentration in soil in mg/kg, NO_3 is nitrate concentration as of N in mg/L, SO_4 is sulfate concentration in mg/L.

This formula was applied onto the four clusters of groundwater sampled in 2007. The predicted probabilities of groundwater arsenic greater than 10 μg/L were 6% in Chelsea, 31% in Sidney, 27% in Litchfield, and 38% in Manchester. Compared with

observed arsenic exceedance rates of 7% in Chelsea, 29% in Sidney, 57% in Litchfield, and 78% in Manchester, this model predicted the order of arsenic occurrence rates but underestimated the quantitative values of arsenic exceedance rates in high arsenic areas. This is not unusual in such complicated fractured bedrock aquifer systems. On the other hand, this suggests that the logistic regression model can very well indicate the anomaly or spatial pattern of arsenic distribution in bedrock aquifers, but requires further improvements to predict arsenic concentrations quantitatively. This can be done by including other factors, such as hydrogeochemical processes in individual wells at very local scales, as well as using finer bedrock geology map and bedrock lithochemistry data.

2.3.4 Arsenic source and mobilization

The strong associations of groundwater arsenic with bedrock geology and horizon C soil arsenic distribution suggest a geologic source of groundwater arsenic rather than anthropogenic activities. Regional studies in New England have found that weathering products from bedrocks are the dominant source of arsenic and the elevated arsenic concentrations in bedrock wells do not show correlations with past agricultural areas (ROBINSON and AYOTTE, 2006). The low nitrate concentrations in the water samples further support the natural source of groundwater arsenic, although it can not be excluded that denitrification under reducing conditions could lower the nitrate concentrations in the well waters.

The strong correlation between arsenic and molybdenum suggests a common sulfidic mineral source because like arsenic, molybdenum is shown to be trapped by sulfide minerals in anoxic marine sediments under sulfide reducing conditions (ZHENG et

al., 2000). Molybdenum may have co-precipitated with arsenic in anoxic marine basins during Silurian, and then later dissolved into groundwater together with arsenic through a set of similar water-rock interactions as it is also an oxyanion with affinity to iron oxyhydroxides. High arsenic contents up to 300 mg/kg have been detected in sulfide minerals such as arsenic-rich pyrite crystals from outcrops in the field (O'SHEA et al., In preparation). The source of arsenic-rich sulfide minerals could be related to the deep hydrothermal fluid circulated upward driven by heat fluxes (FRANCISCA and CARRO PEREZ, 2009), which is reflected by the association between arsenic and fluoride, suggesting the possible same origin of arsenic and fluoride in the sedimentary protolith. In such reducing marine basins, calcium fluoroapatite has been found to be abundant (REIMERS et al., 1996). The most significant metamorphism of Devonian granite intrusion was thought to have caused the desulfidation of Silurian sedimentary rocks (FERRY, 1981), which could convert the association of arsenic with pyrite (FeS_2) to pyrrhotite (FeS), and explain why there is no distinct correlation between arsenic and sulfate and the lower sulfate concentrations in the Manchester cluster than in other areas (Table 2.2).

The mobilization of arsenic in the Augusta aquifers is likely to have begun with oxidation of arsenic rich sulfidic minerals, such as arsenian pyrite and arsenopyrite, at the initial stage of water-rock interactions. The lack of a positive correlation between arsenic and iron in groundwater might be due to the fact that a fraction of arsenic and especially iron was present in colloidal or particulate forms in the unfiltered samples. Furthermore, under oxic conditions, iron was easily oxidized and iron oxyhydroxides ($FeO(OH)_x$) precipitated to remove iron from water and also arsenic by sorption. Nevertheless, this lack of correlation suggests that arsenic is not only controlled by iron sulfide dissolution.

A set of adsorption/desorption and/or precipitation reactions, mostly involving $FeO(OH)_x$ under different pH and redox conditions are likely the key mechanisms regulating arsenic concentration in groundwater (PETERS and BLUM, 2003). The correlations between elevated arsenic and high pH, low dissolved oxygen and low nitrate suggested that reducing environment, perhaps with denitrification (SENN and HEMOND, 2002), favored arsenic mobilization by destabilizing $FeO(OH)_x$ and thus enhancing the desorption of arsenic.

The waters with high arsenic tend to be further down the flow path, and are more geochemically evolved. There are weak positive correlations of the molar sum of cations (corrected by subtracting molar chloride concentration to minimize the effect from road salt) with arsenic ($\rho = 0.10$) and pH ($\rho = 0.17$) in 2006 sampling and somewhat stronger correlations in the clusters sampled in 2007 (Table 2.3). The lack of positive correlations between calcium and arsenic might be because the solubility of calcium carbonate decreases when pH increases to above 8 in carbonate systems. In the groundwater samples with pH > 8, it is observed that calcium concentrations decrease with pH, while sodium concentrations increase.

The groundwater chloride concentrations had a median value of 10 mg/L and a mean value of 30 mg/L, while bromide was only detected in a small number of samples (n=10). This low bromide occurrence and Br^-/Cl^- ratio exclude the possibility that high chloride levels are from seawater intrusion (DAVIS et al., 1998). Because road salt application has increased significantly in the last five decades in the US (ROBINSON et al., 2004), groundwater with high chloride is likely to be recharged recently whereas groundwater with lower chloride is likely to be recharged earlier and thus can be older.

Therefore, presumably aged groundwater samples down along the flow path with low chloride tend to contain elevated arsenic (Figure 2.3). In the Sidney cluster, groundwater with high chloride from the top of a hill showed distinctly lower arsenic than the older water samples with lower chloride down slope further along the flow path of groundwater.

There is a weak positive correlation between arsenic and well depth in the 2006 data set (Table 2.3). When wells were categorized into groups based on well depth, both the median arsenic concentrations and the arsenic exceedance rates (>10 μg/L) increased with well depth (Chapter 2) (YANG et al., 2009). This is probably because those more reducing conditions in the deeper wells favor arsenic mobilization than in the shallower wells where water is more oxic.

Thirty-six wells were sampled in both 2006 and 2007. There is no systematic difference of arsenic concentrations between the two years of sampling (Figure 2.6). The pH, dissolved oxygen, and major ions concentrations are also comparable between the two year sampling. This suggests that ground water chemistry is relatively constant, probably due to the low water withdrawal rates because water is used only for domestic consumption in this rural area.

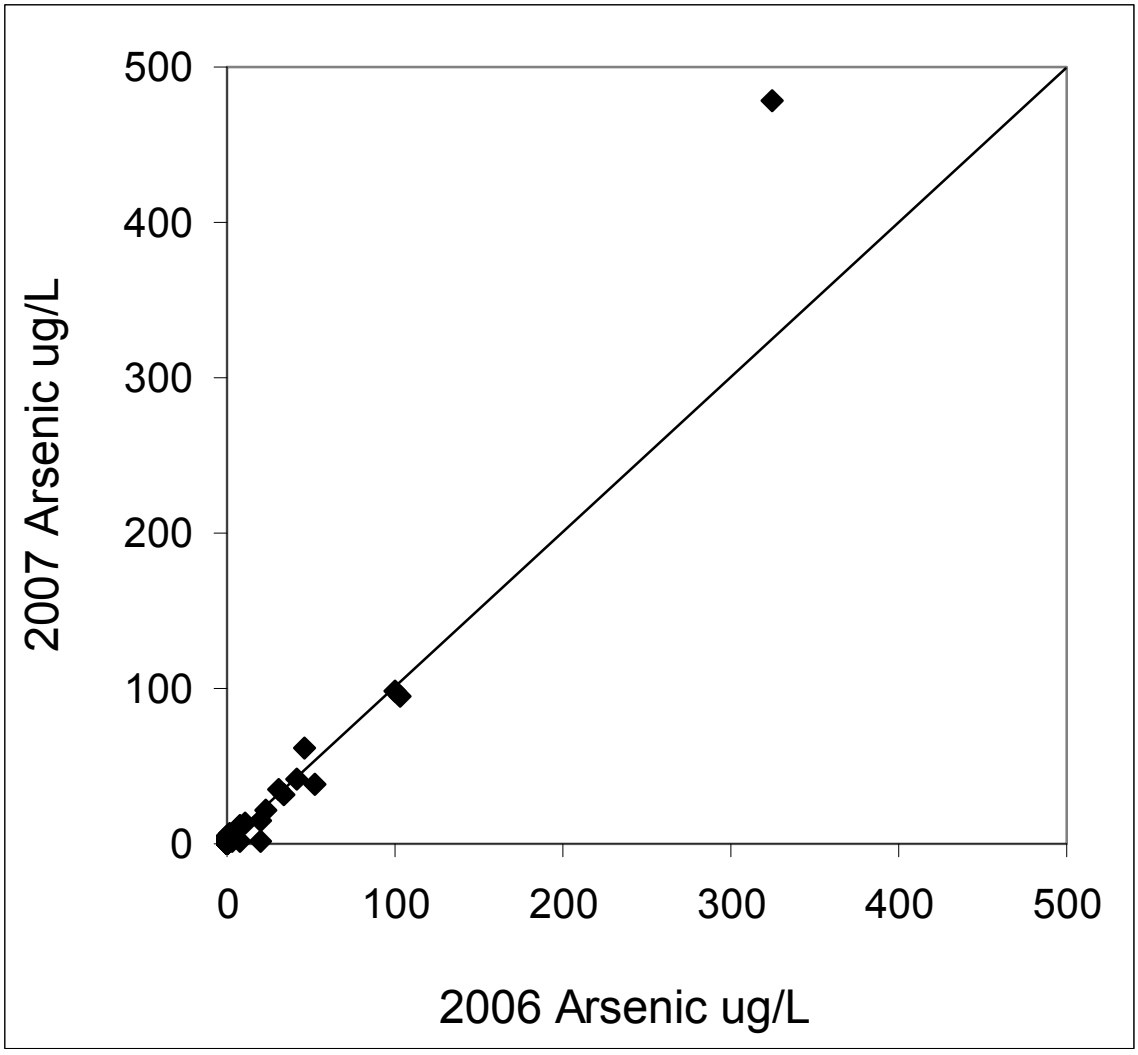


Figure 2.6 Arsenic concentrations in the wells sampled in 2006 and 2007

2.3.5 Implications on arsenic occurrence in bedrock aquifers

Sulfide minerals have been recognized as a very common source of arsenic in bedrock aquifers, although the sequence of geochemical reactions in the aquifers involved in arsenic mobilization remains not well understood. This research shed light on understanding the reactions along groundwater flow paths using spatial and statistical analyses of water chemistry parameters. The desulfidation processes by metamorphisms pre-condition the bedrock, stripping the formations of arsenic rich sulfides and changing

the association between arsenic and pyrite/pyrrhotite minerals. This in part explains the large spatial heterogeneity in groundwater arsenic distribution in fractured bedrock aquifers at local scales. Following the oxidative dissolution, desorption from iron mineral surfaces upon increasing pH offers an important mobilization mechanism of groundwater arsenic evolution. The findings support the geochemical mechanisms proposed based on regional scale studies (AYOTTE et al., 2003; AYOTTE et al., 2006; PETERS, 2008; PETERS and BLUM, 2003) and provide more specifics with regard to evolution of groundwater chemistry. The understanding of geochemical reactions that transport and mobilize arsenic will have implications for groundwater remediation and for homeowners to select appropriate removing devices for arsenic and other metals.

The logistic regression model based on 6 parameters provides a first order estimate of groundwater arsenic occurrence in the greater Augusta area. This could be used to improve the prediction of groundwater arsenic in similar bedrock aquifers in New England at local scale. This means towns, or even sub-county, will be able to identify the potential high arsenic areas with similar geology using some basic water chemistry data. This can guide local communities for water resources management, especially when it comes to the planning of housing development. There are still limitations to the current regression model. The prediction of the arsenic concentrations is not quantitatively accurate but only the spatial pattern at local scales. The spatial heterogeneity of arsenic distribution among individual wells within meters or tens of meters is not addressed here.

2.3.6 Uranium, fluoride and manganese risks

The research also identified the risks from other possible groundwater contaminants in the greater Augusta area, and could shed light on the characterization of these hazards in other areas in New England.

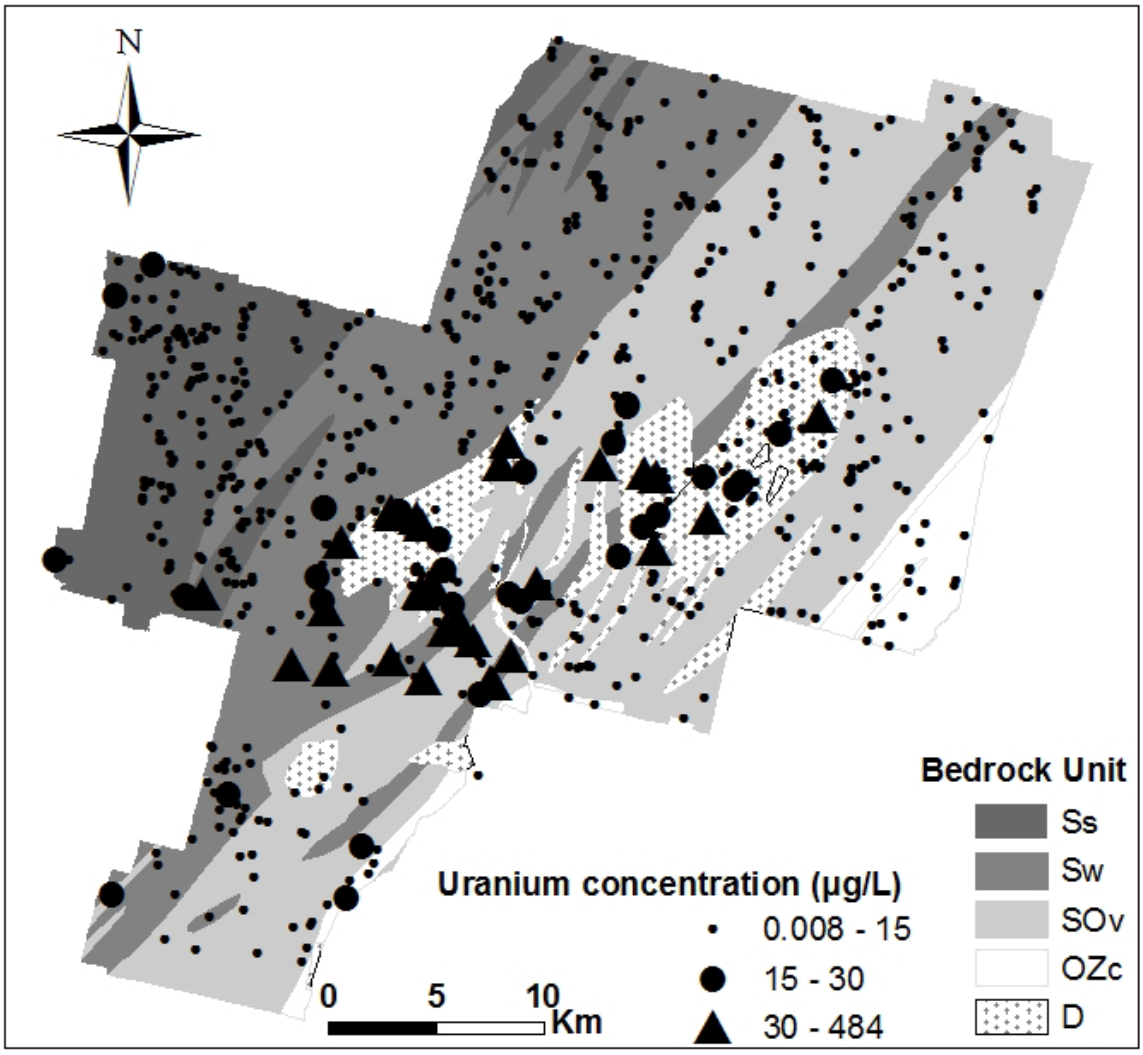


Figure 2.7 Uranium distribution plotted on simplified bedrock geology map in the greater Augusta area, Maine

Uranium in drinking water is an important health hazard in New England, especially in Maine and New Hampshire. In the study area, 62 (or 8%) of 790 water samples showed >15 µg/L of uranium, the WHO's guideline level, and 30 (or 4%) of 790

samples showed >30 μg/L of uranium, the EPA standard. Elevated uranium concentrations are strongly association with the intrusion of Devonian (417-360 Ma BP) plutons of granite, granodiorite, quartz monzonite and syenite (D), located in the center of the study area (Figure 2.7). This association suggests that other granitic plutons in New England are also at higher risks of uranium contamination in groundwater.

Fluoride in drinking water in the US has rarely been considered as a health risk previously. However, 26 (or 3%) of 790 groundwater samples in this research showed fluoride concentrations higher than 1.5 mg/L, the WHO guideline level. There were no water samples with fluoride greater than 4 mg/L, the current US EPA MCL.

Manganese in drinking water has started to attract attentions of environmental scientists with reported effects on intellectual function of children (WASSERMAN et al., 2006). In the greater Augusta area, groundwater manganese concentrations ranged from 0.62 to 7,191 μg/L, with 23% of the samples exceeding 50 μg/L, the EPA's secondary water standard, and 3% exceeding 400 μg/L, the WHO guideline for drinking water. Elevated manganese concentrations are associated with lower pH and lower dissolved oxygen, which is consistent with the well known characteristics of manganese regulated by acid-base and redox reactions in natural water systems.

Chapter 3 Response of Total and Dissolved Arsenic to Pumping in Bedrock Wells from Manchester, Maine, USA

Abstract

Bore hole water samples and those representative of the fractures were collected and analyzed for arsenic under ambient and pumping conditions in two domestic wells in Manchester, Maine, where a high groundwater arsenic occurrence was found in fractured meta-sedimentary bedrock aquifers. Geophysical logging was conducted to characterize fractures and to determine flow rates. Transmissivity of the fractures was estimated at 0.23-10.6 m^2/day by pumping test. Water with high dissolved arsenic and high dissolved solids was coming primarily from high yielding fractures near the bottom of the bore hole. Dissolved arsenic concentrations increased as fracture water was replacing bore hole water with initially low dissolved arsenic concentrations in response to pumping. Iron particulate precipitates were common and were found to be enriched in arsenic. Laboratory experiment on well water samples over a period of 16 days suggested that in the bore hole arsenic was mainly settled with iron enriched particles, probably amorphous ferric oxyhydroxides, with possibly minor adsorption on the iron minerals. The results can improve the understanding of how water flowing through the aquifer enters the bore hole and how arsenic evolves in the bore hole.

3.1 Introduction

Arsenic contamination in fractured bedrock wells has emerged as an important and challenging health problem in African, European and North American countries (ALOUPI et al., 2009; AYOTTE et al., 1999; BOYLE et al., 1998; HEINRICHS and UDLUFT, 1999; KORTATSI, 2007; PIPPIN et al., 2006), especially in rural areas without public water supply. Private wells are not subject to the regulatory mandate to meet drinking water quality standards or regular monitoring. This has posed greater risks for private well users to develop arsenic related diseases and cancers (KARAGAS et al., 2002). In New England region, researches on occurrence, source and transport of arsenic in bedrock aquifers have been reported from regional basin scales to local town or county scales (AYOTTE et al., 2003; LIPFERT et al., 2006; PETERS and BLUM, 2003; SIDLE et al., 2001; YANG et al., 2009). These studies have demonstrated that groundwater arsenic distribution in fractured bedrock aquifers is largely affected by bedrock geology and shows regional patterns and even local patterns. To date, the interactions between flow and water chemistry were considered to be important but not well understood.

One of the pieces of the puzzles is that at the very local scale of < 100 m, arsenic concentrations in bedrock wells could vary greatly from < 1 to hundreds of μg/L. The complexity of flow in inter-connected fractures opens the possibility of fluctuation of water chemistry, and in turn changes arsenic concentrations in individual wells over time or under different pumping conditions. This conjecture is based on a large body of literatures that illuminated the linkage between aquifer transmissivity and chemical transport in inter-connected fracture networks of bedrock aquifers (JOHNSON et al., 2005; LANE JR. et al., 2002; NORDSTROM et al., 1989; PAILLET and KAPUCU, 1989). Fractures

are largely heterogeneous in orientation, length, aperture, depth, connectivity, and more importantly, the water producing capacity. Bedrock wells could penetrate fractures with various water heads and then have inflows or outflows from different depths in bore holes. Under varying hydrogeologic conditions, including those induced by pumping, arsenic concentration is hypothesized to respond to changes of groundwater flow. The changes can be complicated and difficult to predict especially when the rock formations are lithogeochemically heterogeneous, which contribute waters with distinct chemistry. Nevertheless, the connectivity between fractures that yield high arsenic water and those that yield water with little or no arsenic remains a possible explanation for the large degree of spatial heterogeneity of arsenic at very local scales, and may also result in changes of arsenic levels over time in a given bore hole.

To ascertain to what extent arsenic concentrations in bore holes reflects a mixture of water derived from various inter-connected fractures and responds to varying hydrogeologic conditions, bore hole water samples and those collected using methods that intend to collect samples representative of the fractures were analyzed for arsenic and other chemical parameters under ambient and pumping conditions in two domestic wells in Manchester, Maine. The wells are chosen to be representative of high arsenic wells in the greater Augusta area where 790 wells have been screened for arsenic (YANG et al., 2009). Geophysical logging was used to characterize fractures and to determine flow rates at various depths. Transmissivity of the fractures was estimated using pumping test. Laboratory experiment was conducted to simulate oxidation reactions occurring in the bore hole, especially the effect of oxidation on total and dissolved arsenic and iron concentrations over a period of 16 days. The results will improve the understanding of

how water flowing through the aquifer enters the bore hole and what geochemical reactions affect arsenic in the bore hole. Such improved understandings will have implications on examining whether the arsenic concentration of bore hole water collected at a random time of the year after minimal flushing of the bore hole can be used to determine whether it is in compliance with the drinking water standard or not.

