Hydrogeologic Influence on Spatial Variability of Arsenic Levels in Drinking Water[a]

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ABSTRACT

Objective: Geo-spatial models are developed to estimate arsenic concentrations in drinking water at selected locations in 11 counties of Southeast Michigan. Such models depend on an understanding of the sources and mechanisms of arsenic release into water. Arsenic-bearing minerals (including pyrite, arsenopyrite, and oxide/hydroxide phases) have been identified in the primary aquifer formations, namely, Marshall Sandstone and glacial till, but the mechanism responsible for arsenic mobilization into groundwater is unclear. Here it is proposed that arsenic-containing minerals release arsenic in the glacial till into the groundwater. This arsenic, from glacial till may be introduced into the bedrock aquifers during recharge. The profiles of arsenic concentrations in wells in the region seem consistent with this proposition.

Methods: Arsenic measurements (332 from Genesee and 370 from Huron County) supplied by Michigan Department of Environmental Quality and Genesee County Health Department (GCHD), were linked to well characteristics by the United States Geological Survey and GCHD. The relationship between arsenic and estimates of recharge, proximity to Marshall Sandstone, and distance between casing-depth and bedrock-surficial interface were evaluated in linear and exponential regression models.

Results: Significant associations were found between arsenic and proximity to recharge zone, distance between casing-depth and bedrock-surficial interface, higher elevation, and proximity to Marshall Sandstone in Genesee ($F=135.97$, $p<0.0001$, $R^2=0.81$) and Huron County ($F=36.48$, $p<0.0001$, $R^2=0.34$) using exponential and linear regression models.

Conclusion: Elevated arsenic levels are found in areas of greatest recharge potential, high elevation, and in close proximity to bedrock-surficial interface and Marshall Sandstone. Detailed chemical analyses in individual wells are necessary to better understand the influence of redox

cycle in the spatial distribution of arsenic. This application of geo-spatial methods to estimate arsenic concentrations can be used with ecological models to assess the risks of exposure to arsenic in groundwater in the region.

INTRODUCTION

In the United States, an estimated 54,200 cases of urinary bladder cancer are diagnosed which result in 12,100 deaths each year (McKean-Cowdin et al., 2000). Although epidemiological studies have suggested that chronic ingestion of inorganic arsenic in drinking water is associated with bladder cancer, few studies have assessed the risks associated with exposure to low levels of arsenic (typically 5-100 μg/L) most commonly found in drinking water in the United States (Cantor, 2001; Calderon, 2000). In 2001, the U.S. Environmental Protection Agency (USEPA) recommended a maximum contaminant level (MCL) of 10 μg/L for arsenic in US public drinking water supplies scheduled to go into effect in 2006 (USEPA, 2001). The new MCL of 10 μg/L is similar to the provisional guideline recommended by the World Health Organization (WHO, 1993). The new MCL is being contested on the grounds that it is not supported by sound science. The National Cancer Institute is currently funding a case-control study at the University of Michigan to study the relationship between bladder cancer and exposure to arsenic in the 5-50 μg/L range.

Elevated levels of naturally-occurring arsenic have been identified in regional patterns within the United States and are attributed to geochemistry, geology, climate, and glacial history (Welch et al., 2000). In the Michigan thumb region, arsenian pyrite has been identified in the bedrock of the Marshall Sandstone aquifer, one of the region's most productive aquifers (Westjohn et al., 1998). Geochemical analyses, however, reveal that arsenic is not likely to be oxidized out of the bedrock since the groundwater is reducing (Kolker et al., 1998). Most of the arsenic (53-98%) is in the reduced, As(III) form (Kim et al., 2002). Arsenian pyrite grains have also been identified in the glacial till, where the conditions are more favorable for the oxidation of arsenic into the water (Kolker et al., 2001). The oxidation of arsenopyrite is well established and may be written as

$$FeAsS + 7/2O_2 + 4H_2O \rightarrow Fe(OH)_3 + H_3AsO_4 + H_2SO_4$$

The presence of the bacteria *Thiobacillus ferrooxidans* enhances the oxidation reaction (Fernandez et al., 1995) by facilitating the oxidation of ferrous ion to ferric ion:

$$4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_20$$

The ferric ions generated by the biologic activity can oxidize arsenopyrite grains and release arsenate to solution as follows:

$$FeAsS + 7Fe^{3+} + 4H_20 \rightarrow H_3AsO_4 + 8Fe^{2+} + S^0_{(surface)} + 5H^+$$

In addition to arsenian pyrite, arseniferrous iron oxy-hydroxides have been identified in Marshall Sandstone till fragments (Kolker et al., 2001). A complimentary explanation to the arsenian pyrite oxidation is the reduction of arsenic-rich iron oxy-hydroxides in Marshall Sandstone fragments in the zone of fluctuating oxidation and reduction, close to the water table.