3.2 Material and Methods

3.2.1 The bedrock wells

Arsenic in domestic wells sampled at a density of 5-24 wells per square kilometer in 13 towns of the greater Augusta area, Maine, has identified that the calc and calc-silicate meta-sedimentary rock formations, namely Sangerville and Waterville Formations, display high rates of arsenic occurrence (YANG et al., 2009). Two 6-inch bedrock wells in Manchester, Maine in the Waterville Formation of Silurian pelite and sandstone or limestone, adjacent to granitic intrusions are chosen based on a detailed survey of 113 wells in 6 square kilometer (YANG et al., 2009) that found 78% of the wells having > 10 µg/L of arsenic (Figure 3.1). The wells are situated on a slope from the topographic high point of the granite hill (elevation 149 m) to Lake Cobbosseecontee shore (elevation 52 m) with a regional groundwater flow direction from east to west. The total arsenic concentrations of groundwater (not filtered) from well MA70076 (elevation 88 m) and MA70138 (elevation 85 m) sampled in 2007 were 38 µg/L and 73 µg/L, respectively. The two wells are about 50 meter apart.

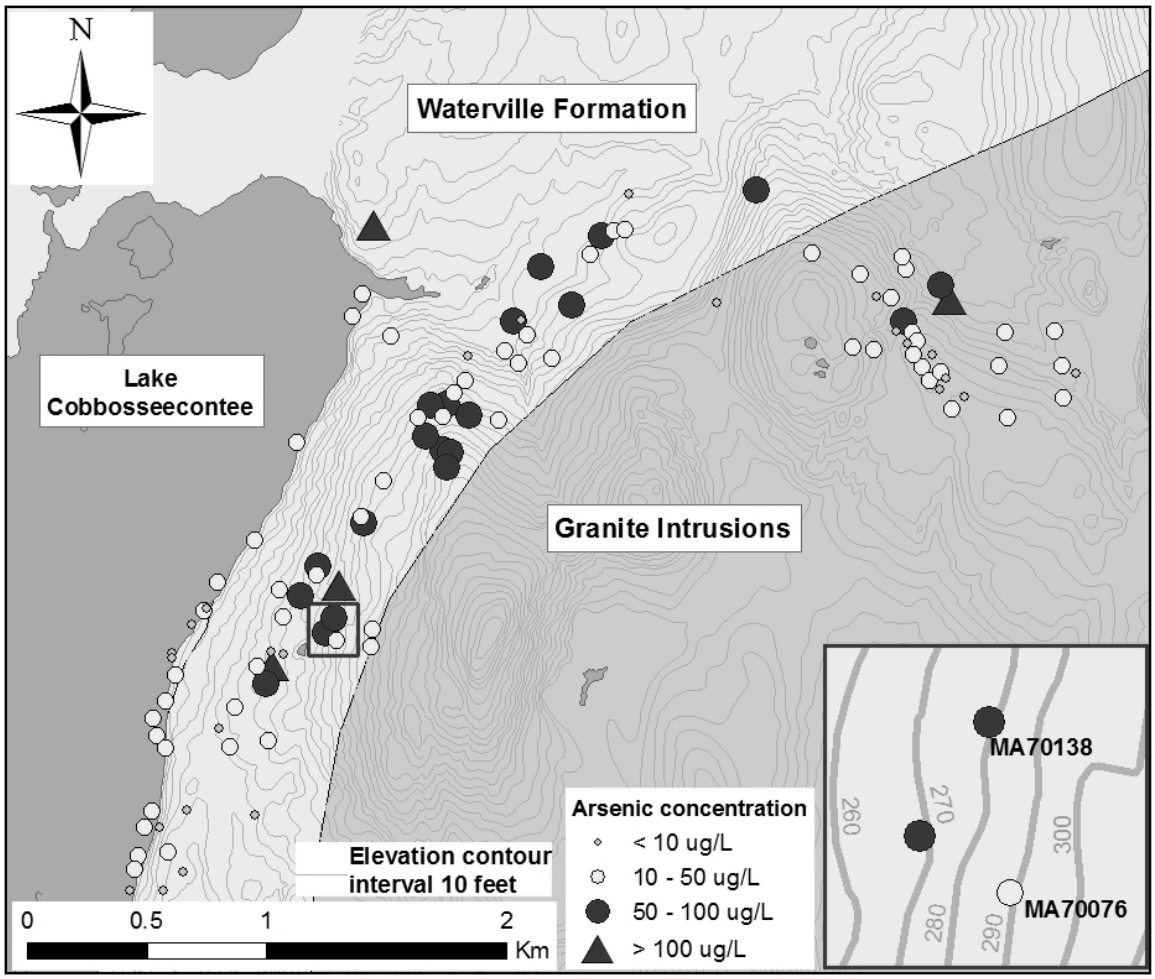


Figure 3.1 Arsenic distribution plotted on bedrock geology and topographic map in Manchester, Maine
* Insert indicates the location of wells in this research.

These domestic wells penetrate sand-gravel overburdens into deeper fractured bedrock formations. They are cased at shallow depths, such that water is drawn only from the deep open bore hole in the bedrock. In the study area, sparse sand-gravel glacial aquifers, with thickness ranging from 0 to 50 meter, have relatively high transmissivity, with hydraulic conductivity ranging from 10-300 meter per day. The bedrock aquifers have lower transmissivity with typical hydraulic conductivity ranging from 8×10^{-5} to 8 meter per day (HARTE, 1992; HSIEH et al., 1993; PAILLET and KAPUCU, 1989). Fractures

are widely distributed in the bedrocks. The rock formations mostly strike in the NE-SW direction and dip greater than 80 degrees to northwest or southeast. There are also cross-cutting joints which strike NW-SE and dip steeply based on the observation of outcrops.

3.2.2 Geophysical logging

In October 2008, caliper and conductivity logging was conducted to determine the well depth and the length of well casing, as well as the apparent fractures which can be reflected from changes of well radius, water temperature and conductivity. Acoustic televiewer logging was used to attain the vertical profile of the bore hole, providing information regarding the depth and orientation of fractures. Heat-pulse flow meter logging was performed to measure flow rates under ambient and pumping conditions and then to determine the proportion of water contribution from fractures at various depths. Interpretation of flow rates under the two scenarios led to the estimate of bore hole and fracture transmissivities.

3.2.3 Pumping test

Pumping test was carried out in October 2008 (a pilot study) and August 2009 (Tables 3.1 and 3.2) to estimate the aquifer transmissivity following the Cooper-Jacob straight line method. Water table drawdown and recovery were recorded manually by water level meter and continuously by pressure transducer. Pumping rate was kept as constant as possible and measured by flow meter and calibrated using volume certified buckets.

Table 3.1 Pumping and sampling history, geochemistry of groundwater samples in well MA70076

year	start time	pumping time (min)	pumping rate (gpm)	sample ID	sampling depth (m)	pH	DO (mg/L)	total [As] (ug/L)	dissolved [As] (ug/L)	dissolved As(III)	total [Fe] (ug/L)	dissolved [Fe] (ug/L)	particulate As/Fe molar ratio	F (mg/L)	Cl (mg/L)	SO4 (mg/L)	alkalinity (mmol/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Ca (mg/L)
2007		15	from hose	MA70076	hose	7.50	3.0	37.7	ND	ND	2190	ND		0.54	1.67	7.15	1.07	5.61	1.50	1.07	17.28
2008	13:40	92	0.2																		
	15:13	44	0, water recovery																		
	15:57	30	4.2																		
	16:27	83	4.2	MA70076.0	30.5	7.80	4.1	20.0	14.1	ND	155347	563		0.52	1.44	6.65	1.07	4.93	1.22	0.85	22.33
	17:50			MA70076.1	52	7.85	3.9	ND	24.1	2.3	9739	232		0.51	1.43	6.46	1.16	5.56	1.24	0.86	21.69
2009	11:05	35	1.0																		
	11:40	70	1.0	70076.01	30	7.17	8.7	67.1	7.7	0.0	14625	22	0.003	0.51	1.61	6.11	ND	3.03	1.12	0.32	13.37
	12:50	110	1.0	70076.02	30	7.12	5.4	55.3	17.4	0.5	5908	28	0.005	0.52	1.51	6.62	ND	5.16	1.80	0.92	22.84
	14:40	8	1.0	70076.03	30	7.06	4.0	31.4	28.0	0.1	1217	7	0.002	0.50	1.54	6.86	ND	5.35	1.94	1.03	25.24
	14:48	18	0, water recovery																		
	15:06	84	0.9																		
	16:30	22	0.8	70076.1	54	7.22	5.0	42.8	36.7	0.3	2652	112	0.002	0.50	1.51	7.04	ND	4.64	1.72	0.84	22.51
	16:52	25	0.7	70076.2	52	7.21	5.0	103.8	30.4	0.1	23425	19	0.002	0.52	1.50	7.08	ND	4.30	1.65	0.76	20.93
	17:17	25	0.7	70076.3	49	7.18	5.0	77.0	32.5	0.6	10960	18	0.003	0.51	1.45	6.95	ND	4.58	1.70	0.84	22.22
	17:42	23	0.7	70076.4	39	7.21	4.0	51.8	31.3	0.4	5846	11	0.003	0.55	1.66	6.78	1.01	4.80	1.65	0.79	22.23
	18:05	10	0.7	70076.5	32	7.20	4.0	52.8	29.8	0.5	6624	24	0.003	0.50	1.54	6.88	1.07	ND	ND	ND	ND
	18:15			70076.04	30	7.22	4.0	41.4	24.7	0.8	5103	17	0.002	0.51	1.52	6.88	1.15	4.99	1.78	0.87	23.54

* ND – no data

Table 3.2 Pumping and sampling history, geochemistry of groundwater samples in well MA70138

year	start time	pumping time (min)	pumping rate (gpm)	sample ID	sampling depth (m)	pH	DO (mg/L)	total [As] (ug/L)	dissolved [As] (ug/L)	dissolved As(III)	total [Fe] (ug/L)	dissolved [Fe] (ug/L)	particulate As/Fe molar ratio	F (mg/L)	Cl (mg/L)	SO4 (mg/L)	alkalinity (mmol/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Ca (mg/L)
2007		15	from hose	MA70138	hose	8.18	1.0	73.1	ND	ND	50	ND		1.08	1.15	5.77	1.12	5.57	0.43	0.62	24.51
2008	9:50	60	2.1																		
	10:50	295	2.1	MA70138.0	0	7.91	5.2	649.5	10.0	ND	174834	1390		0.88	1.14	6.45	1.13	7.30	1.25	1.01	23.10
	15:45	67	6.0																		
	16:52	33	2.0																		
	17:25	15	8.2																		
	17:40	80	8.2	MA70138.1	57	8.03	0.7	117.4	21.0	4.2	26242	564		0.71	1.30	5.84	1.30	7.32	1.29	1.04	24.69
	19:00			MA70138.2	52	7.93	2.2	47.4	46.2	5.3	3181	67		0.81	1.13	5.50	1.36	8.52	1.29	1.08	24.74
2009	9:45	11	2.4																		
	9:56	49	2.4	70138.01	35	7.46	2.0	119.4	19.4	2.2	11047	40	0.007	0.89	1.12	5.68	1.31	ND	ND	ND	ND
	10:45	62	2.4	70138.02	35	7.49	3.0	83.0	50.0	1.0	3682	36	0.007	0.89	1.26	5.70	1.34	ND	ND	ND	ND
	11:47	116	0, water recovery	70138.03	35	7.54	3.0	71.2	54.3	0.7	2382	10	0.005	0.86	1.14	5.83	1.40	ND	ND	ND	ND
	13:43	7	0.9																		
	13:50	50	1.2																		
	14:40	30	1.4																		
	15:10	20	1.4	70138.1	56.5	7.72	1.0	93.1	51.5	0.5	4944	26	0.006	0.94	1.06	5.58	1.34	6.10	1.46	0.69	19.47
	15:30	30	1.4	70138.2	53	7.71	2.0	51.0	51.7	0.0	867	4		0.85	1.15	5.64	1.32	5.32	1.37	0.66	18.70
	16:00	25	1.4	70138.3	50	7.56	1.0	59.6	50.7	0.6	1301	11	0.005	0.82	1.13	5.81	1.30	4.77	1.26	0.58	17.09
	16:25	25	1.4	70138.4	46	7.43	1.0	84.5	53.1	0.0	4303	15	0.005	0.83	1.15	5.74	1.28	4.11	1.13	0.41	15.34
	16:50	10	1.4	70138.5	40	7.74	1.0	98.1	52.5	0.1	4435	15	0.008	0.86	1.18	5.75	1.27	4.13	1.12	0.41	15.09
	17:00			70138.04	35	7.75	2.0	78.5	54.4	0.6	3173	12	0.006	0.85	1.17	5.83	ND	5.98	1.60	0.83	21.88

* ND – no data

3.2.4 Groundwater sampling

In 2008 and 2009, filtered and unfiltered bore hole water samples were collected 3-4 times at the beginning, middle and end of the pumping test from the depth right below the well casing. In addition, water samples were collected from selected depths where fractures have been identified by geophysical logs using a dual pumping technique. A pump was placed below the well casing and pumped at higher rates to keep the bore hole flushed, while a second pump was placed at the desired depth to draw water at lower pumping rates. After the pH, dissolved oxygen and conductivity monitored by an YSI 600QS multiprobe in a flow cell were stabilized, four aliquots of samples were collected from each depth. The 1st aliquot was filtered through a 0.45 μm membrane filter into a vial that is acidified for cation analyses. The 2nd aliquot was also filtered but not acidified for anion analyses. An arsenic speciation cartridge was attached after the filter to collect the 3rd acidified aliquot for the dissolved arsenic (III) analysis. The 4th aliquot was the unfiltered water sample, often with visible iron-oxide particles, that was later digested with nitric acid for the total arsenic analysis.

3.2.5 Cubitainer experiment

Experiments were conducted to evaluate the kinetic and equilibrium of adsorption processes that can modify total and dissolved arsenic concentrations of groundwater in the bore hole. In 2009, two water samples from each well were collected into 4 liter cubitainers. One was collected from the main pump placed at the depth below the casing towards the end of pumping test, while another was from the bottom of the bore hole

from the slower pump. For each sample, two cubitainers were filled, placed in thick walled plastic bags immediately, and kept in dark for the duration of the experiment. One cubitainer was kept sealed while another was purged with air to promote oxidization. The same four types of aliquots were collected for the total arsenic, dissolved arsenic and arsenic(III) at 7 time points, i.e. 8 hours, 16 hours, 1 day, 2 days, 4 days, 8 days and 16 days, with the volume of water taken out from the cubitainer recorded. At each sampling time, pH, conductivity and dissolved oxygen were recorded using the YSI 600QS multiprobe.

At the end of the experiment, the entire volume of water and particles in the cubitainers were filtered through 0.7 μm glass fiber filters (Whatman GF/F). The particles together with the filters were dried and weighed, then digested by concentrated nitric acid on a hot plate. The digests were diluted and analyzed for arsenic and iron. The mass loss of arsenic due to sampling and evaporation during the experiment was considered when reconstructing the mass balance.

3.2.6 Analytical methods

Anions of water samples were measured using the Ion Chromatography (IC) following the EPA method 300. Major cations and trace elements, including arsenic, were analyzed using the High Resolution Inductively Coupled Plasma Mass Spectrometry (HR ICP-MS). Arsenic speciation in selected samples was measured in the field using the differential pulse cathodic stripping voltammetric method (HE et al., 2004). Alkalinity was titrated using the Gran titration method.

3.3 Results and Discussions

3.3.1 Water producing fractures

Well MA70076 is 54.3 m deep with the casing extended to 28.3 m depth (Figure 3.2). The initial water table was at 6.60 m in October 2008 and 6.99 m in August 2009. The caliper, conductivity and acoustic televiewer logs suggest three fracture zones. The first is a group of relatively high angle fractures from the casing to 34 meter depth, as indicated by large variations in well diameter from the caliper log, fluid resistance and electromagnetic conductivity. The second fracture zone is composed of messy fractures between 36 and 41 meter depth. The third zone is the deep fractures from 47 meter depth to the bottom of the bore hole where water temperature and conductivity increased with depth (Figure 3.2). Under the ambient condition, flow meter did not show significant inflows or outflows, except a very slight downward flow (0.04 liter per minute) between 48 and 52 meter depth. When the well was pumped at a rate of approximately 0.68 liter per minute, more than 90% of flow to the well was estimated from the deepest fracture zone with a flow rate of about 0.53 liter per minute near the bottom. The two shallower fracture zones contributed very little water to the borehole. The flow rate of groundwater from deep fractures was estimated to be about 3.0 liter per minute under stressed conditions with a pumping rate of 3.8 liter per minute.

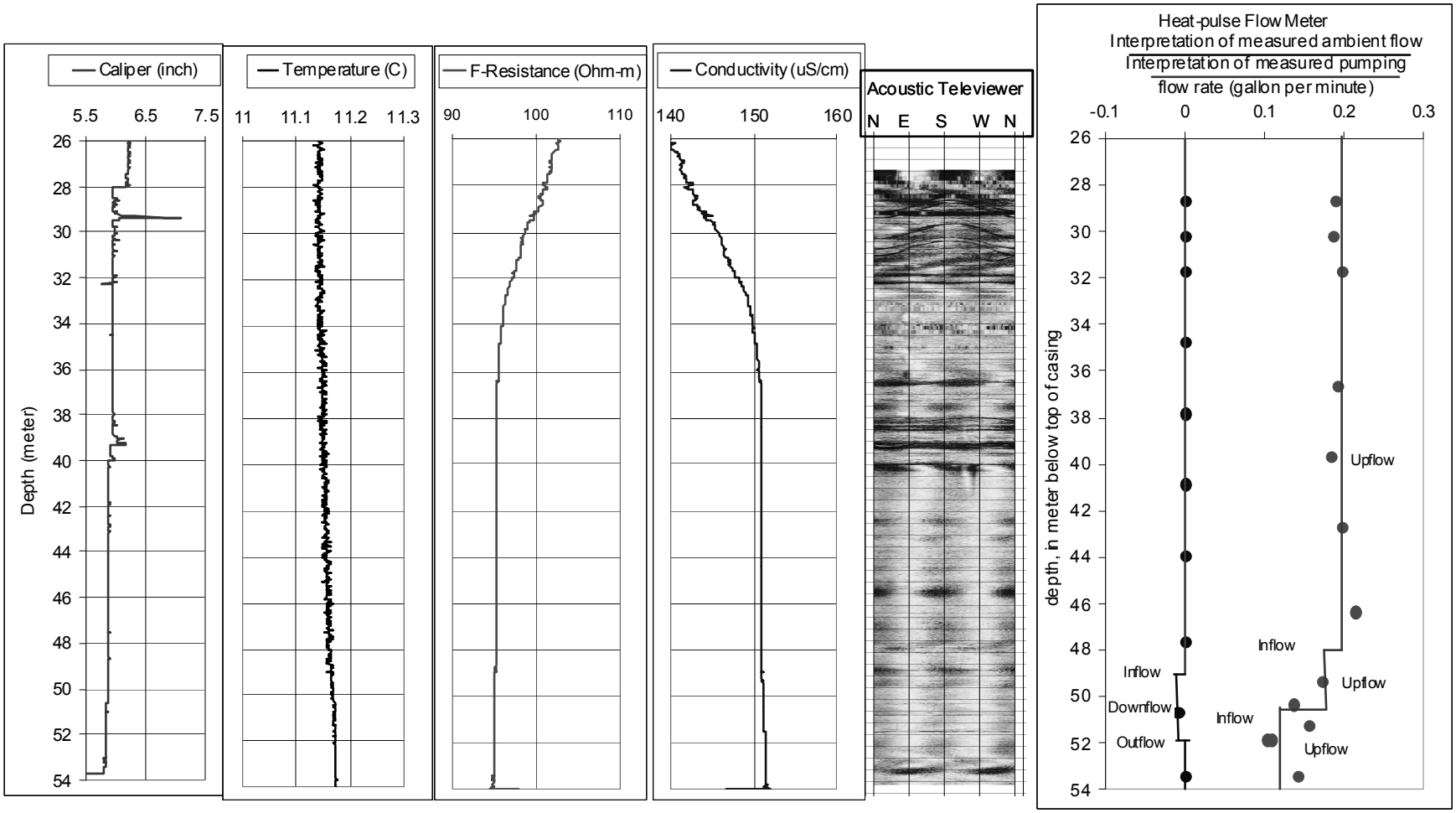


Figure 3.2 Composite logs of caliper, water temperature, fluid resistance, electromagnetic conductivity, acoustic televiewer, and heat-pulse flow meter logs from well MA70076 in Manchester, Maine

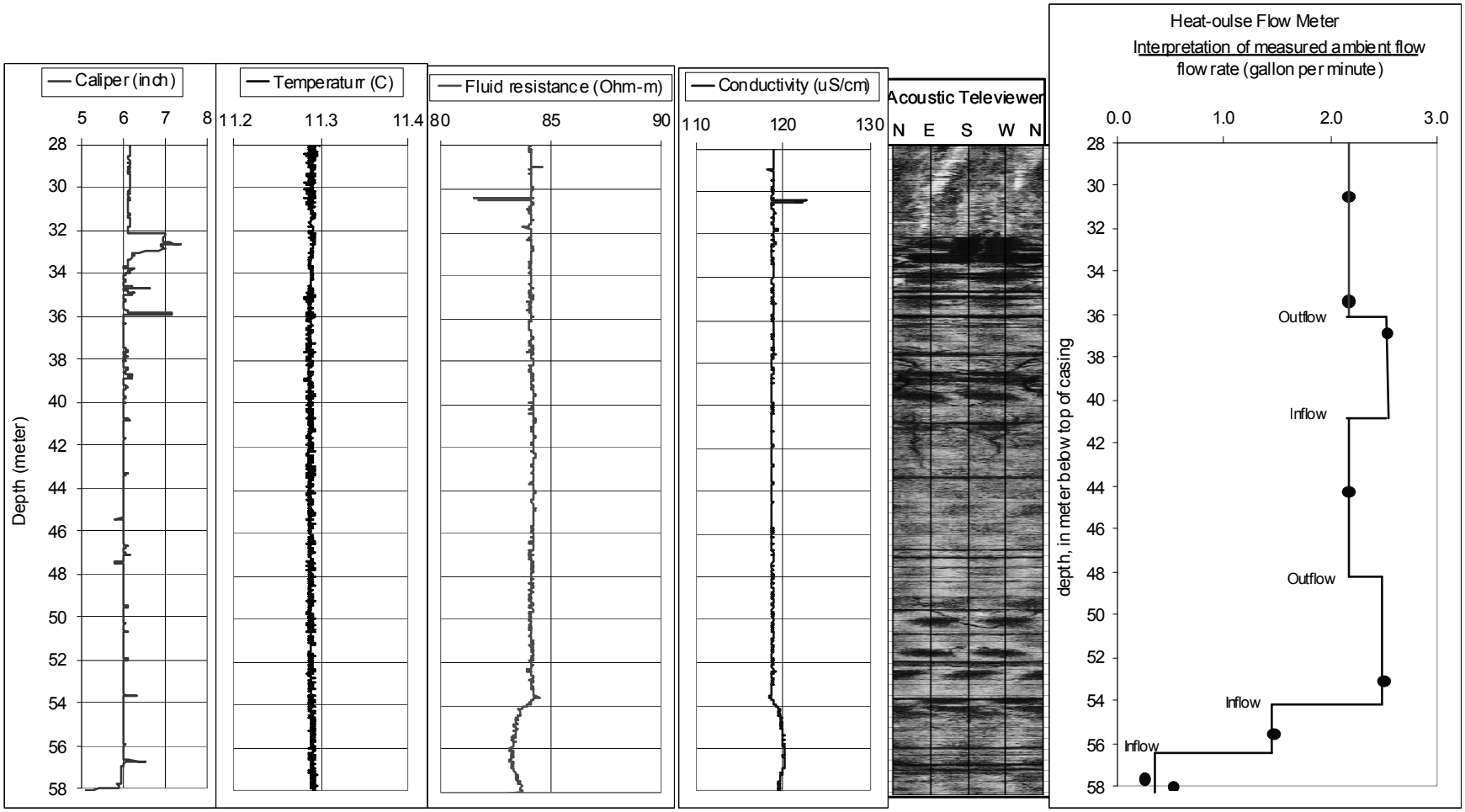


Figure 3.3 Composite logs of caliper, water temperature, fluid resistance, electromagnetic conductivity, acoustic televiewer, and heat-pulse flow meter logs from well MA70138 in Manchester, Maine

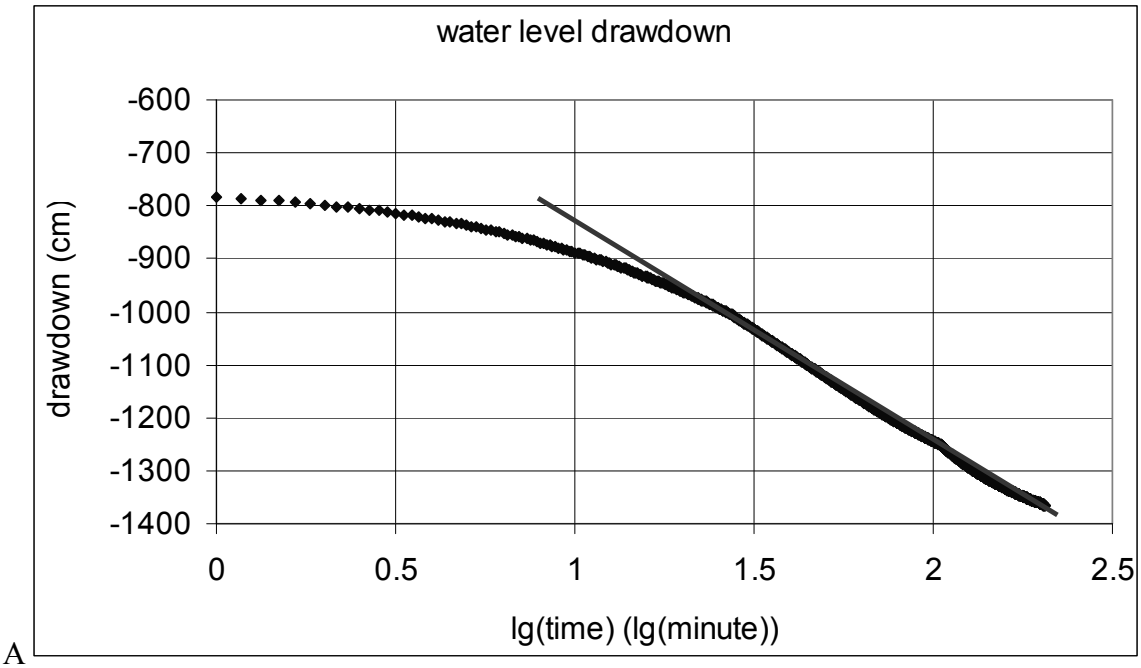
Well MA70138 is 58.2 m deep with the casing extended to a depth of 32.1 m (Figure 3.3). This well was artesian with an ambient flow rate of approximately 7.6 liter per minute in October 2008. The water table was 0.3 meter from the top of casing in August 2009 after the family returned to full time residency. There are again three major fracture zones. The shallow fracture zone is from the bottom of the casing to 36 meter depth featured by many open fractures as indicated by abruptly enlarged well diameters. The second fracturezone is between 37 and 52 meter depth with many poorly oriented fractures. The deep fracture zone is below 53 meter with large fractures corresponding to a sudden increase of conductivity (Figure 3.3). The ambient flow rates were way beyond the dynamic range of measurement by the heat pulse flow meter. The best estimate was that the deep fractures below 53 meter contributed more than 70% of water flow to the bore hole. The flow rate of groundwater from the deep fractures was estimated to be about 9.1 liter per minute when pumped at a rate of 9.1 liter per minute in August 2009.

For both wells, water is coming primarily from deep fractures near the bottom of the bore hole, consistent with the fact that drillers usually stop drilling and complete the well installation at depths where productive fractures with sufficient yield were found.

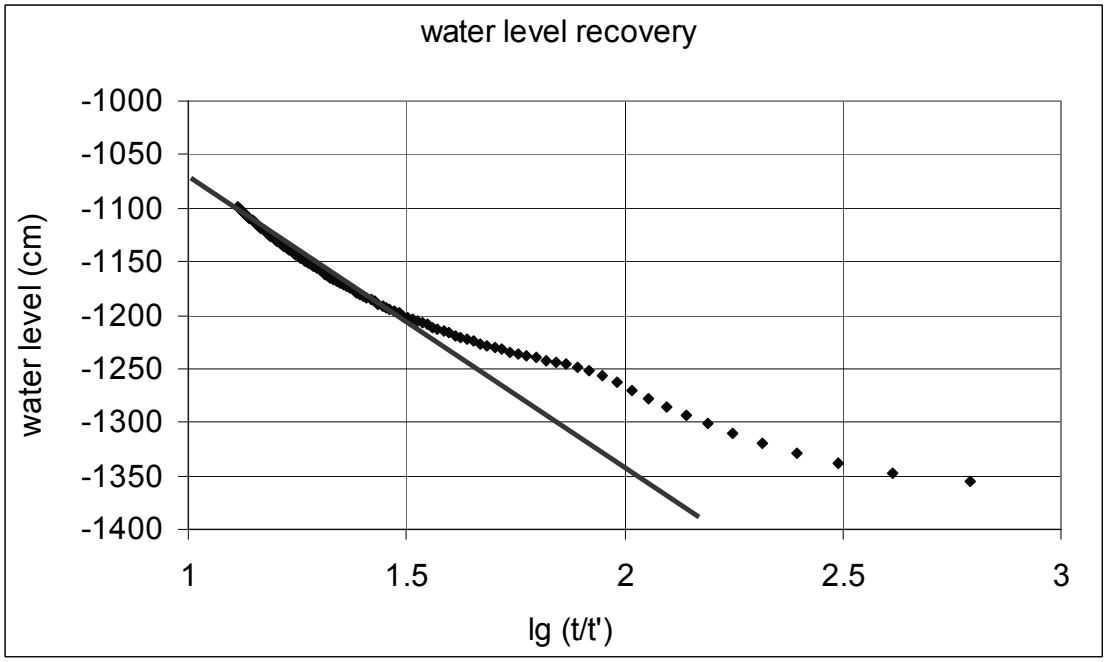
3.3.2 Bore hole transmissivity

The bore hole transmissivity of well MA70076 was 0.23 square meter per day (m^2/d) estimated from the drawdown data collected by pressure transducers in 2009 (Figure 3.4-A). Water level recovery did not show an ideal linear trend, the best educated guess of the bore hole transmissivity was 0.31 m^2/d (Figure 3.4-B). The transmissivity estimated from a few manually collected water level drawdown and recovery data in

2008 was 0.7-0.9 m^2/d, but this might be biased because the pumping test was conducted only very briefly for 90 minutes.



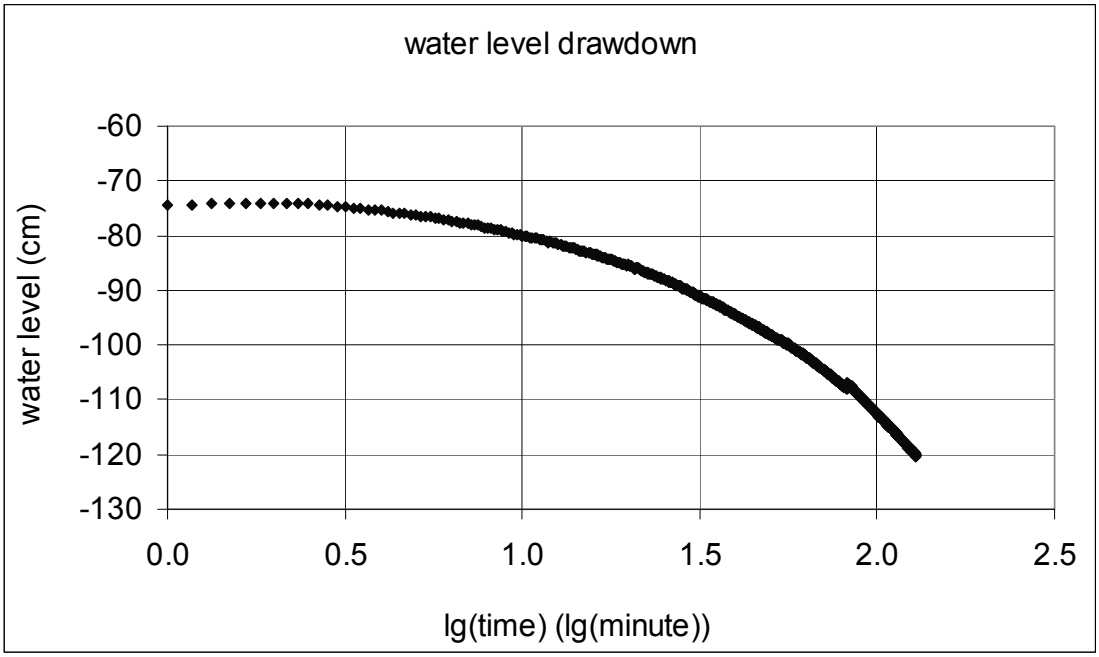
A



B

Figure 3.4 Cooper-Jacob method to estimate bore hole transmissivity of well MA70076

A



B

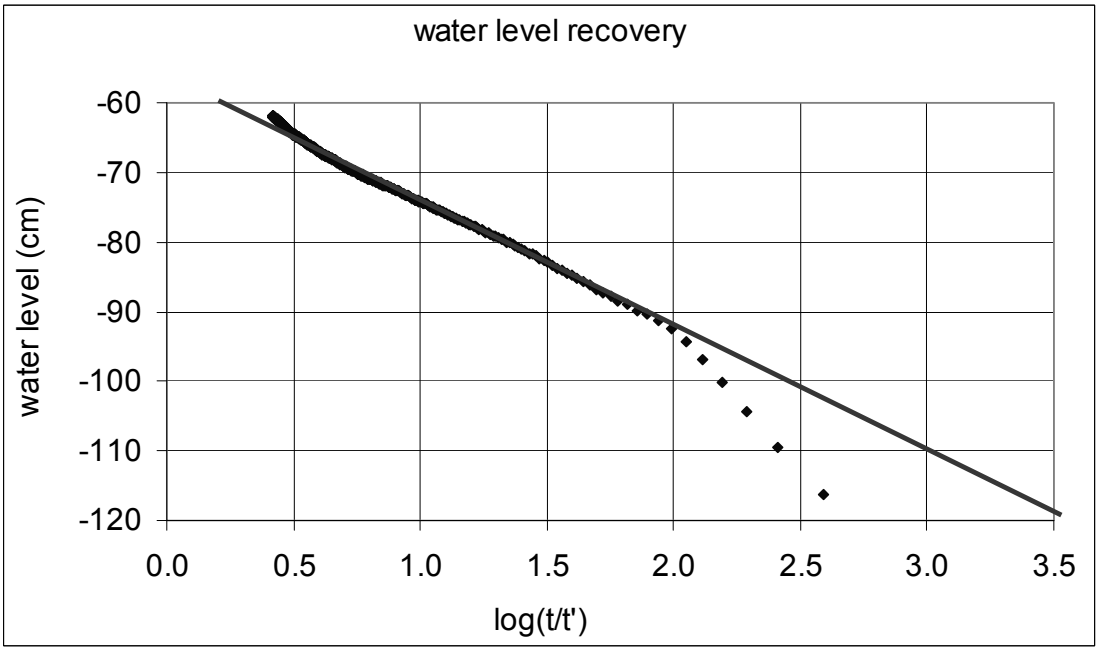


Figure 3.5 Cooper-Jacob method to estimate bore hole transmissivity of well MA70138

The drawdown curve of well MA70138 was typical when a barrier boundary was reached by pumping (Figure 3.5-A). It was very likely that a less productive fracture or a

poorly inter-connected network of fractures existed in the vicinity of the well. Based on the water level recovery data (Figure 3.5-B), the bore hole transmissivity was estimated to be 10.6 m^2/d.

The estimated bore hole transmissivities are comparable to those determined in similar bedrock units in New England. In Bigelow Brook Formation of meta-sedimentary sillimanite gneiss in Storrs, CT, bore hole transmissivities ranged from 0.46 to 2.8 m^2/d (JOHNSON et al., 2005). In a fractured granitic gneiss and micaceous schist formation of Cambrian-Ordovician age in Norwalk, CT, bore hole transmissivities ranged from 0.19 to 8.0 m^2/d (LANE JR. et al., 2002). In Mirror Lake, NH, where the bedrock is pelitic schist intruded by the granite and overlain by the glacial drift, the transmissivities of fractures measured by flow meter ranged from 0.01 to 10 m^2/d, and most bore holes had at most 2 or 3 highly transmissive fractures (transmissivity > 0.1 m^2/d) (PAILLET, 1998; SHAPIRO, 2001).

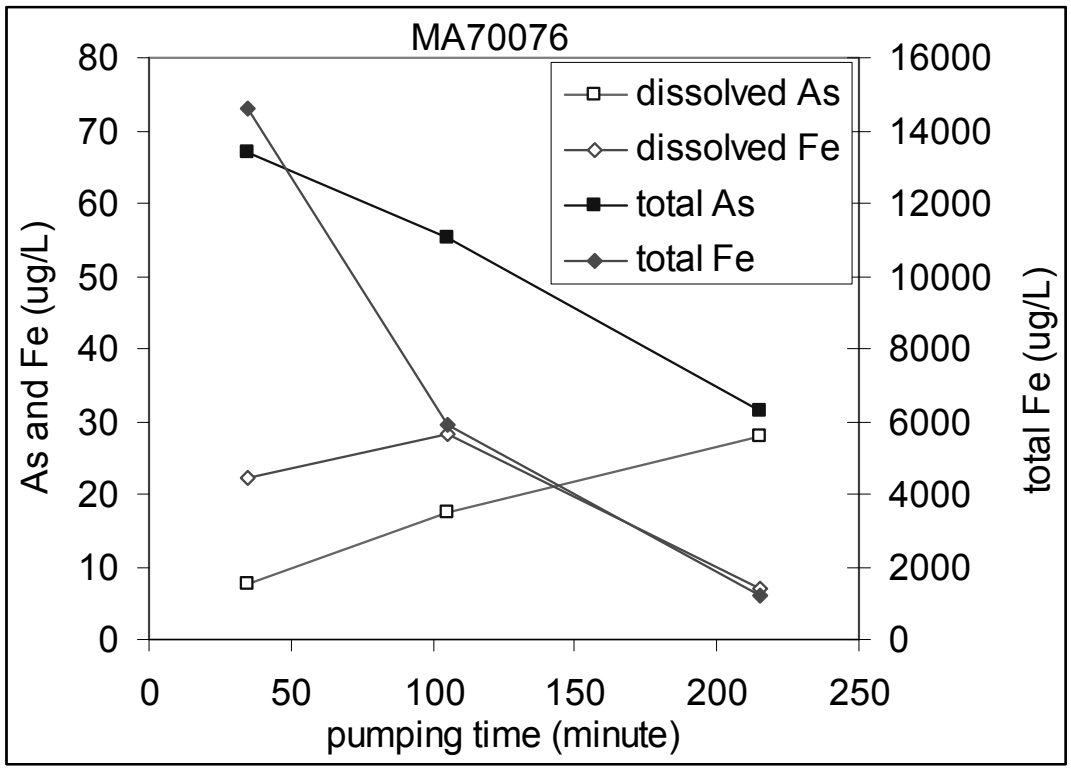
3.3.3 Arsenic and water chemistry under minimum pumping

In well MA70076, the total arsenic concentration in the unfiltered well water sample MA70076 collected in 2007 from garden hose after pH (7.5) and dissolved oxygen (3.0 mg/L) stabilized in a flow cell (pumping time unkown, but was < 30 minutes) was 37.7 µg/L. The total iron concentration was 2,190 µg/L. In 2009 sampling, the first bore hole water sample 70076.01 collected after 35 minute of pumping had 67.1 µg/L of total arsenic, and 7.7 µg/L of dissolved arsenic, mostly in As(V). The dissolved arsenic was a very small fraction of the total arsenic. The total iron concentration was 14,625 µg/L, with a very small fraction as in dissolved forms (22 µg/L). Dissolved

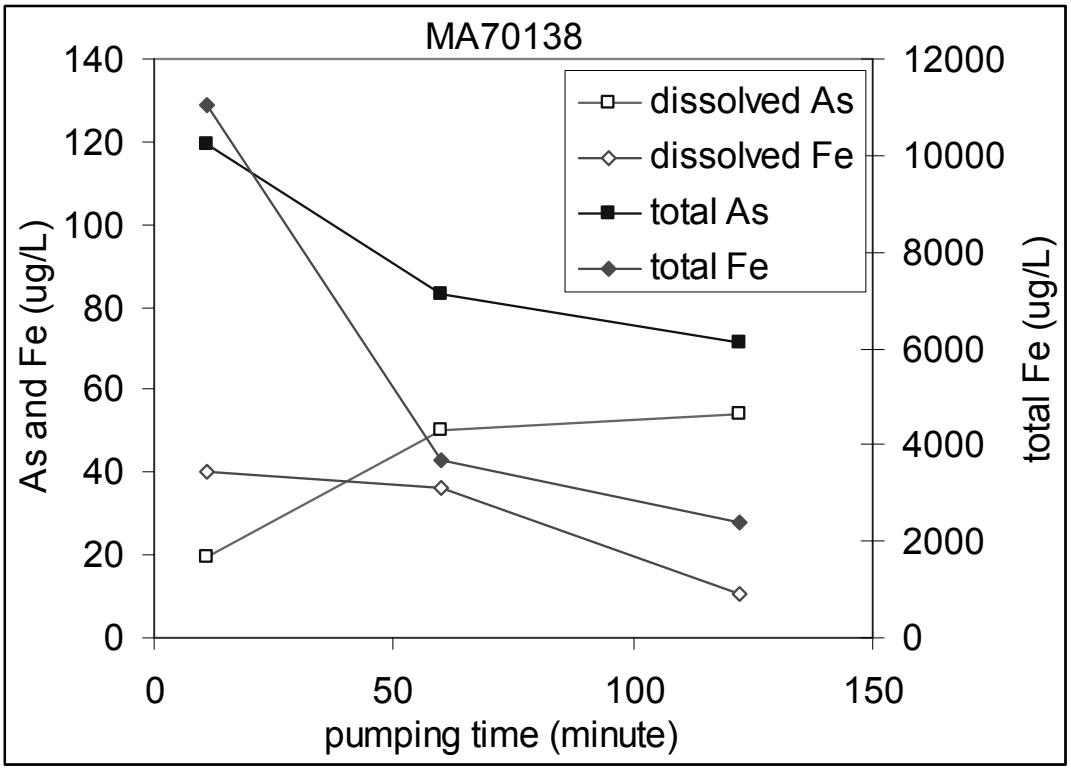
oxygen was initially 8.7 mg/L, but decreased to 5.4 and 4.0 mg/L as pumping proceeded, indicating an oxic environment in the bore hole and consistent with the high As(V) fraction of dissolved As. The major ions, especially cations, i.e. Ca, K, Na, Mg, in the sample 70076.01 were significantly lower than those samples after pumping over a longer time (> 2 hrs). This suggests that the high yielding fracture water with high arsenic and high dissolved solids was diluted by the bore hole water with low arsenic and low total dissolved solids at the beginning of pumping. As pumping going on, the bore hole water is being replaced by the water from high yielding fractures near the bottom.

In well MA70138, the total arsenic concentration in the water sample MA70138 collected in 2007 from garden hose also after pH (8.2) and dissolved oxygen (1.0 mg/L) were stabilized was 73.1 µg/L. The total iron concentration was 50 µg/L. The water sample MA70138.0 collected in 2008 from garden hose after 1 hour of artesian overflow had 649.5 µg/L of total arsenic and only 10 µg/L of dissolved arsenic, 174,384 µg/L of total iron and 1,390 µg/L of dissolved iron (e.g., the fraction that passed through the 0.45 um filter and may contain colloidal iron). In 2009 sampling, the first bore hole water sample 70138.01 collected after 11 minute of pumping had 119.4 µg/L of total arsenic with 19.4 µg/L of dissolved arsenic as mostly in As(V), and 11,047 µg/L of total iron with 40 µg/L of dissolved iron.