While the mechanisms responsible for arsenic release are not known, we propose that arsenic is released into the groundwater in the glacial till and introduced into the bedrock aquifers during recharge. If the recharge proposition is correct, then higher levels of arsenic are expected in shallow bedrock wells beneath recharge zones. Arsenic concentrations are expected to decrease both as water infiltrates deeper into the bedrock aquifer and as water flows away from the recharge zone. This paper will illustrate geo-spatial hydrogeologic models of arsenic in drinking water, designed to assist in the estimation of arsenic concentrations at selected locations in 11 counties of Southeast Michigan.

METHODS

Historic arsenic data were acquired from the Genesee County Health Department (GCHD) and Michigan Department of Environmental Quality (MDEQ). The GCHD database links arsenic data from 1988-1989 with characteristics of 332 wells, and categorizes the aquifers that supply the water for those wells. The Genesee County data were collected as part of the Michigan Groundwater Survey and were analyzed at Michigan State University. The sample design accomplished a fairly uniform geographic spread of approximately 20 wells from each of the 18 townships in Genesee County. The MDEQ database encompasses 14,588 arsenic measurements (requested by home owners) in the 11-county study area. As the database only includes samples requested by home owners, some areas are densely sampled while others have sparse sampling. The analysis was done in the MDEQ state laboratory with ICP/MS (Inductively coupled plasma/mass spectrometry) procedure, which limited the database to samples collected between 1993 and 2002. The United States Geological Survey (USGS) created a database (N=2179) which geocoded the MDEQ database from January, 1997 through February, 1999 in 9 of the 11 counties in the study area. In Huron County, the USGS arsenic database was linked to a database with well characteristics for 370 drinking wells. Non-detects were assigned a value equal to half of the detection limit (2.5 μg/L for GCHD and 0.5 μg/L for other datasets).

To visualize the spatial pattern throughout the study area, the MDEQ arsenic data were aggregated at the township-level. The township is the smallest geographic unit in the database. The mean, median, maximum, minimum, and standard deviation were calculated for all 288 townships in Genesee, Huron, Ingham, Jackson, Lapeer, Livingston, Oakland, Sanilac, Shiawassee, Tuscola, and Washtenaw Counties. Probability distribution functions also were created for each township. Spatial autocorrelation at the township-level was evaluated using Moran's I, first order neighbors, available in the S-Plus spatial analysis extension of ArcView 3.3. The Moran's I is a spatial correlation test that evaluates if points near each other are more similar than would be expected at random (Cullen et al., 2001).

Arsenic values in Huron and Genesee Counties were compared with surficial material and bedrock geology to evaluate spatial pattern with underlying geology. Geology layers are available from Michigan Center for Geographic Information, Geographic Data Library, and were generated by Michigan Department of Natural Resources. The shape file of surficial rock formation represents the top layer of surficial material, beneath the topsoil. The bedrock geology shapefile represents the subcrop of the bedrock geology beneath the surficial geology. Neither of these shape files includes information about the depth of the geologic types. In ArcGIS 8.2, these geology files were overlain with arsenic data to determine if a spatial pattern exists. Using SAS "proc glm", a 2-way analysis of variance was conducted on Huron and Genesee datasets. Surficial material, bedrock geology, and aquifer were evaluated for bedrock and surficial wells. Spatial autocorrelation at the individual wells was evaluated by constructing a semivariogram using Gslib software package. Anisotropy was evaluated and the lag size was chosen such that no lag size was greater than one-half the maximum lag between observations.

Estimates of recharge in the 11-county study area were provided by a USGS-developed model of ground-water recharge rates in the lower peninsula of Michigan (Holtschlag et al., 1997). The recharge model accounts for discrete changes in recharge rate associated with streamflow, rainfall, basin characteristics, land-use classifications of deciduous and coniferous forests, and surficial material classifications of outwash sand and coarse-textured till. In the study area, the model estimates ranged from 0-13 inches per year (Figure 1) with an associated uncertainty of 4.2-5.5 inches per year. The computed output was provided by the USGS and georectified in ArcGIS 8.2. The recharge model was overlain by the Marshall Sandstone subcrop and different arsenic datasets. Using tools from the spatial analysis extension in ArcGIS 8.2 (zonal statistics), each arsenic location was assigned a recharge estimate. Buffering and selecting with different options was employed for the following recharge estimates: continuous estimate (inches per year), categorical estimate (<5, 5-8, >8 inches per year), and proximity to the >8 inches per year recharge zone (kilometers).