In both wells, dissolved arsenic was a small fraction of total arsenic, which favored the arsenic removal efficiency of filtration devices typically installed by homeowners for water treatment. The treated tap water from well 70076 had only 0.02 µg/L of arsenic and 0.86 µg/L of iron.



A



B

Figure 3.6 Arsenic and iron concentrations in bore hole water during pumping test

3.3.4 Arsenic response to pumping

In both wells, during the pumping test in 2009, total arsenic and total iron concentrations in water samples collected below well casing decreased, while dissolved arsenic concentrations increased with pumping (Figure 3.6). The increase of dissolved arsenic is attributed to displacing the low arsenic bore hole water by the high arsenic fracture water supplied mostly from the fractures at the bottom of both holes. The decrease of total iron and arsenic most likely reflect the settling of existing iron particles in the bore hole caused by the disturbance when the homeowner's pump was pulled and the sampling pumps and other instruments were deployed.

After 3.5 hours of pumping, dissolved arsenic concentrations decreased from 36.7 to 24.7 μg/L in well MA70076 as the pump was being pulled up from deeper depths to shallow depths. This was consistent with the displacement mechanism suggested above, and further implies that the flux of high dissolved arsenic water from the deep fracture zone was small, so the dilution effect by the bore hole water with low dissolved arsenic is still evident. In well MA70138, dissolved arsenic showed constant concentrations from deep to shallow depths as the pump was raised. This is attributed to the high transmissivity of the bottom fractures in this well, which supplied a large flux of high arsenic water that completely displaced the bore hole water in 2 hours.

In well MA70076, the molar ratios of particulate As/Fe were 0.002-0.005 with a mean value of 0.003. Based on this ratio, even if all of the dissolved iron entering the bore hole from the fractures was as high as 112 μg/L and all the iron formed particles and fully adsorbed arsenic, this would only result in a very little arsenic removal of bore hole

water (0.4 μg/L). Even in well MA70138, which had higher molar ratios of particulate As/Fe (mean value 0.006), arsenic adsorption on iron particles would not contribute much to arsenic removal in the bore hole (0.3 μg/L) because of the low dissolved iron concentrations in fracture water. This suggested that there was no or only a very small fraction of arsenic adsorption during pumping, while the settling iron particles already had arsenic sorbed to them before entering the bore hole, probably in the fractures.

Because of the lack of arsenic sorption in the bore hole, the low initial dissolved arsenic concentrations could be from other fractures at other depths supplying water with low arsenic and low total dissolved solids. Another possibility is that there are other fractures supplying dissolved iron, so when the water was sitting in the bore hole for a long time, it had ample time to be oxidized and thus adsorb arsenic on iron particles.

It is worthwhile notifying that only 0.45 μm membrane filters were used, so when the total iron concentrations were really high, the dissolved iron probably had a fraction that was really colloidal. This could be the reason of high dissolved iron concentrations in the samples of MA70076.0, MA70076.1, MA70138.0 and MA70138.1.

3.3.5 Arsenic evolution in bore holes from cubitainer experiment

Dissolved arsenic concentrations (mostly in the form of As(V) consistently) did not change apparently over time during the cubitainer experiment, except there was a small decrease in the bore hole water from well MA70076 at the beginning stage of the experiment (Table 3.3 and Figure 3.7). Dissolved iron concentrations were high in the initial water samples with high levels of particulate iron, then decreased and kept constantly low (mostly below 10 μg/L) over the experiment period when iron particles

were settling down. These high initial dissolved iron concentrations and decrease over time might be due to the colloidal iron not being filtered out when the total iron concentrations were high. The high initial dissolved arsenic concentrations in the bore hole water from well MA70076 might be also caused by this reason, which was the artifact presence of colloidal iron enriched in arsenic. At the end of the experiment, the final dissolved arsenic concentrations in the air-purged water samples were slightly higher than those in the non-air-purged water samples, probably affected by the higher pH in the former than in the later.

Total iron and arsenic concentrations decreased with time, following a logarithmic trend (Table 3.3 and Figure 3.7). Because iron was mostly in particulate forms and dissolved arsenic levels did not show much variation with time, both particulate iron and arsenic decreased with time. This is consistent with the settling process of arsenic rich iron particles in the bore hole. The molar ratios of As/Fe in particulates kept constant in each experiment (Table 3.3, samples with total iron <500 μg/L not included due to low particle contents), which further suggested that the most significant process was coagulation and settling of iron particles that might be already enriched in arsenic. In the water samples from well MA70076, there was a slight increase in particulate As/Fe ratios in the first few hours (Table 3.3), which might indicate a small fraction of arsenic adsorption on iron particles.

The sorption coefficient of arsenic on iron particles, Kd value, was calculated by dividing the dissolved arsenic concentration from the arsenic concentration in particulate, assuming that particulate arsenic was adsorbed on iron minerals. The Kd values were in the range of 90,000~260,000 L/kg except the bore hole water from well MA70076

showed relatively higher values of 300,000 - 400,000 L/kg. The Kd values did not show apparent changes over time in each water sample except slightly lower in the initial water samples from well MA70076, which further proved that there was no or very little adsorption in the bore hole.

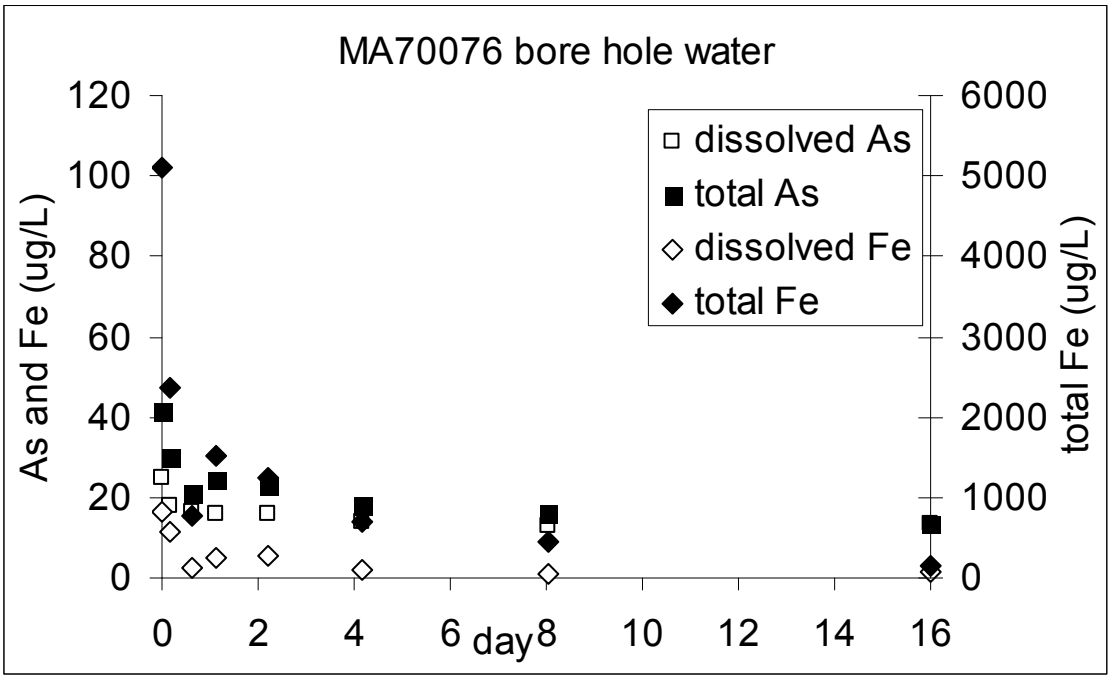
All the water samples had more than 95% As(V) out of dissolved arsenic throughout the experiment, indicating there was no or very little oxidation, or a quick oxidation process before water samples were collected.

The particles were highly enriched of iron (15% - 35% in weight), which were possibly in the mineral forms of amorphous ferric oxyhydroxides. Arsenic concentrations ranged from 775 to 1,178 mg/kg in those particles from well MA70076 water samples, and from 1,568 to 3,016 mg/kg in MA70138 particles (Table 3.4). The molar As/Fe ratios were 0.006-0.008 in MA70138 particles, higher than 0.003-0.004 in MA70076 particles. These ratios were also consistent with the ratios found in the particulates of the bore hole water during pumping test and those during the cubitainer experiment. The different As/Fe ratios between the water samples in two wells were probably because that the initial pH, dissolved oxygen and major ion concentrations affected the composition of iron particles and thus the arsenic adsorption capacity of them. Most samples showed a mass balance within 10% range before and after experiment. Two samples showed larger loss of arsenic (-26% and -33%), probably because some arsenic was adsorbed on the wall of the cubitainers.

Table 3.3 Arsenic and iron concentrations in the cubitainer experiment

Sample	Time	pH	Iron (Fe)		Arsenic (As)			molar ratio	As sorption Kd
			total	dissolved	total	dissolved	diss.As(III)	particulate As/Fe	adsorb.As/diss. As
	day		µg/L	µg/L	µg/L	µg/L	µg/L	mol/mol	L/kg
MA70076	0	7.22	5103	16.6	41.4	24.7	0.8	0.002	1.E+05
bore hole water	0.2	ND	2373	11.3	30.0	17.7	0.1	0.004	3.E+05
	0.6	7.25	783	2.6	21.0	16.5	0.1	0.004	4.E+05
	1.1	7.91	1514	4.8	24.4	15.8	0.1	0.004	4.E+05
	2.2	7.34	1244	5.3	22.7	15.7	0.1	0.004	4.E+05
	4.2	7.58	698	1.9	17.7	13.9	0.1	0.004	4.E+05
	8.0	7.52	459	1.0	16.0	13.1	0.0		
	16.0	7.78	150	1.7	13.7	13.4	0.2		
MA70076	0	7.22	5103	16.6	41.4	24.7	0.8	0.002	1.E+05
bore hole water	0.6	7.67	2260	2.5	31.6	20.8	0.2	0.004	2.E+05
with air purging	1.1	7.98	1670	1.2	28.0	21.1	0.1	0.003	2.E+05
	2.2	7.87	847	1.9	25.1	21.0	0.5	0.004	2.E+05
	4.2	7.70	420	1.8	21.2	20.8	0.2		
	8.1	7.61	160	0.4	20.0	20.8	0.3		
	16.0	8.19	335	3.6	21.0	20.5	2.4		
MA70076	0	7.22	2652	111.9	42.8	36.7	0.3	0.002	7.E+04
fracture water	0.2	ND	1185	44.4	42.4	35.3	0.1	0.005	2.E+05
	0.7	7.53	601	3.5	38.2	35.0	0.1	0.004	2.E+05
	1.2	7.53	1109	2.0	39.5	34.1	0.1	0.004	1.E+05
	2.3	7.57	848	1.9	38.4	33.7	0.3	0.004	2.E+05
	4.2	7.59	448	1.4	35.4	32.8	0.6		
	8.1	7.46	233	3.0	32.8	33.0	0.1		
	16.1	7.82	134	0.7	32.1	32.5	<DL		
MA70076	0	7.22	2652	111.9	42.8	36.7	0.3	0.002	7.E+04
fracture water	0.7	7.72	943	1.3	40.8	37.6	0.1	0.003	9.E+04
with air purging	1.2	8.02	862	1.2	42.2	38.7	0.1	0.003	1.E+05
	2.3	7.87	466	3.8	39.4	37.8	0.9		
	4.3	7.73	240	0.3	38.2	38.0	1.0		
	8.1	7.89	128	0.4	37.5	38.3	1.3		
	16.1	8.23	101	0.3	37.4	39.1	2.2		
MA70138	0	7.75	3173	12.3	78.5	54.4	0.6	0.006	1.E+05
bore hole water	0.3	7.76	1441	1.9	68.9	54.9	0.6	0.007	2.E+05
	0.7	8.23	882	12.6	61.5	54.4	1.4	0.006	2.E+05
	1.2	8.63	633	13.1	58.3	53.3	0.5	0.006	2.E+05
	2.2	8.36	679	9.5	56.8	50.9	0.5	0.007	2.E+05
	4.7	8.38	402	4.6	54.4	50.6	0.2		
	8.1	8.16	240	4.3	51.7	49.7	0.8		
	15.0	8.12	114	0.4	49.2	49.4	0.1		
MA70138	0	7.75	3173	12.3	78.5	54.4	0.6	0.006	1.E+05
bore hole water	0.7	7.85	1489	2.6	69.3	54.3	0.5	0.008	2.E+05
with air purging	1.2	7.85	984	1.9	64.9	53.8	0.9	0.008	2.E+05
	2.2	7.87	550	0.7	58.4	54.4	1.2	0.005	1.E+05
	4.7	8.07	198	0.4	55.8	54.3	0.8		
	8.1	8.05	28	<DL	53.0	55.1	0.5		
	15.0	8.28	35	<DL	53.7	56.5	0.9		
MA70138	0	7.71	4944	25.6	93.1	51.5	0.5	0.006	2.E+05
fracture water	0.4	7.85	2373	5.0	77.7	52.5	1.3	0.008	2.E+05
	0.8	7.90	1791	7.0	70.0	52.2	1.4	0.007	2.E+05
	1.3	7.98	1409	9.2	65.3	51.1	1.0	0.008	2.E+05
	2.3	7.99	1073	5.2	62.8	49.2	0.4	0.009	3.E+05
	4.8	7.90	899	4.0	58.7	49.4	0.2	0.008	2.E+05
	8.2	7.90	491	4.7	52.4	48.5	0.5		
	15.1	8.10	236	5.6	49.3	47.7	0.1		
MA70138	0	7.71	4944	25.6	93.1	51.5	0.5	0.006	2.E+05
fracture water	0.8	7.85	2629	6.9	79.6	50.5	1.0	0.008	2.E+05
with air purging	1.3	7.85	2209	7.0	73.3	50.5	0.8	0.008	2.E+05
	2.3	7.88	1402	3.8	64.7	50.9	0.7	0.007	2.E+05
	4.8	8.12	832	2.6	58.9	49.2	0.2	0.009	2.E+05
	8.2	8.12	282	1.2	53.0	50.6	0.2		
	15.1	ND	310	<DL	51.5	51.0	0.4		

* ND – no data; <DL – below detection limit


MA70076 bore hole water
As and Fe (ug/L)
total Fe (ug/L)
day
dissolved As
total As
dissolved Fe
total Fe
0
20
40
60
80
100
120
0
1000
2000
3000
4000
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6000
0
2
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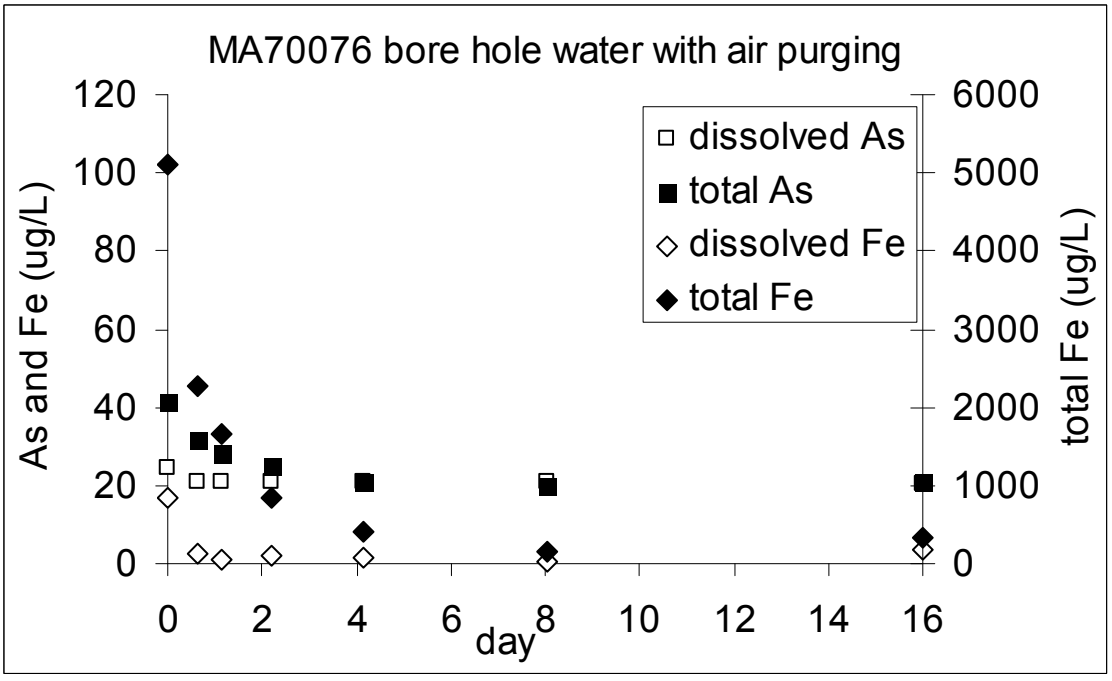
16


MA70076 bore hole water with air purging
As and Fe (ug/L)
total Fe (ug/L)
day
dissolved As
total As
dissolved Fe
total Fe
0
20
40
60
80
100
120
0
1000
2000
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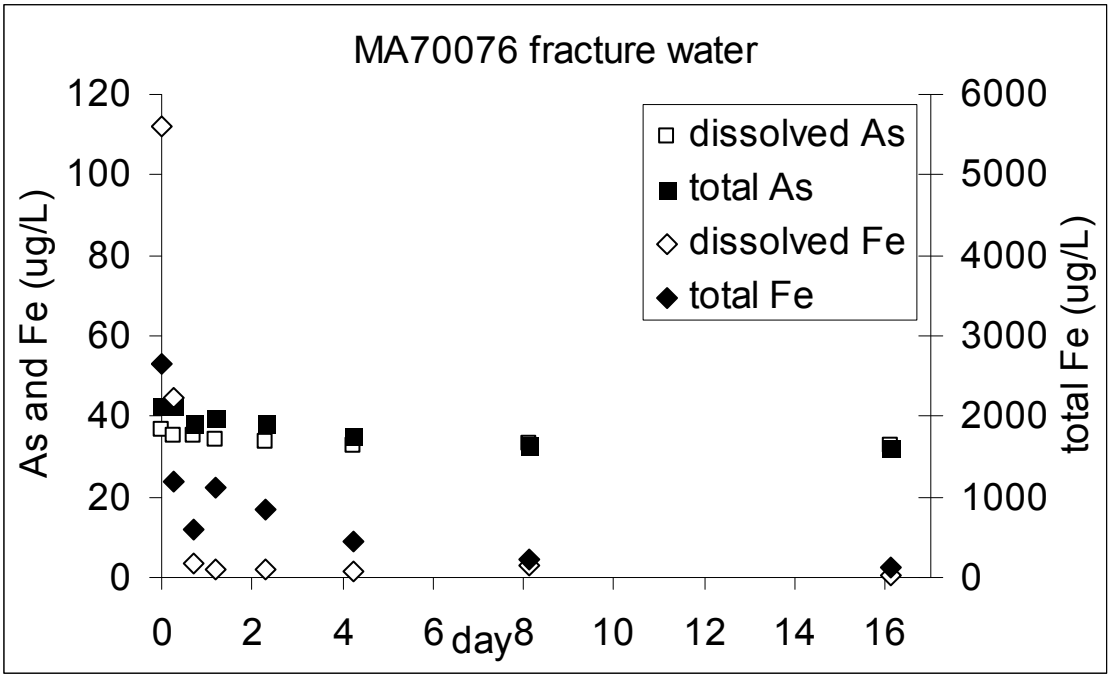
MA70076 fracture water
As and Fe (ug/L)
total Fe (ug/L)
day
dissolved As
total As
dissolved Fe
total Fe
0
20
40
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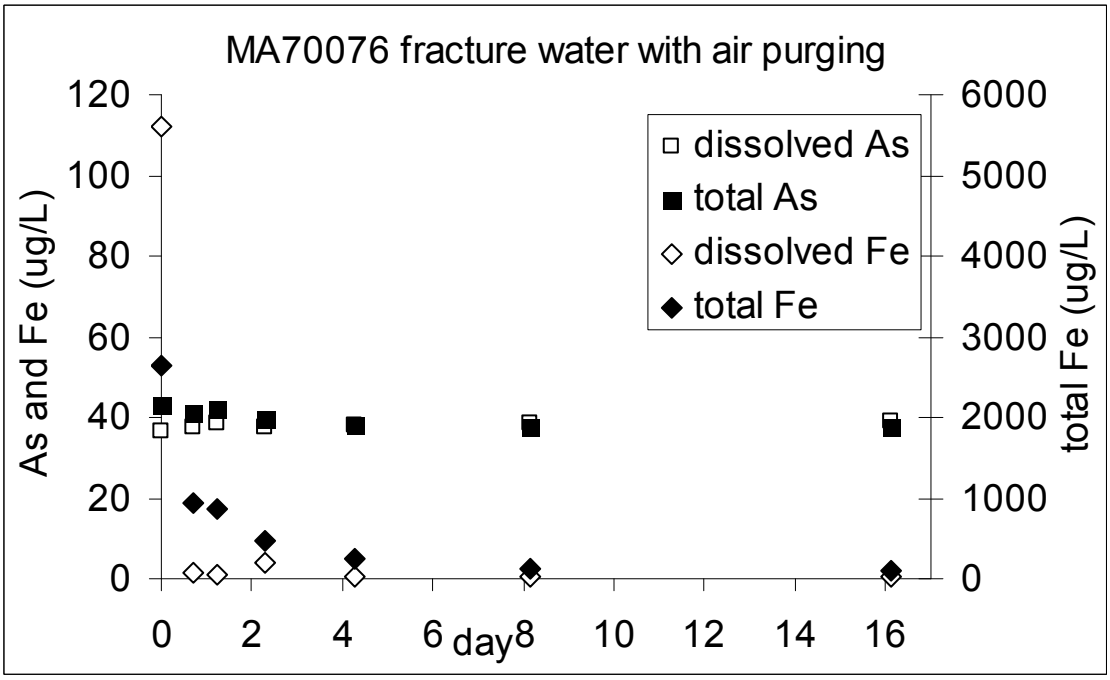
MA70076 fracture water with air purging
As and Fe (ug/L)
total Fe (ug/L)
day
dissolved As
total As
dissolved Fe
total Fe
0
20
40
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80
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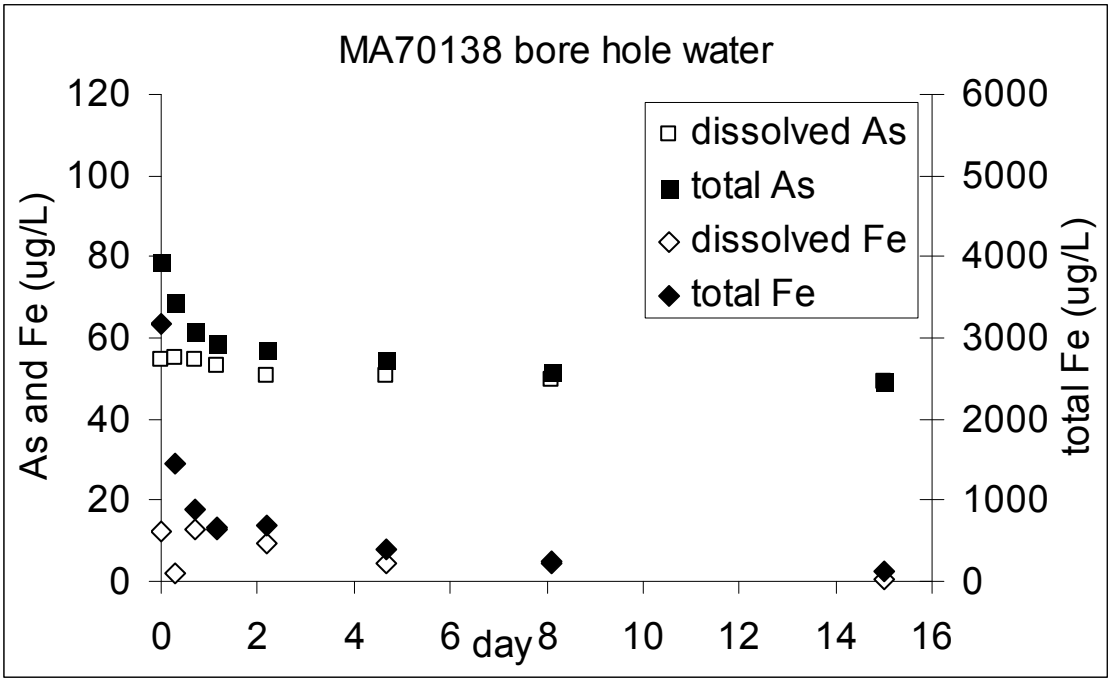
MA70138 bore hole water
As and Fe (ug/L)
total Fe (ug/L)
day
dissolved As
total As
dissolved Fe
total Fe
0
20
40
60
80
100
120
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1000
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0
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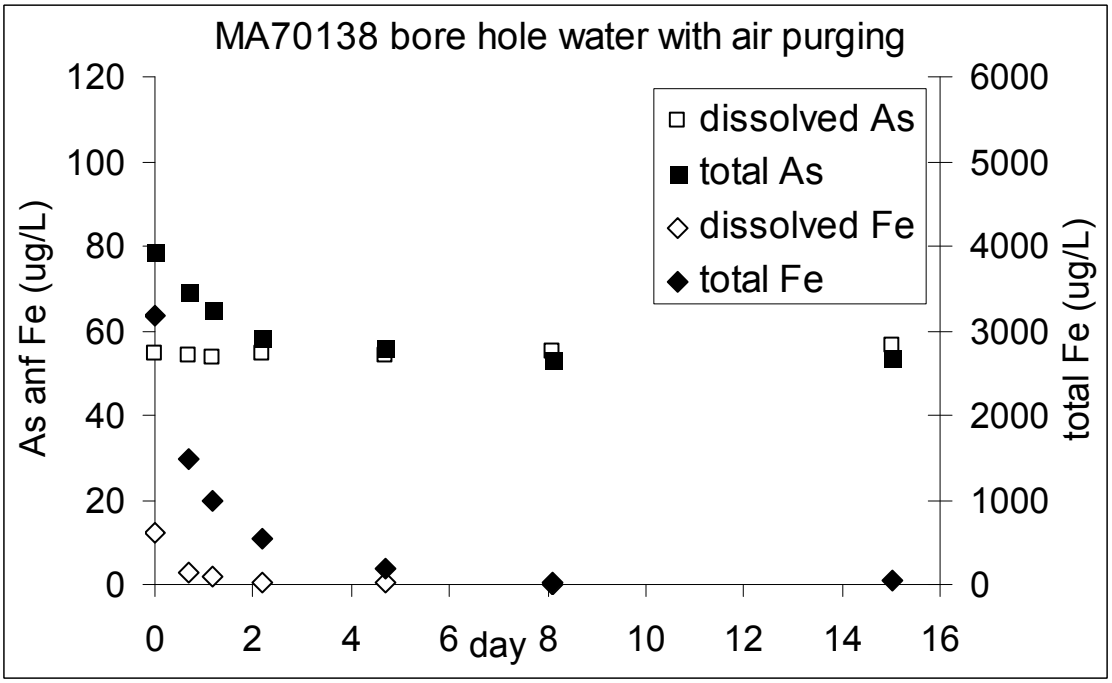
MA70138 bore hole water with air purging
As anf Fe (ug/L)
total Fe (ug/L)
day
dissolved As
total As
dissolved Fe
total Fe
0
20
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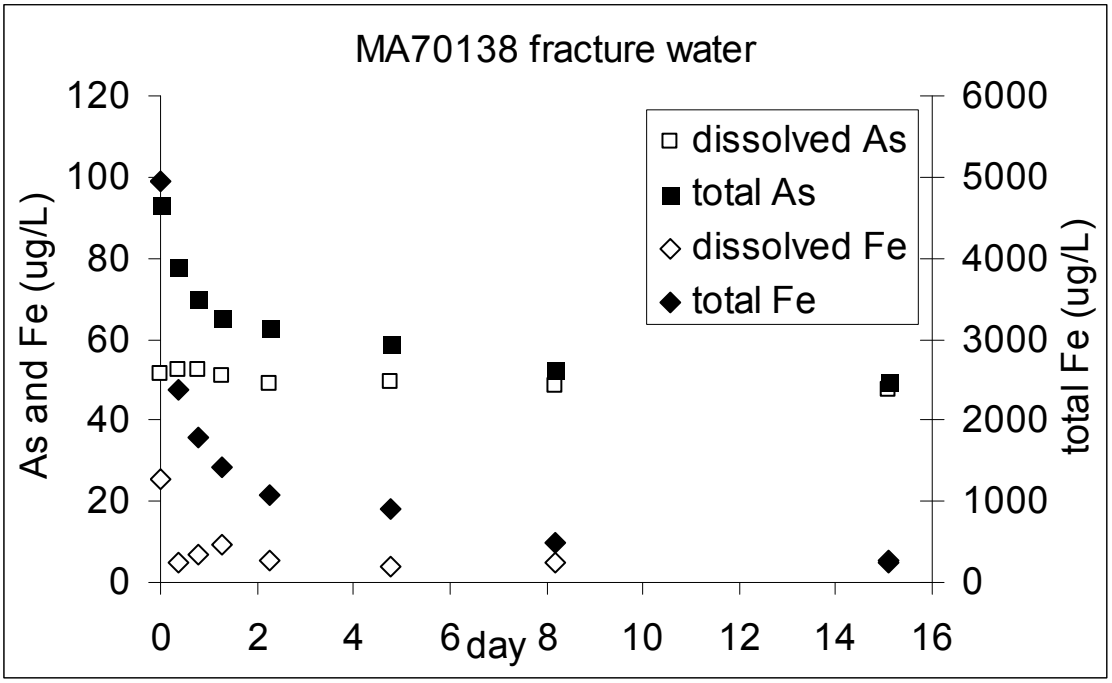


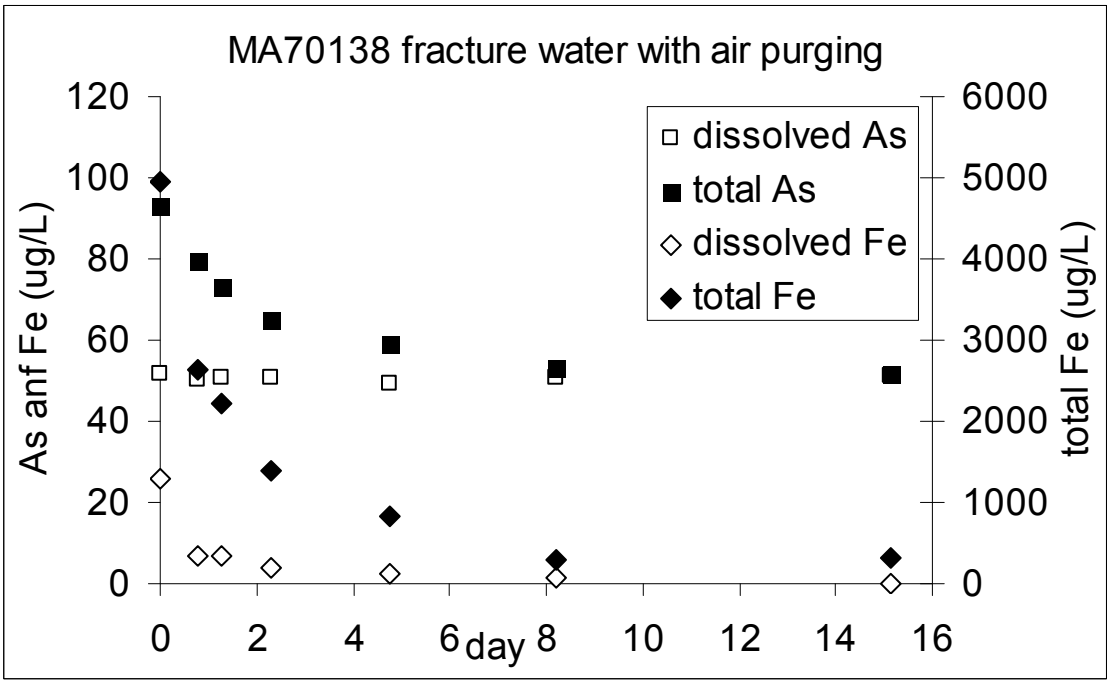


Figure 3.7 Arsenic and iron concentrations in the cubitainer experiment

Table 3.4 Arsenic and iron concentrations in the precipitated particles and mass balance estimate

	particle Fe (ug/g)	particle As (ug/g)	particle As/Fe molar ratio	As in particle (ug)	As left in solution (ug)	As loss during sampling (ug)	Initial total As (ug)	mass balance error
Well 70076								
bore hole water	276527	1137	0.003	40	46	29	174	-33%
fracture water	242549	1178	0.004	22	92	59	180	-3%
bore hole water - air	202621	775	0.003	40	57	66	174	-6%
fracture water - air	185246	867	0.003	14	97	98	180	16%
Well 70138								
bore hole water	346688	3016	0.006	76	132	92	330	-9%
fracture water	272127	2933	0.008	60	111	118	391	-26%
bore hole water - air	191359	1911	0.007	57	117	154	330	-1%
fracture water - air	144387	1568	0.008	71	102	209	391	-2%

3.3.6 Summary

In the two domestic bedrock wells in the greater Augusta area, arsenic in the bore hole water is mainly supplied by water producing fractures near the bottom of bore hole. The arsenic concentrations of the bore hole water reflects the mixing between the high arsenic water from the productive fractures and the low arsenic ambient bore hole water. Pumping increases the supply of arsenic to the bore hole water from the productive fractures at the bottom, and thus increases the dissolved arsenic concentrations in the wells. The reason of why the bore hole water was initially low in arsenic remains to be explored but it is unlikely due to the sorption or co-precipitation reactions with iron supplied from the productive fractures because the dissolved iron concentrations in fracture water samples were simply too low. The lower dissolved arsenic concentrations of the ambient bore hole water compared to that supplied by the fracture water suggests that there must be additional sources of water with low arsenic percolating to the bore hole.

3.3.7 Future work

This research can be improved by, 1) further quantifying the groundwater flow rates from various fractures to reconstruct the vertical flow profile in the bore hole, 2) collecting more water samples during pumping test to reproduce the mixing process and estimate the fractions of arsenic and iron in dissolved, colloidal and particulate phases, 3) collecting water samples from specific bore hole intervals using inflatable packers to minimize the mixing effect, 4) conducting cubitainer experiments with high dissolved iron water samples to better define the oxidation and adsorption rates of arsenic, 5) conducting researches in wells with even higher arsenic concentrations to better estimate the arsenic evolution processes. Another domestic well, with up to 478 μg/L of arsenic in the unfiltered well water, in the similar bedrock formation in the greater Augusta area, Maine, has been proposed to estimate the groundwater flow by advanced geophysical logs and to collect fracture specific water samples using inflatable packers to investigate arsenic evolution in the bore hole.

Chapter 4 A Comparison of Spatial Distributions of Arsenic in Groundwater, Soil and Stream Sediment in the Conterminous US

Abstract

Arsenic distributions in soil, stream sediment and groundwater in the conterminous United States from PLUTO, NURE and NAWQA data sets were interpolated at the national scale. Western and Southwestern states showed the highest arsenic occurrence, High Plains and Southeastern states showed the lowest. The soil arsenic concentrations (n=12,705) ranged from 0.1 to 5,667 mg/kg with a median value of 10 mg/kg. The sediment arsenic concentrations (n=49,034) ranged from 0.1 to 100,000 mg/kg with a median value of 10 mg/kg. The association of arsenic distributions among different media examined by logistic regression suggested that soil and stream sediment arsenic distributions had significant effects on groundwater arsenic occurrence at the national scale. At regional scales, the association between soil/sediment and groundwater arsenic distribution was quantified in Florida and Nevada where the sampling density is > 1 per 200 km^2. At local scales, the association between soil and groundwater arsenic distributions in fractured bedrock aquifers in the greater Augusta area, Maine suggested that the soil arsenic distribution was indicative of the groundwater arsenic pattern when sampling density was > 1 per 20 km^2. A comparison of data at different spatial scales showed stronger associations between arsenic in groundwater and in soil/sediment when sampling density was higher. Soil and sediment arsenic data should be included in regression models used to predict arsenic occurrence in groundwater.

4.1 Introduction

High concentrations of arsenic in drinking water have increased the risks of skin, bladder, kidney, liver, lung diseases and cancers to an estimated 51.1 million person-years in the past fifty years in the United States (FROST et al., 2003; KARAGAS et al., 2002). Like many other countries, population in the United States relying on groundwater, especially from private wells, is subjected to the greatest health risk. The source of arsenic in groundwater is mostly geogenic with the exception of a few localized cases where groundwater was polluted by mining activities or by the application of arsenic containing pesticides.

Evidences are emerging that arsenic contents and chemical composition of sedimentary or bedrock aquifer materials play important roles on groundwater arsenic distributions in the U.S. (AYOTTE et al., 1999; WELCH et al., 2000). Studies from Bangladesh (AZIZ et al., 2008; VAN GEEN et al., 2008), India (PATEL et al., 2005), and the United Kingdom (BREWARD, 2007) have found that examining the correlation of arsenic spatial patterns in groundwater, soil, and stream sediment can be very helpful to understand groundwater arsenic occurrence and transport on regional scales. To date, few studies have attempted to compare the spatial patterns of groundwater arsenic occurrence with arsenic anomalies in soils and stream sediments despite the fact that economic geologists have extensively used soil arsenic anomalies to pinpoint areas with subsurface precious metal (and arsenic) mineralization (BOYLE and JONASSON, 1973; KESLER et al., 2005; ZHOU et al., 2002). This has been done for two reasons. First, the mineral contents and chemical composition of stream sediments and soils reflected the weathering of underlying parent materials (JOHNSON et al., 2004). Second, sampling and analyzing soils

or stream sediments for arsenic is easier and less costly than dealing with hard rocks or consolidated samples. In the Malcantone watershed of southern Switzerland, soil arsenic concentrations, especially those in the C horizon, have been shown to be a promising indicator of arsenic concentrations in underlying bedrocks and groundwater (PFEIFER et al., 2004). Studies are needed to ascertain on what spatial scales soil or stream sediment arsenic anomalies are indicative of sub-surface aquifer sediment or rock arsenic anomalies and elevated groundwater arsenic concentrations.

Fortunately, tens of thousands of groundwater, soil and stream sediment samples have been collected and the data are available for the conterminous U.S. The spatial distribution of groundwater arsenic (n=20,000) shows a distinguished pattern that the west generally has substantially higher values than the east (LOCKWOOD et al., 2001; O'CONNOR, 2002; RYKER, 2001; WELCH et al., 2000). Researches have also been carried out at basin scales to examine the spatial patterns of groundwater arsenic distribution (AYOTTE et al., 2006; GOOVAERTS et al., 2005).

In this research, geostatistical analyses are performed to delineate the arsenic spatial distribution in groundwater, soil and stream sediment in the conterminous U.S. utilizing the best available data sets that allow the comparison especially for areas with sufficient sampling density. The spatial patterns of arsenic among different media are compared using logistic regression models to understand to what extent and at what scales groundwater arsenic distribution can be explained by soil and/or stream sediment arsenic occurrence. This research has implications on risk assessment and evaluation of arsenic occurrence in groundwater and soil/sediment, as well as resource management. It also

identifies the gaps in national geochemical databases that are needed to determine soil arsenic background values to establish appropriate cleanup goals (DAVIS et al., 2001).

4.2 Materials and Methods

4.2.1 National arsenic data

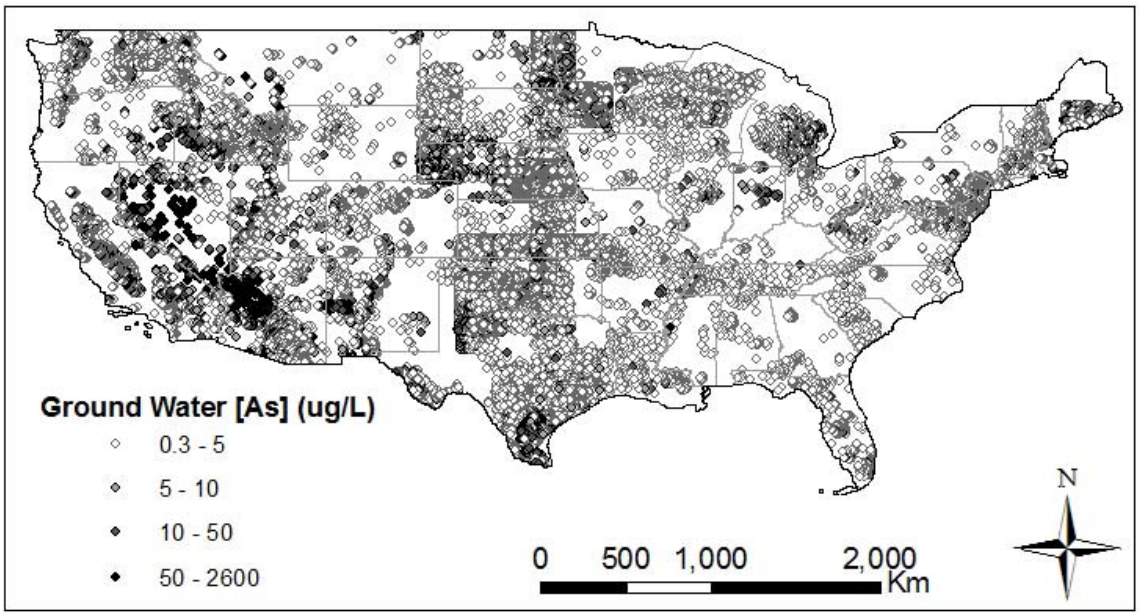
Arsenic concentrations in groundwater, soils and stream sediments are complied from 5 national data sources (Table 4.1). Average arsenic concentrations are used for those sites sampled multiple times and by multiple programs, thus the final combined data sets have fewer data points.

Groundwater: Data (n=41,120) are combined from two sources in the ArcGIS according to the latitude and longitude coordinates. The first is arsenic in potable groundwater resources (n=19,760) analyzed by the U.S. Geological Survey (USGS) National Water Quality Assessment program (NAWQA). The second is arsenic in well water samples (n=23,254) collected during the hydrogeochemical and stream sediment reconnaissance phase (HSSR) of the National Uranium Resource Evaluation program (NURE). The combined data set has an overall sampling density of 1 per 200 km^2, although the sampling density can be as low as 1 per 6000 km^2 to as high as 1 per 20 km^2 in different states (Figure 4.1 and Table 4.2).

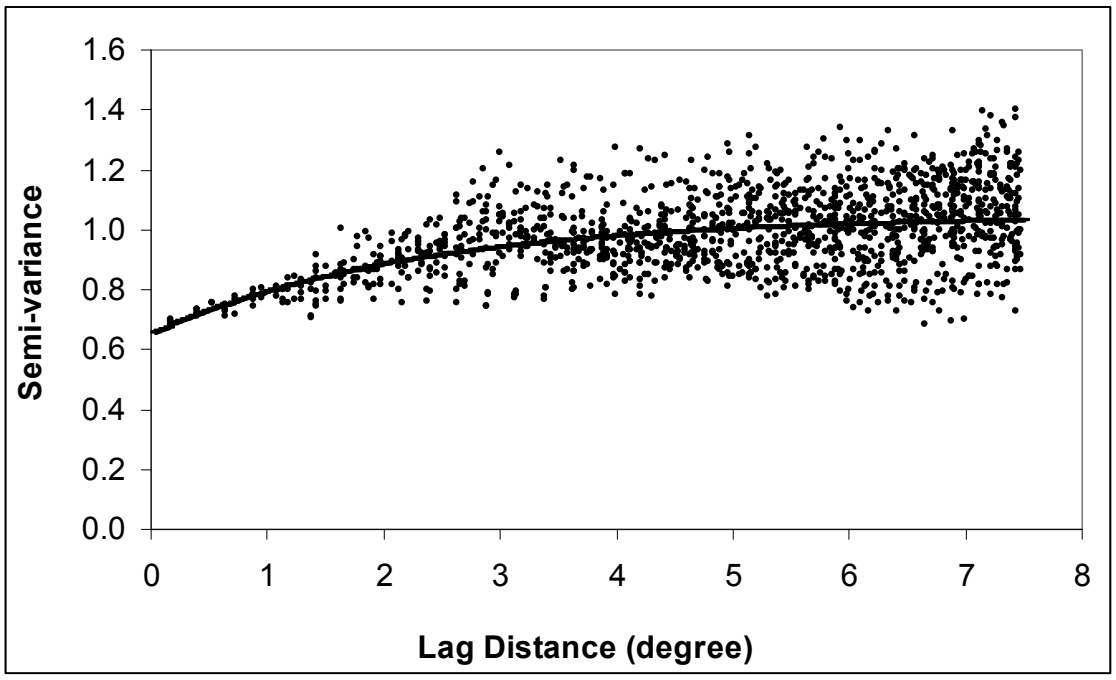
Soil: The updated PLUTO database (USGS, 2001a) is consisted of 30,323 soil arsenic concentrations with part of sites analyzed for multiple times. The sample size of the final data set is reduced to 12,705 after averaging. The sampling density is 1 per 600

km^2. Sampling density is high (greater than 1 per 150 km^2) in the states of California, Colorado, Missouri, Nevada, North Dakota and Oregon, but is low (1 per 2000 km^2) in most of other states (Figure 4.2 and Table 4.2). The original PLUTO database (SHACKLETTE and BOERNGEN, 1984) has 1,323 soil samples collected from a depth of about 1 foot, primarily from non-cultivated fields during the 1960s and 1970s at a density of one sample per 6000 km^2. The interpretation of this "Shacklette data set" indicated regional anomalies of soil arsenic distributions (GUSTAVSSON et al., 2001). The USGS and Natural Resources Conservation Service (NRCS) have proposed a national soil geochemical survey that will increase the sampling density of the PLUTO data set by at least a factor of 10 (SMITH et al., 2003).