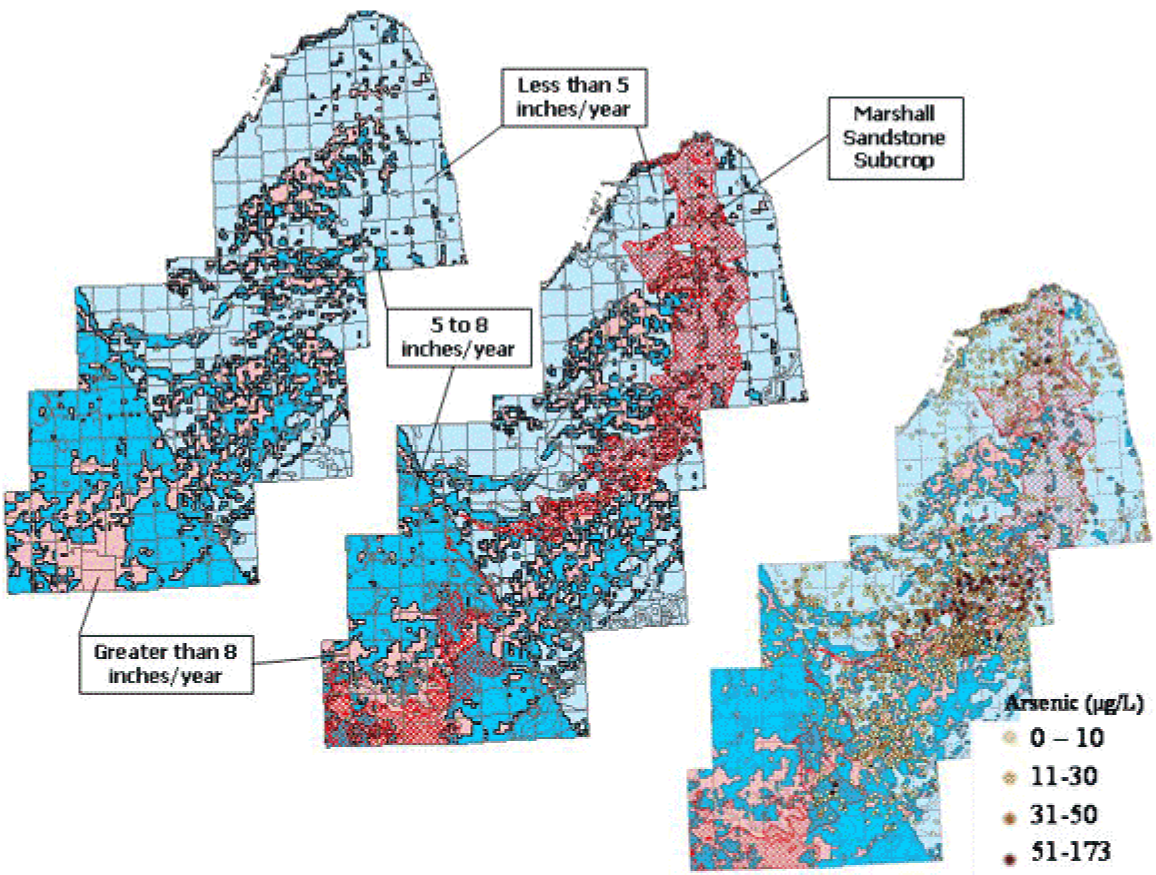

Figure 1: The USGS-developed recharge model in units of inches per year (Holtschlag et al., 1997), overlain by Marshall Sandstone subcrop (from Michigan Center for Geographic Inofrmation) and arsenic data (N= 2179) in units of μg/L, analyzed by MDEQ and geocoded by USGS. Note the apparent association between arsenic and the higher recharge zone along with the Marshall Sandstone subcrop.

With large uncertainty in the recharge model, other surrogates of recharge were evaluated. One indication of recharge potential is the hydraulic head, defined as the difference between elevation and standing water level, which is used to calculate the potentiometric surface specific to an aquifer. Since groundwater flows down a hydraulic gradient from points of higher to lower hydraulic head, water can generally be thought of as recharging close to the higher hydraulic head values. Our hydraulic head estimate, however, is not aquifer-specific since different aquifers are not categorized throughout the study area. Elevation, which is highly correlated with hydraulic head is also evaluated; this surrogate for recharge does not need to be aquifer-specific. In addition to its relationship with recharge, elevation may also indicate areas where there is a greater distance for oxidation to occur during infiltration. The water table is a subdued replica of the ground surface elevation; therefore, in general, there is a greater distance between ground surface and water table in higher elevation areas.