Stream sediment: The data set of stream sediment arsenic distribution (n=49,034) is combined from two sources. The first is the unconsolidated sediment arsenic data (n=56,660) analyzed by various USGS programs and stored in the PLUTO database (USGS, 2001b). This data set includes arsenic concentrations in lake sediments and other uncategorized sediments besides stream sediments, and lacks the coverage for those states around the Gulf of Mexico. The second is the arsenic data in stream sediment samples (n=21,202) collected under the HSSR phase of NURE program (GROSZ et al., 2004; SMITH, 1997). The NURE data set is clustered in a number of regions in High Plains states and Texas. The average sampling density is one sample per 150 km^2, although the distribution is not even (Figure 4.3).

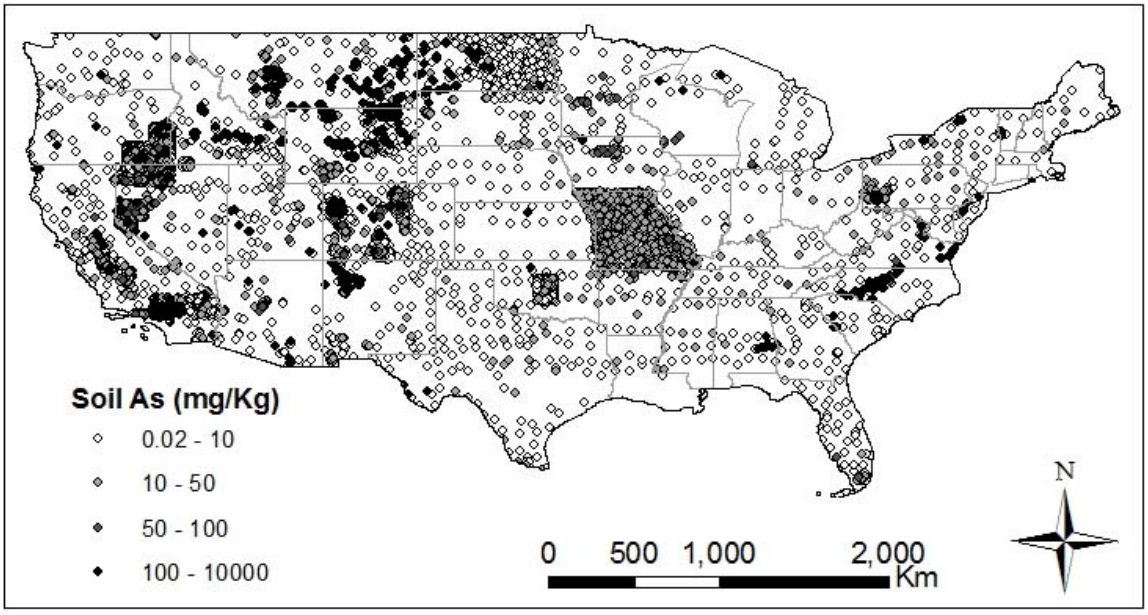


* number of observations =41,120

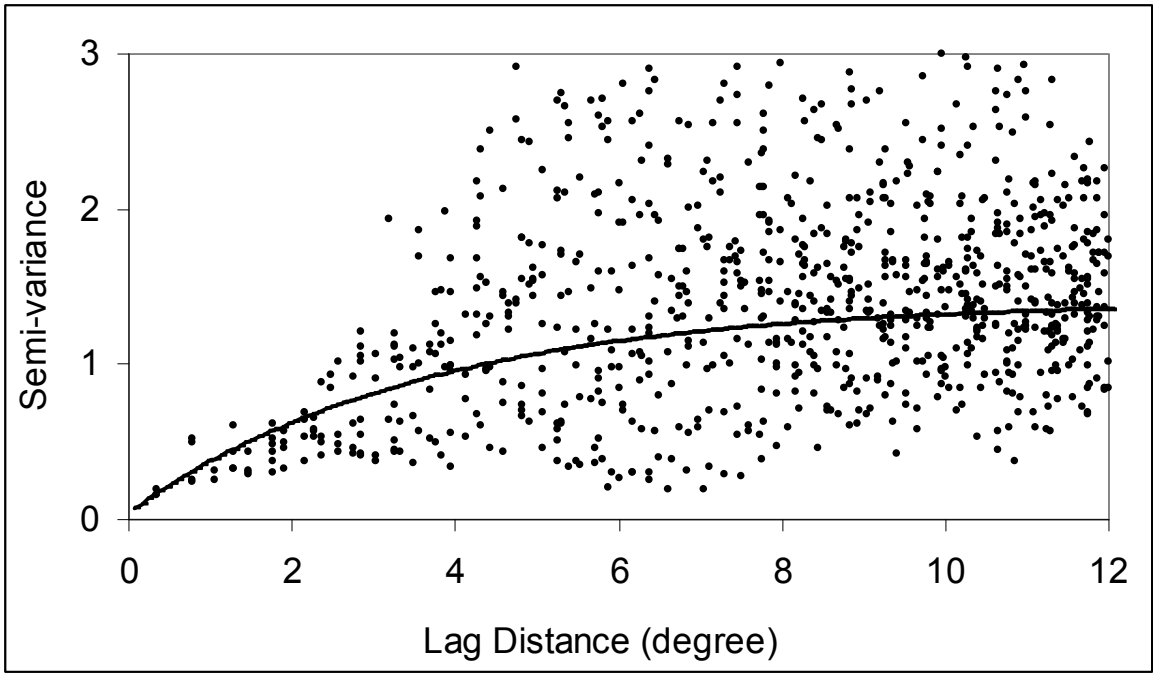


Isotropic exponential model $r_{(h)} = 0.40 \times (1 - e^{-h/6.72}) + 0.65$

Figure 4.1 Groundwater arsenic distribution and semi-variogram in the conterminous U.S.

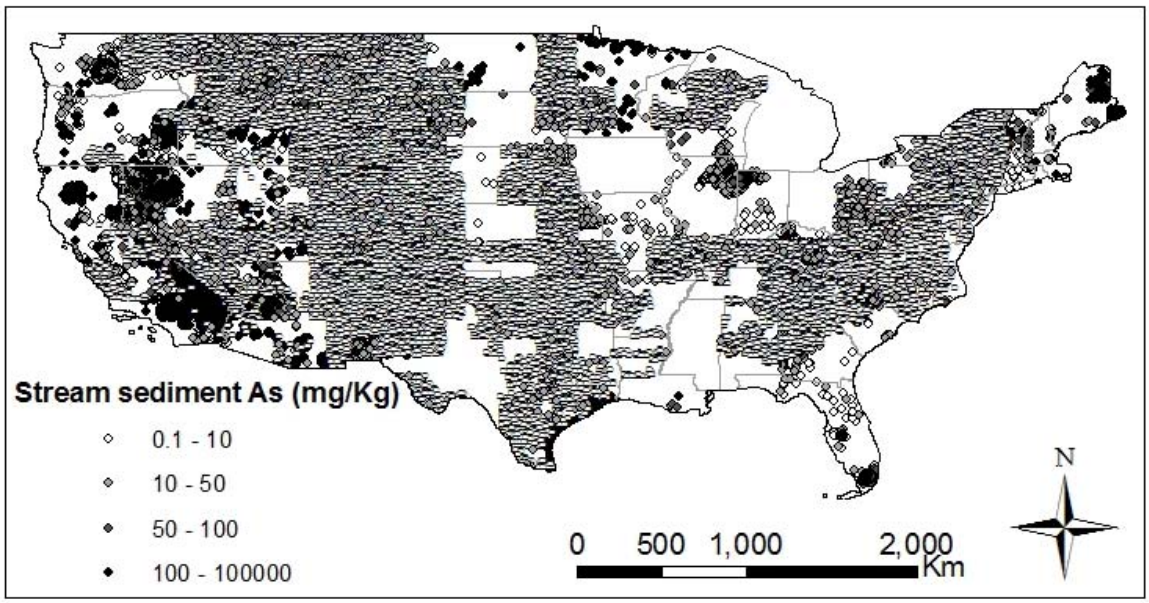


* Number of observations =12,705

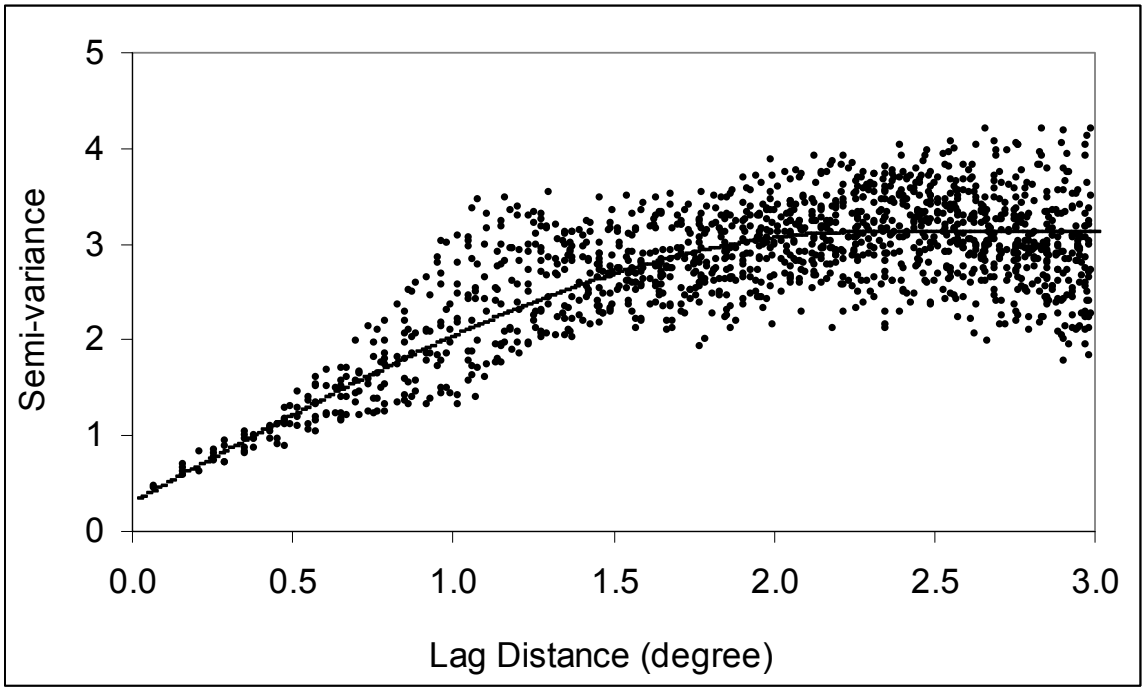


Isotropic exponential model $r_{(h)} = 1.36 \times (1 - e^{-h/10.81}) + 0.05$

Figure 4.2 Soil arsenic distribution and semi-variogram in the conterminous U.S.



* Number of observations =49,034



Isotropic spherical model $r_{(h)} = 2.81 \times (1.5 \times \frac{h}{2.27} - 0.5 \times (\frac{h}{2.27})^3) + 0.31$ when $h \le 2.27$

$r_{(h)} = 2.81 + 0.31$ when $h > 2.27$

Figure 4.3 Stream sediment arsenic distribution and semi-variogram in the conterminous U.S.

Table 4.1 Data sets of arsenic in the conterminous United States

	Data Sources	Number of Entry	Sample size after reduction	Mean [As], median [As], [As] range	Sample size (combined)	Sample density	Mean [As], median [As], [As] range	Mean [As], median [As] (interpolated)
Ground water	USGS NAWQA	19,760	18,358	7.2, 1.0, 0.9 – 2600	41,120	1 out of 200 km^2	6.1, 1.6, 0.3-2600	4.7, 2.1
	HSSR – NURE	23,254	22,762	5.2, 1.8, 0.3 – 1238				
Soil	PLUTO	30,323	12,705	33.6, 10.0, 0.1 – 5667	12,705	1 out of 600 km^2	33.6, 10.0, 0.1-5667	17.2, 7.8
Stream sediment	PLUTO	56,660	28,369	124.7, 15.0, 0.1 – 100,000	49,034	1 out of 150 km^2	73.8, 10.0, 0.1-100,000	101.4, 14.8
	HSSR - NURE	21,202	20,666	4.0, 3.0, 0.1 – 117				

* USGS NAWQA: U.S. Geological Survey National Water Quality Assessment program
* HSSR-NURE: the Hydrogeochemical and Stream Sediment Reconnaissance phase of the National Uranium Resource Evaluation program
* PLUTO: national geochemical database

4.2.2 Regional arsenic data

Three regions that represent different principal aquifers (USGS) are selected for comparison because they show an even sampling strategy and also a sufficient sampling density of both groundwater and soil/sediment (greater than one sample per 200 km^2). They are, 1) Florida, primarily unconsolidated sand/gravel aquifers and secondarily carbonate-rock aquifers, 2) New England, fractured crystalline bedrock aquifers with sporadically glacial deposited sand/gravel aquifers, 3) Nevada, extensively interlaced unconsolidated sand/gravel aquifers and igneous rock aquifers, in the order of from low to high in groundwater arsenic occurrence rates.

4.2.3 Local arsenic data

At the local scale, the greater Augusta area, Maine, has a groundwater data set (n=790) at a very high sampling density of 1 per 1.4 km^2 (YANG et al., 2009). Soil samples (n=67), mostly from horizon C or B which represent the highly weathered products of bedrocks, have been collected throughout the study area with a sampling density of 1 per 20 km^2. They were subjected to the total digestion by mixed concentrated perchloric acid, hydrofluoric acid and nitric acid in a microwave digestion system before arsenic concentrations were analyzed (YANG et al., In preparation). The sampling density of stream sediment in this area in the existing arsenic data sets is too low.

4.2.4 Statistical and spatial analysis

At the national scale, the log-normal ordinary kriging was used in the ArcGIS - Geostatistical Analyst for interpolation of each combined data set. Kriged surface maps of arsenic distributions in groundwater, soil and stream sediment were then converted into raster maps, with a grid size of 1 degree by 1 degree. Average groundwater, soil and stream sediment arsenic values were calculated in each grid. The logistic regression models, which used arsenic exceedance rates (transferred binary variables using 10 μg/L as the threshold value) in each grid as the dependent parameter, soil and stream sediment arsenic concentrations or transferred binary variables (using median concentrations as threshold values) as explanatory parameters, were used to estimate the impact of soil and stream sediment arsenic distributions on groundwater arsenic occurrence rates.

At regional and local scales, similar interpolation and logistic regression methods were applied, except that the interpolated arsenic concentrations in groundwater, soil and/or stream sediment were compared in each county and town, respectively.

A final logistic regression model using the combined data sets from different scales and using the spatial scale as an additional variable was performed to determine how the spatial scale and sampling density affected the correlation between groundwater and soil/sediment arsenic.

Results of logistic regression models in this research are as follows.

The form of logistic regression model is $P[y=1|x]=\frac{e^{(\beta_0+\beta_1x_1+\beta_2x_2+...+\beta_nx_n)}}{1+e^{(\beta_0+\beta_1x_1+\beta_2x_2+...+\beta_nx_n)}}$. In this research, P[y=1] represents the dependent variable, probability of groundwater [As] >10 μg/L; x1, x2, … xn represent independent variables or parameters; β0 represent intercept, β1, β2, … βn represent estimate; standard error is the prediction error of each estimate; z value is estimate divided by standard error; Pr(>|z|) is the two-tailed p value, parameters having p-values less than alpha (usually 0.05) are statistically significant.

1) Logistic regression model on national scale

Probability of groundwater [As] _binary ~ soil [As] + stream_sediment [As]

Parameter	Estimate	Std. Error	z value	Pr(>|z|)
(Intercept)	-2.771e+00	1.504e-01	-18.425	<2e-16
soil [As]	9.619e-06	1.454e-05	0.662	0.508
sed [As]	3.525e-06	2.691e-06	1.310	0.190

Convert soil/stream_sediment [As] into binary variable using median value
(0 when [As] < median, 1 when [As] > median)

Probability of groundwater [As] _binary ~ soil [As] _binary + stream_sediment [As] _binary

Parameter	Estimate	Std. Error	z value	Pr(>|z|)
(Intercept)	-3.4110	0.3489	-9.777	<2e-16
soil_binary	0.3914	0.2909	1.346	0.1784
sed_binary	0.7236	0.3777	1.916	0.0554

The odds ratio of sediment vs. soil = exp(0.7236-0.3914) = 1.4

2) Generalized linear regression model on national scale

Groundwater [As] ~ soil [As] + stream_sediment [As]

Parameter	Estimate	Std. Error	t value	Pr(>|t|)

(Intercept)	4.444e+02	5.112e+01	8.693	<2e-16
soil [As]	1.529e-03	7.566e-03	0.202	0.840
sed [As]	2.261e-03	1.557e-03	1.452	0.147

3) Logistic regression model on regional scale - Florida

Probability of groundwater [As] _binary ~ soil [As] + stream_sediment [As]

Parameter	Estimate	Std. Error	z value	Pr(>|z|)
(Intercept)	-0.2253	0.6017	-0.374	0.708
soil [As]	0.2699	0.2148	1.256	0.209
sed [As]	-0.2427	0.4668	-0.520	0.603

Convert soil/stream_sediment [As] into binary variable using median value
(0 when [As] < median, 1 when [As] > median)

Probability of groundwater [As] _binary ~ soil [As] _binary + stream_sediment [As] _binary

Parameter	Estimate	Std. Error	z value	Pr(>|z|)
(Intercept)	-0.1234	0.4138	-0.298	0.7654
soil_binary	1.0699	0.5275	2.028	0.0425
sed-binary	-0.7631	0.5276	-1.446	0.1481

The odds ratio of soil vs. sediment = exp(1.0699-(-0.7631)) = 6.3

4) Logistic regression model on regional scale - Nevada

Probability of groundwater [As] _binary ~ soil/stream_sediment [As]

Parameter	Estimate	Std. Error	z value	Pr(>|z|)
(Intercept)	-5.5203	2.8541	-1.934	0.0531
soil/sed [As]	0.5078	0.2657	1.912	0.0559

5) Logistic regression model on local scale – the greater Augusta area, Maine

Probability of groundwater [As] _binary ~ soil [As]

Parameter	Estimate	Std. Error	z value	Pr(>|z|)
(Intercept)	-2.083733	0.240847	-8.652	< 2e-16
soil [As]	0.053883	0.008915	6.044	1.5e-09

6) Logistic regression model on combined data from different scales

Probability of groundwater [As] _binary ~ area + soil [As] _binary

Parameter	Estimate	Std. Error	z value	Pr(>|z|)
(Intercept)	0.02985	0.24437	0.122	0.9028
area_Augusta	1.07666	0.84436	1.275	0.2023
area_FL	0 (defaulted)			
area_NV	-0.35993	0.57898	-0.622	0.5342
area_US	-3.00026	0.30969	-9.688	<2e-16
soil_binary	0.66016	0.27304	2.418	0.0156

4.3 Results and Discussion

4.3.1 Arsenic distribution in groundwater, soil and stream sediment in US

In the combined groundwater data set, arsenic concentrations range from 0.3 to 2,600 μg/L, with a mean value of 6.1 μg/L and a median value of 1.6 μg/L (Table 4.1). Approximately 9.3% of the samples have more than 10 μg/L of arsenic, similar to the finding based on about 30,000 groundwater samples (WELCH et al., 2000). The distribution of arsenic concentrations is highly skewed. Logarithmic transformation of the data reduces the skewness from 30.7 to 1.4. The semi-variogram of arsenic data shows a high nugget effect (0.7 out of 1.1), indicating a weak spatial autocorrelation in the distance of major range of 6.7 degree, or approximately 500 km (Figure 4.1). Western states show the highest arsenic concentrations, followed by southwestern, mid-west, High Plains states, and northeastern states. The lowest occurrences are found in southeastern states (Figure 4.4-A and Table 4.2). This spatial pattern from the kriging interpolation (Figure 4.4-A) is consistent with previous research results based on the area average method (RYKER, 2001) on the national scale, but differs in regional or local areas especially where the sample density is low or the sample distribution is not even.

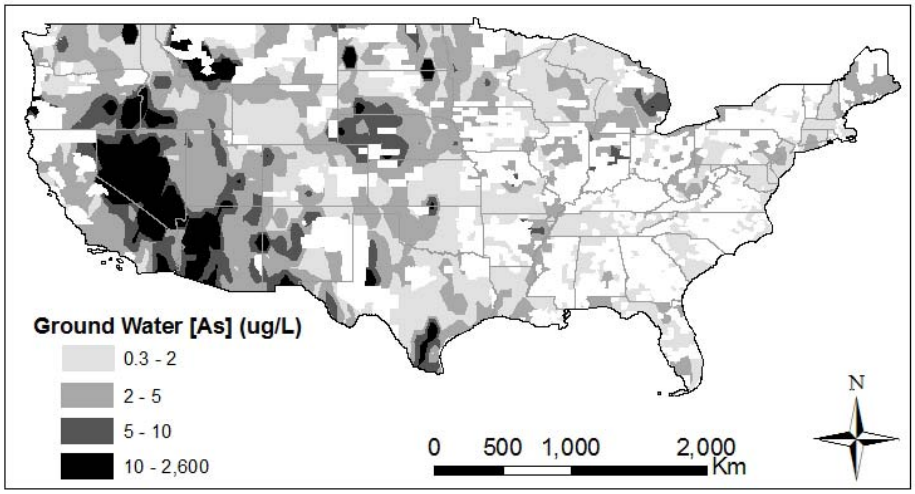
In the final soil data set, arsenic concentrations range from 0.1 to 5,667 mg/kg, with a mean value of 33.6 mg/kg and a median value of 10.0 mg/kg (Table 4.1). The distribution of arsenic concentrations is again highly skewed. Logarithmic transformation of the data reduces the skewness from 30.4 to 1.5. The semi-variogram of soil arsenic concentrations shows a low nugget effect (0.1 out of 1.4), indicating a strong spatial

autocorrelation in the distance of major range of 10.8 degree, or approximately 900 km (Figure 4.2). Compared with the previous interpolated maps based on "Shacklette data set" only (GUSTAVSSON et al., 2001; SHACKLETTE and BOERNGEN, 1984), western states and states in northern Great Plains display higher arsenic concentrations (Figure 4.4-B and Table 4.2).

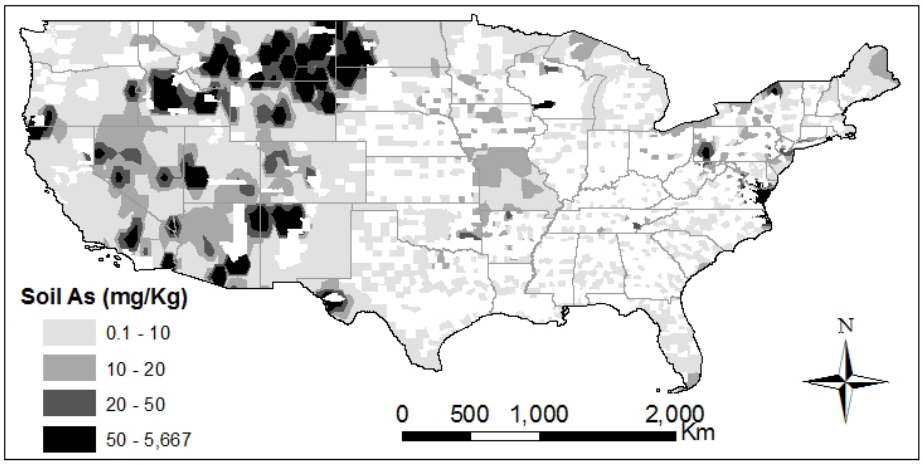
In the combined stream sediment data set, arsenic concentrations range from 0.1 to 100,000 mg/kg, with a mean value of 73.8 mg/kg and a median value of 10.0 mg/kg (Table 4.1). The distribution of arsenic data is extremely skewed and the skewness (110.9) can be reduced to 0.6 by the logarithmic transformation. The semi-variogram shows a low nugget effect (0.3 out of 3.1), indicating a strong spatial autocorrelation in the distance of major range of 2.3 degree, or approximately 200 km (Figure 4.3). Western states and the mid-west states show higher arsenic concentrations than other regions (Figure 4.4-C and Table 4.2).

The map generated in this research shows a better representation of the groundwater arsenic distribution because, 1) kriging can minimize the prediction bias from the uneven sampling, 2) kriging can estimate distributions in those areas with very few or even no samples based on the spatial autocorrelation of available data, although the prediction uncertainty and errors in those areas could be relatively large. Due to the large prediction uncertainty, those counties without any available arsenic data were left blank (Figure 4.4 and 4.5).

A



B



C

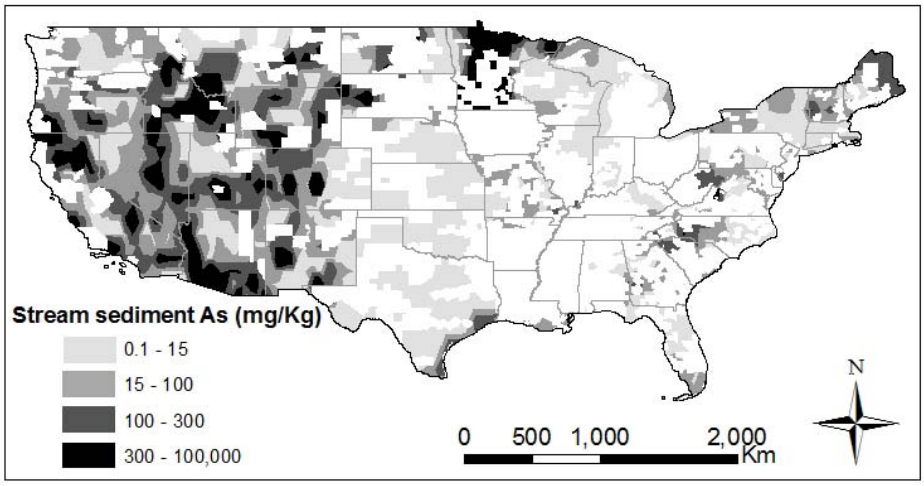


Figure 4.4 Interpolated arsenic distributions in groundwater, soil and stream sediment plotted on the state map of the conterminous U.S.
* Blank areas are counties without available arsenic data.

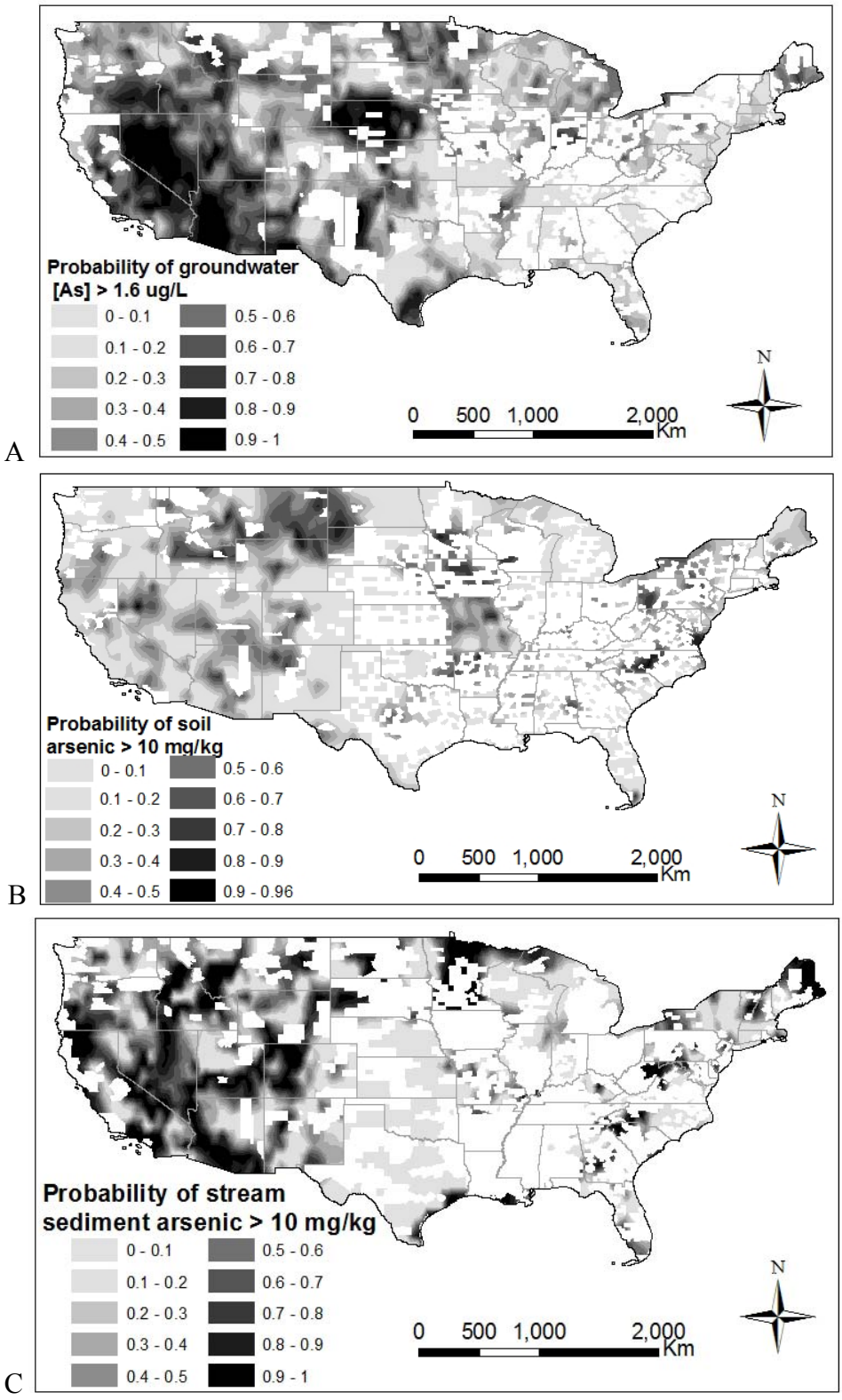


Figure 4.5 Probability maps of arsenic in groundwater, soil and stream sediment greater than median values plotted on the state map of the conterminous U.S.

* Blank areas are counties without available arsenic data.

4.3.2 Correlation of groundwater, soil, stream sediment arsenic on the national scale

The interpolated arsenic maps of groundwater, soil, and stream sediment show similar patterns at the nationwide scale (Figure 4.4 and 4.5) except in the High Plains aquifers where there is a high occurrence of groundwater arsenic but low arsenic in soil or stream sediment. This research was in part motivated by a first order, visually noticeable similarity between the spatial patterns of arsenic in soils from the earlier PLUTO database (GUSTAVSSON et al., 2001; USGS, 2001a) and in stream sediments from the NURE database (GROSZ et al., 2004) with that in groundwater (RYKER, 2001). Despite of the visual similarity, a logistic regression model using soil and stream sediment arsenic values as explanatory variables did not show significant correlations ($p=0.58$ and $p=0.19$, respectively) between groundwater and soil or stream sediment arsenic concentrations. However, when the soil and stream sediment arsenic values were transferred into binary data, stream sediment arsenic showed a significant association ($p=0.05$) with groundwater arsenic, while soil arsenic was still not significant ($p=0.18$). This suggested that soil or stream sediment arsenic concentrations, at the present sampling density, are not useful predictor of groundwater arsenic concentrations. Instead, categorical values, or anomalies in soil or stream sediment arsenic patterns, can be used to indicate high groundwater arsenic anomalies on the national scale. Stream sediment arsenic has a 1.4 times greater association with groundwater arsenic than soil arsenic does, which may be due to the higher sampling density of the stream sediment data set.

4.3.3 Correlation of groundwater, soil, stream sediment arsenic on regional scales

In Florida, arsenic concentrations in 448 soil samples had been interpolated into a surface map and in the county grid using geometric mean values (CHEN et al., 2001). Soil arsenic levels were generally the highest in the south, followed by the north, and were the lowest in the central Florida. We find here that soil arsenic values (n=1,345) range from 0.3 to 39 mg/kg, with a mean value of 1.8 mg/kg and a median value of 1.1 mg/kg. The sampling density is 1 per 130 km^2. Stream sediment arsenic values (n=913) range from 0.3 to 16.9 mg/kg, with a mean value of 1.2 mg/kg and a median value of 0.8 mg/kg. The sampling density is 1 per 190 km^2, but the data coverage is poor in the southern Florida. Groundwater arsenic values (n=468) range from 1 to 110 µg/L, with a mean value of 2.3 µg/L and a median value of 1.0 µg/L. The sampling density is 1 per 360 km^2, but the sampling is highly scattered with two denser clusters. Interpolated soil and stream sediment arsenic data show similar patterns as that of groundwater arsenic (Figure 4.6). The logistic regression model on soil and stream sediment arsenic values does not show significant correlations between groundwater and solid media arsenic at the county level. However, when soil and stream sediment arsenic values are transferred into binary data based on median values, soil turns out as a significant indicator of groundwater arsenic anomalies, which may be due to a more even data coverage and a higher sampling density of soil arsenic.

In New England, a regional study (ROBINSON and AYOTTE, 2006) compared interpolated maps of stream sediment arsenic (n=1,597, sampling density ~ 1 per 100 km^2) and groundwater arsenic (n=2,041, sampling density ~ 1 per 90 km^2), and found that among bedrock geology, stream sediment, and land use factors, the distribution of

arsenic in bedrock groundwater wells had a weak but positive correlation with the distributions of elevated stream sediment and bedrock arsenic.

In Nevada, soil and stream sediment arsenic values (n=5,640) range from 0.65 to 2140 mg/kg, with a mean value of 14.1 mg/kg and a median value of 7.0 mg/kg. The sampling density is 1 per 50 km^2. Groundwater arsenic values (n=868) range from 0.3 to 1400 μg/L, with a mean value of 49.2 μg/L and a median value of 9.0 μg/L. The sampling density is 1 per 330 km^2 (Figure 4.7). The Logistic regression model on soil and stream sediment arsenic values shows that groundwater arsenic anomalies can be indicated by the variation of arsenic distribution in soil and stream sediment at the county level. This stronger correlation than in Florida may be due to the better data coverage and even sampling strategy, as well as the higher sampling density.

Soil and stream sediment arsenic data can be a good indicator of groundwater arsenic distribution at regional scales given the sufficient sampling density and well designed sampling strategy. This correlation is independent of arsenic concentrations or aquifer types.

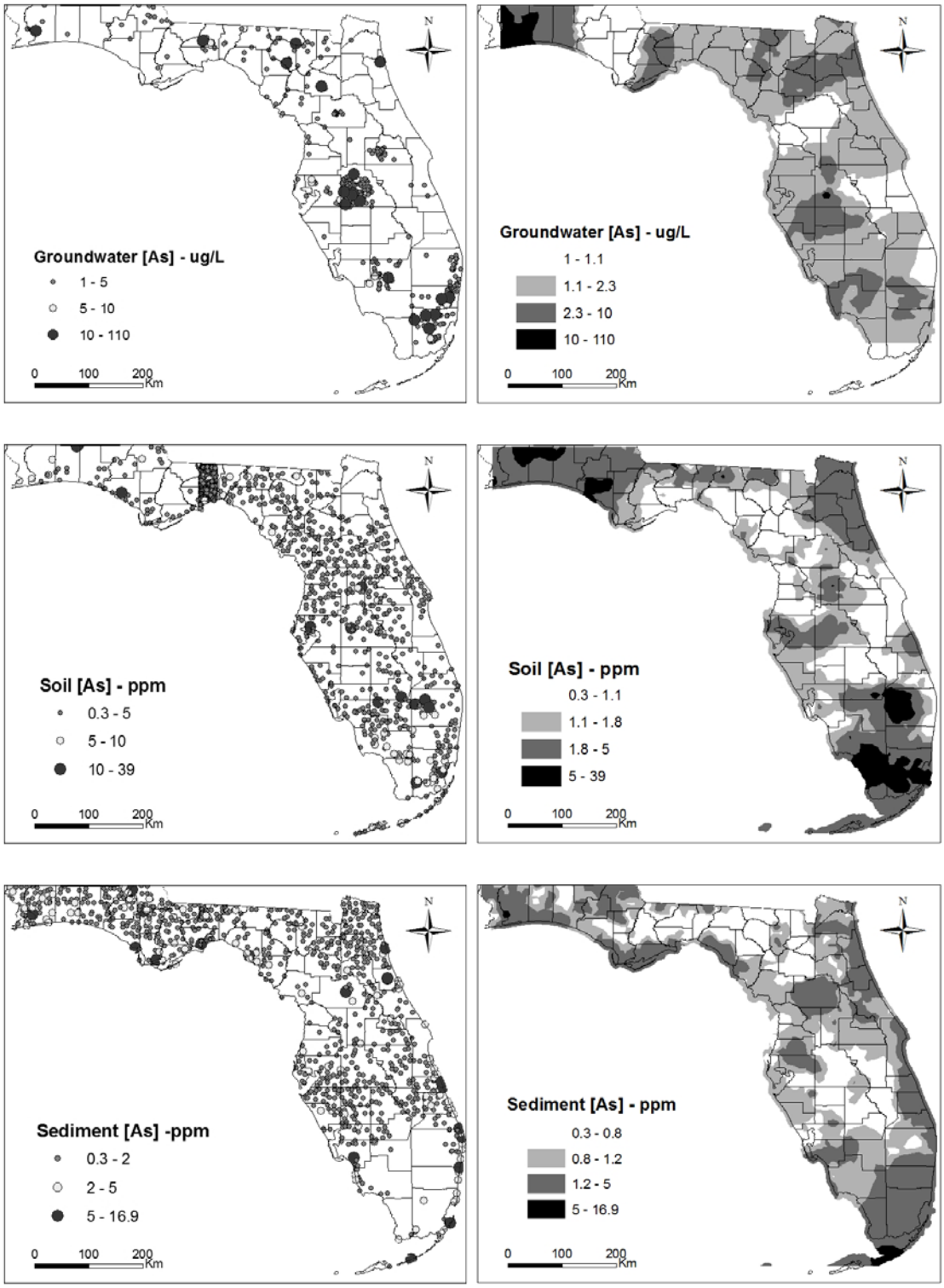


Figure 4.6 Distribution and interpolated maps of groundwater, soil and stream sediment arsenic in Florida

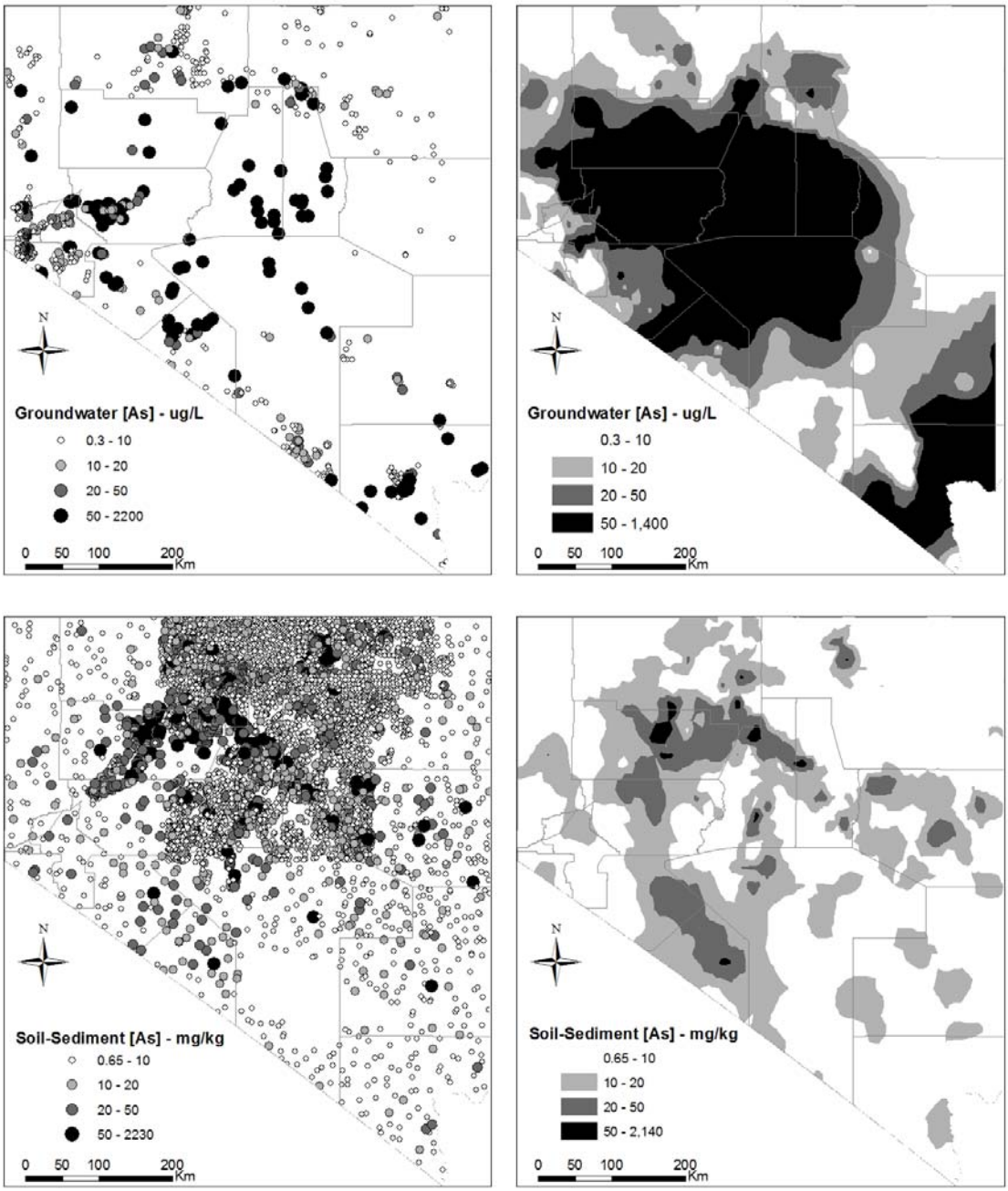


Figure 4.7 Distribution and interpolated maps of groundwater and soil/stream sediment arsenic in Nevada

4.3.4 Correlation of groundwater and soil arsenic on the local scale

In the greater Augusta area, Maine, groundwater arsenic distribution (n=790, sampling density of 1 per 1.4 km^2) shows distinct difference in the western and eastern parts in the fractured bedrock aquifers (YANG et al., 2009), which has been considered to be mainly controlled by the bedrock geology (AYOTTE et al., 2003; YANG et al., 2009). Arsenic distribution in soil samples (n=67, sampling density of 1 per 20 km^2), which reflect arsenic levels in the underlying bedrocks, displays a very similar spatial pattern in the study area after kriging (Figure 4.8).

The logistic regression model on soil arsenic values shows that the groundwater arsenic distribution can be indicated by soil arsenic concentrations. Soil arsenic is still a significant factor of groundwater arsenic distribution even when all the other geochemical and hydrogeological parameters are included in the model (YANG et al., In preparation). Furthermore, there is a strong positive correlation between groundwater arsenic and soil arsenic for each town (Figure 4.9). This suggests that at the local scale, soil arsenic data can be used to indicate groundwater arsenic distribution in bedrock aquifers when the sampling density is high enough.

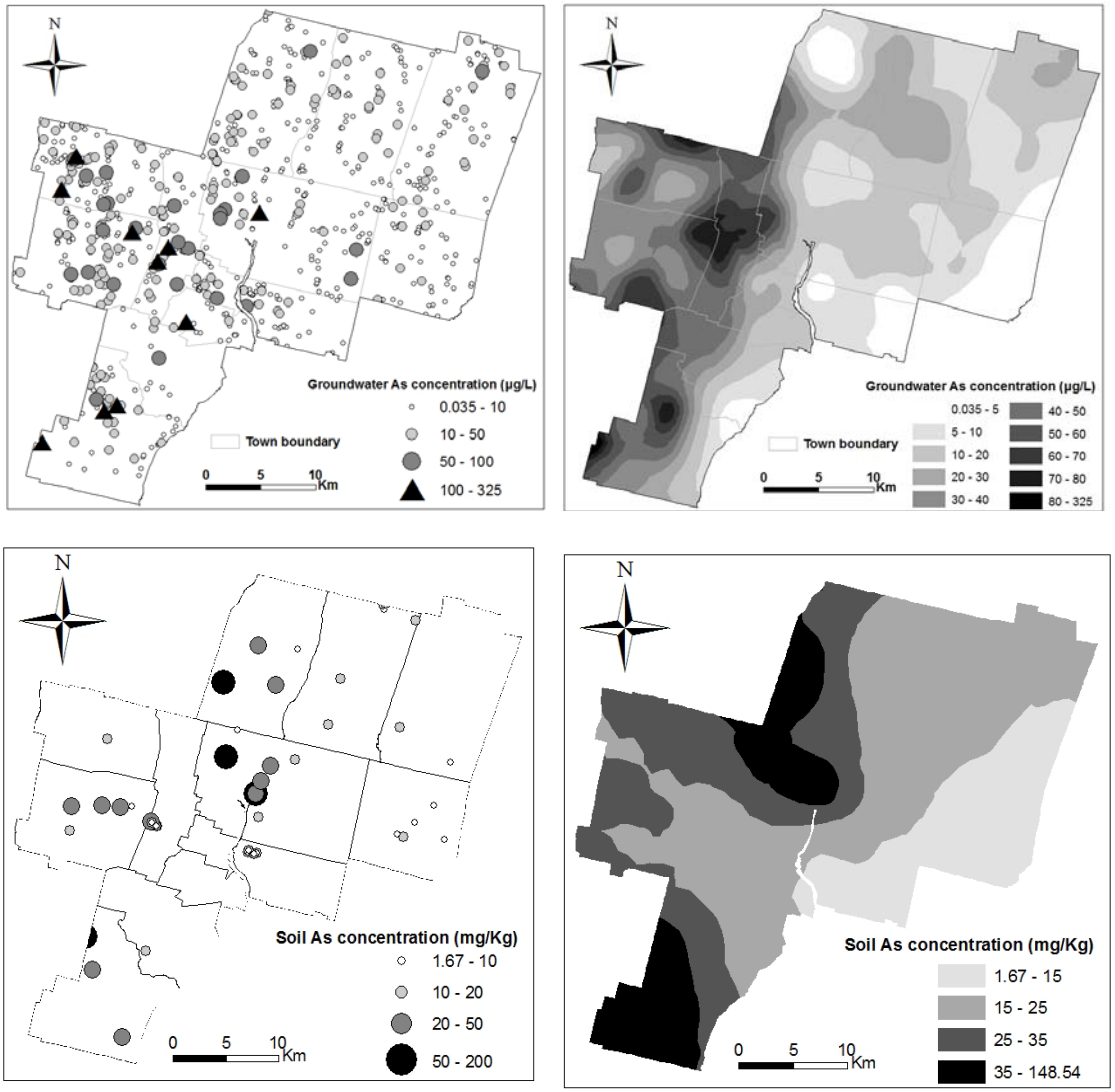
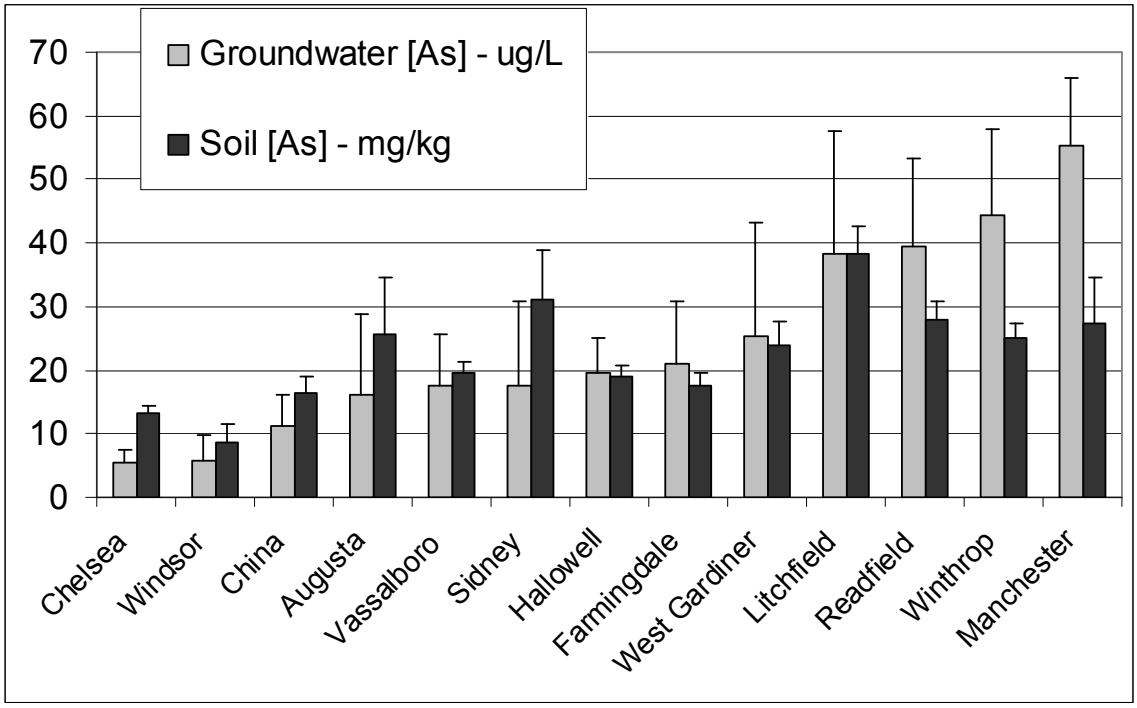
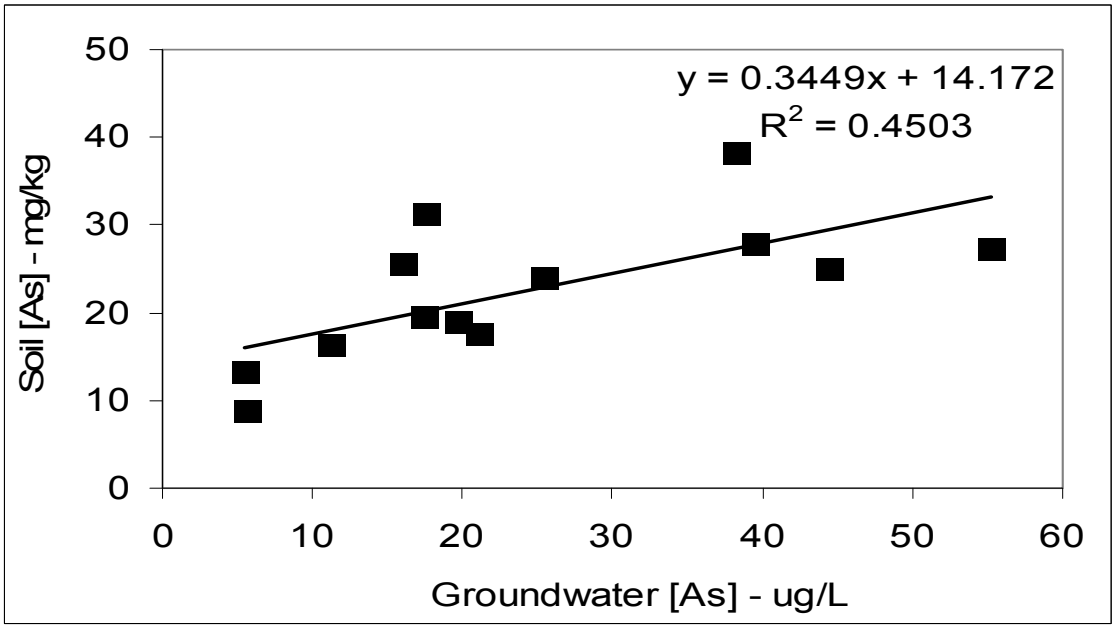


Figure 4.8 Distribution and interpolated maps of groundwater and soil arsenic concentrations in the greater Augusta area, Maine



* Error bars stand for one standard deviation.



* Each point represents a town.

Figure 4.9 Interpolated groundwater and soil arsenic concentrations in each town in the greater Augusta area, Maine

4.3.5 Significance of the correlations

When comparing the significance of the correlations between groundwater and soil/sediment arsenic distributions at different scales, the strongest correlation is observed at the local scale with the highest sampling density and the best data coverage, while the weakest correlation was found at the national scale.

The analyses suggest that soil and/or stream sediment can be used as an indicator of groundwater arsenic distribution at different scales given a sufficient sampling density and even spaced sampling strategy. Current national geochemical data bases have reasonable sample size to identify arsenic anomalies in groundwater, soil and stream sediment at the nationwide scale. However, a more systematic sampling, especially aiming at those areas with sparse data, will be helpful to develop a better national pattern. At state or similar regional scales, even sampling of soil and stream sediment at a density of 1 per 100-200 km^2 is needed to help identify areas with groundwater arsenic problems. At local scales, even higher sampling density, 1 per a few or tens of km^2, is desirable. Sparse or scattered sampling has a large negative effect on the analyses, which exists in many regional or local researches unfortunately.

We do not exclude the impacts on groundwater arsenic distribution from other important parameters, such as geology, land use, and water chemistry. Those parameters were shown to have stronger and more important influences in some cases (AMINI et al., 2008; AYOTTE et al., 2006; WINKEL et al., 2008). This research suggests that adding soil and/or stream sediment arsenic data, which are often available from geochemical surveys,

into the models can improve the prediction of groundwater arsenic occurrence (AYOTTE et al., 2006).

4.3.6 Implications on background levels of arsenic

The median arsenic concentrations of groundwater in each state range from 1.0 to 9.0 µg/L, while the mean values between 1.0 and 53 µg/L. The median arsenic concentrations of soil in each state range from 1.4 to 200 mg/kg, while the mean values between 1.4 and 291 mg/kg. The median arsenic concentrations of stream sediment in each state range from 1.8 to 200 mg/kg, while mean values between 2.4 and 753 mg/kg. The median arsenic concentrations of groundwater, soil and stream sediment in each state are significantly lower than the mean concentrations (Table 4.2) as the mean values can be affected by the extremely large measurements.

The interpolated mean arsenic concentrations in each state range from 1.3 to 33 µg/L in groundwater, from 0.8 to 93 mg/kg in soils, and from 2.9 to 445 mg/kg in stream sediments. These interpolated values can be used as better estimates of background arsenic distributions because the kriging methods minimize the bias from uneven sampling and extreme values.

The statistics of arsenic concentrations in the national databases and each state offer a reference for the determination of background values and then the cleanup goals of arsenic driven by the background levels in soil and stream sediment (DAVIS et al., 2001).

Table 4.2 Arsenic distributions in groundwater, soil and stream sediment in each state of the conterminous US

State	Groundwater						Soil						Sediment						Interpolated mean arsenic distribution			
	n	density	min	max	median	mean	n	density	min	max	median	mean	n	density	min	max	median	mean	groundwater	probability of groundwater	soil	sediment
		1 per km^2	µg/L	µg/L	µg/L	µg/L		1 per km^2	mg/kg	mg/kg	mg/kg	mg/kg		1 per km^2	mg/kg	mg/kg	mg/kg	mg/kg	µg/L	[As] >10 ug/L in percent	mg/kg	mg/kg
Alabama	159	854	1.0	4	1.0	1.3	59	2301	0.8	150	150.0	105.8	365	372	0.5	150	2.0	9.1	1.8	2.2	13.8	8.0
Alaska	167	10287	1.0	94	3.0	11.6	1990	863	0.1	12000	10.0	131.2	8004	215	0.2	100000	200.0	752.7				
Arkansas	216	638	1.0	80	1.0	3.4	42	3279	2.6	61	13.0	16.1	22	6261	3.2	26	10.0	11.1	2.7	9.4	9.2	21.9
Arizona	1649	179	0.5	980	4.0	18.1	626	472	1.2	1000	55.0	100.7	4785	62	1.1	20000	10.0	144.0	14.7	27.4	26.6	204.5
California	2626	161	0.5	2600	2.0	10.7	7384	57	0.2	1000	10.0	31.0	9048	47	0.1	43000	20.0	169.0	6.0	16.2	11.7	343.1
Colorado	898	300	1.0	110	1.0	2.3	4531	60	0.0	1000	9.7	26.1	2767	97	0.1	100000	13.0	210.9	2.4	1.4	10.3	76.8
Connecticut	188	76	1.0	18	1.0	1.3	0						54	266	0.8	32	5.7	6.6	1.3	0.0	7.7	12.4
Delaware	120	54	1.0	14	1.0	1.2	2	3223	0.1	2.68	1.4	1.4	26	248	100	100	100.0	100.0	1.5	0.0	0.8	253.7
Florida	581	293	1.0	110	1.0	2.4	277	615	0.1	97	10.0	16.6	602	283	1.3	460	20.0	41.3	1.9	2.2	2.7	18.4
Georgia	109	1412	1.0	4	1.0	1.1	116	1327	0.2	150	2.8	28.8	500	308	0.6	1200	10.0	23.9	1.4	0.0	5.0	24.9
Hawaii	0						0						0									
Iowa	130	1121	1.0	16	1.0	2.0	516	282	0.8	620	20.0	23.8	6	24291	4.9	11	10.0	9.4	2.2	2.7	10.4	150.7
Idaho	2533	85	1.0	950	2.0	6.4	979	221	1.1	10000	120.0	291.3	4397	49	1	20000	200.0	207.6	4.1	13.1	92.6	231.7
Illinois	189	794	1.0	42	1.0	4.3	25	6000	2.7	13	7.5	7.4	1394	108	1	200	10.0	16.5	2.1	3.9	9.9	34.5
Indiana	287	329	1.0	89	2.0	5.4	8	11790	3.6	10	6.6	6.4	240	393	1.4	140	10.0	19.3	4.4	16.3	8.2	15.2
Kansas	2604	82	0.5	661	1.0	2.2	41	5197	2.4	200	8.7	31.7	2044	104	0.1	31	4.0	5.3	2.1	1.3	7.4	6.6
Kentucky	22	4757	1.0	1	1.0	1.0	14	7476	2.0	14	8.5	7.9	1526	69	0.1	200	10.0	18.0	2.2	6.2	7.3	33.6
Louisiana	299	449	1.0	200	1.0	2.5	8	16783	1.4	11	5.1	5.6	273	492	10	130	20.0	20.2	1.8	4.4	6.4	15.6
Massachusetts	179	153	1.0	560	1.0	13.4	6	4556	2.0	22	6.9	8.6	1029	27	1	200	3.0	8.8	1.5	0.0	7.6	4.6
Maryland	426	75	1.0	72	1.0	1.6	35	918	1.1	13	12.2	11.0	113	284	3.5	100	14.0	23.8	1.6	4.7	7.3	20.3
Maine	388	236	1.0	270	2.0	6.1	13	7050	1.4	19	8.7	9.4	1816	50	1	411	100.0	113.1	3.2	10.2	8.6	95.3
Michigan	842	297	0.5	360	1.0	3.5	121	2070	0.1	150	10.0	66.8	218	1149	0.1	70	2.8	8.1	2.2	4.9	5.1	15.5
Minnesota	2279	99	0.5	340	1.7	3.5	482	467	0.2	100	10.0	12.8	858	262	0.3	3040	93.5	230.5	2.6	1.5	7.0	445.0
Missouri	417	433	0.5	52	1.0	2.5	2569	70	1.6	170	9.9	11.2	387	466	0.9	220	6.4	11.5	2.3	7.1	9.6	17.4
Mississippi	56	2240	1.0	56	1.0	2.7	17	7378	2.4	21	8.8	9.5	0						1.7	2.6	8.4	14.0
Montana	181	2104	0.9	1900	2.0	25.6	1514	252	0.5	5600	10.0	102.9	5293	72	0.5	5000	10.0	81.5	8.3	14.8	35.3	144.3
North Carolina	148	942	1.0	21	1.0	1.5	401	348	1.0	260	150.0	149.7	1219	114	1	500	10.0	87.1	1.6	1.4	41.1	52.3
North Dakota	961	191	0.5	1500	1.9	8.6	1210	151	0.0	500	10.0	26.5	816	224	0.3	500	4.1	14.8	2.5	6.6	19.4	158.8
Nebraska	3509	57	0.5	85	3.0	4.0	21	9540	1.6	13	5.2	5.6	1711	117	0.1	200	4.5	12.3	5.1	7.6	6.2	9.8
New Hampshire	255	95	1.0	30	1.0	1.7	3	8072	1.6	6	4.2	3.9	99	245	5.8	100	100.0	95.4	1.5	0.0	3.8	88.4
New Jersey	1427	16	1.0	57	1.0	2.0	57	396	0.1	150	12.6	52.2	202	112	2.3	4100	10.0	181.5	2.5	9.3	10.0	73.6
New Mexico	783	402	1.0	200	2.0	9.0	708	445	0.1	220	10.0	39.8	3374	93	0.8	3000	10.0	81.9	3.7	7.9	22.2	76.0
Nevada	914	313	0.3	2200	9.0	52.8	2627	109	0.6	5300	10.0	24.6	10312	28	1	20000	200.0	236.9	33.0	34.8	20.0	145.3
New York	58	2436	1.0	16	1.0	2.4	294	481	1.1	200	11.6	65.1	1509	94	1	500	6.0	20.4	1.9	2.4	11.2	23.9
Ohio	273	425	1.0	21	1.0	2.1	9	12900	5.2	27	9.9	11.9	0						2.7	10.3	10.6	39.6
Oklahoma	2320	78	0.5	110	1.4	2.8	622	291	0.1	1000	10.0	12.7	1948	93	0.1	14.3	2.1	2.4	2.0	2.2	9.6	4.6
Oregon	455	560	0.5	1100	2.0	11.0	2146	119	1.1	1000	10.0	14.7	1502	170	0.3	7000	11.0	139.7	5.7	19.4	19.2	151.2
Pennsylvania	600	199	1.0	24	1.0	1.8	327	365	1.0	215	13.2	38.9	350	341	1	29	8.0	8.6	2.1	5.7	13.6	19.8
Rhode Island	5	800	1.0	1	1.0	1.0	0						0						1.3	0.0	6.5	2.9
South Carolina	102	813	1.0	9	1.0	1.1	64	1296	1.0	220	10.0	62.4	350	237	0.4	500	30.0	78.4	1.4	0.0	11.1	72.8
South Dakota	1230	162	0.5	125	1.2	4.4	183	1091	1.7	500	10.0	38.3	262	762	4.3	30000	20.0	746.4	2.6	3.0	14.1	87.9
Tennessee	455	240	1.0	190	1.0	2.1	17	6421	3.1	73	8.6	12.9	180	606	1	100	3.0	4.7	1.5	2.1	11.0	52.2
Texas	7905	88	0.5	868	1.8	4.3	168	4141	1.1	220	7.1	45.8	6362	109	0.1	170	3.0	27.4	3.4	6.4	9.2	24.9
Utah	804	273	0.5	730	2.0	13.1	192	1145	1.5	200	200.0	114.7	3595	61	0.7	100000	5.0	133.6	3.9	10.4	20.0	158.8
Virginia	111	998	1.0	8	1.0	1.4	173	640	0.7	200	10.0	77.3	654	169	0.1	1000	4.0	152.5	1.9	0.0	31.7	23.6
Vermont	4	6225	1.0	1	1.0	1.0	29	859	2.4	200	200.0	179.7	202	123	2.3	500	20.0	56.5	1.8	0.0	6.0	69.2
Washington	1768	104	1.0	280	1.0	4.1	96	1924	0.4	135	4.9	8.9	2022	91	0.8	1000	10.0	14.2	2.4	2.9	6.0	24.8
Wisconsin	996	170	0.5	59	1.0	1.9	40	4241	2.8	150	150.0	112.4	1914	89	0.1	150	1.8	9.4	1.6	0.8	17.7	15.4
West Virginia	224	280	1.0	110	1.0	3.1	12	5230	4.3	100	6.7	23.0	660	95	5.9	200	200.0	178.0	2.4	6.6	12.3	130.3
Wyoming	329	770	0.5	36	1.0	1.9	1537	165	0.1	500	10.0	51.5	817	310	0.6	6100	11.0	186.2	2.5	5.1	36.2	152.0

4.3.7 Limitations

The combined national data sets of groundwater and stream sediment still do not have a full spatial coverage of the conterminous U.S. (Figure 4.1 and 4.3). National soil data set has a better coverage but in most states the sampling density is as low as of the "Shacklette data set". The two national sediment data sets combined have different arsenic distributions, higher in the PLUTO database than in the HSSR-NURE database. Soil and stream sediment data sets were not combined into one data set as surficial materials (GROSZ et al., 2004) because soil and stream sediment data distributions are very different in terms of mean and median values, and also the soil data set already has a decent spatial coverage.

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