Other parameters evaluated include proximity of the well to Marshall Sandstone subcrop and distance between casing depth and interface between bedrock and surficial rock formations. Marshall Sandstone was evaluated because of high levels of arsenic in sandstone bedrock and in arsenian pyrite grains and arseniferrous iron oxy-hydroxides, located in the surficial material, above or close to the sandstone bedrock. Proximity to Marshall Sandstone was calculated with a buffer technique, similar to that described above for recharge, and was calculated in units of kilometers. Databases of well logs were required to calculate casing depth, depth of interface between bedrock and surficial rock formations, and hydraulic head. The distance between casing depth and bedrock-surficial interface is an indication of proximity of well intake to glacial till material and was previously identified as a significant parameter in our study area (Haack, 2002). Well logs were also utilized to distinguish wells drilled into bedrock from those drilled into surficial rock formations.

The proposition that arsenic is introduced into the bedrock aquifers during recharge was evaluated in wells of Huron (N=370) and Genesee (N=332) counties and in the 9 counties of the USGS database (N=2179). A stepwise linear regression procedure, performed in SAS, enabled selection of the most significant parameters. Both linear and exponential regression models were adopted to evaluate the relationship between the selected parameters and arsenic. Linear regression was performed with SAS, “reg” procedure, using log-transformed arsenic values, while exponential regression utilized untransformed arsenic values with SAS, “proc nlin”. For the exponential model, exponential decay was combined with exponential growth. Elevation and hydraulic head follow an exponential growth curve; their values were subtracted by the maximum value for each variable in a county, such that all hydraulic head and elevation values were assigned a negative value, except for the maximum value which was assigned a value of zero. By reassigning the values of elevation and hydraulic head in this manner, the arsenic level will be at its maximum when all parameters equal zero. For the exponential models, the intercept was assigned the maximum observed value: 161 μg/L in Huron; 69 μg/L in Genesee; 173 μg/L in USGS 9 Counties.

RESULTS

Available data indicates a regional pattern of the arsenic concentration accompanied by local variability within the study area. This short-range variability results in a semivariogram with large nugget effect and unreliable kriging estimates (Figure 2).

Directional semivariograms indicate that anisotropy is not present in the first 15 kilometers. The upward trend between the nugget and the sill, indicates some regional spatial trend in the arsenic data. The regional pattern can be characterized using township-level estimates of arsenic (Figure 3), as confirmed by a Moran's I value of 0.47 ($p<0.05$). The arsenic value in Figure 1 is the township mean + 2 standard deviations. The low-arsenic townships tend to have small amounts of variance, suggesting that a township-level estimate may be satisfactory for these townships. The high-arsenic townships are accompanied by high levels of variance, however, indicating the need for better understanding of the mechanism of arsenic release and transport to enhance predictive capability.

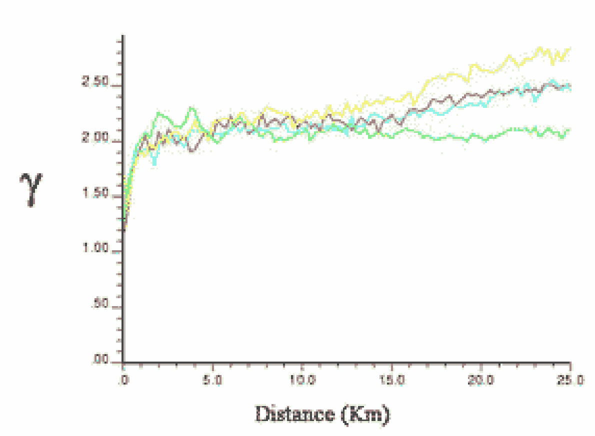

Figure 2: Directional semivariograms of log (Arsenic) created with Gslib software package Minimal anisotropy exists during the first 15 kilometers and high nugget effect exemplifies extreme short-range variability.

In Genesee County, GCHD categorized 332 wells by aquifer, as part of the Michigan Groundwater Survey in 1987 (Michigan Groundwater Survey, 1989). Stratifying the arsenic values by aquifer (Table 1) demonstrates that there is elevated arsenic in most aquifers, be they bedrock or surficial. Aquifers A1, A2, A3, A4, Drift, and Unclassified Drift are surficial aquifers; Coldwater, Marshall, Michigan, and Saginaw are bedrock aquifers. In the GCHD database, the non-detect limit was 5 µg/L, and was reported in each aquifer. The Saginaw aquifer is home to both the lowest mean and the highest maximum arsenic value in Genesee County. The largest mean arsenic value is in the Marshall aquifer, followed by the A2 surficial aquifer.

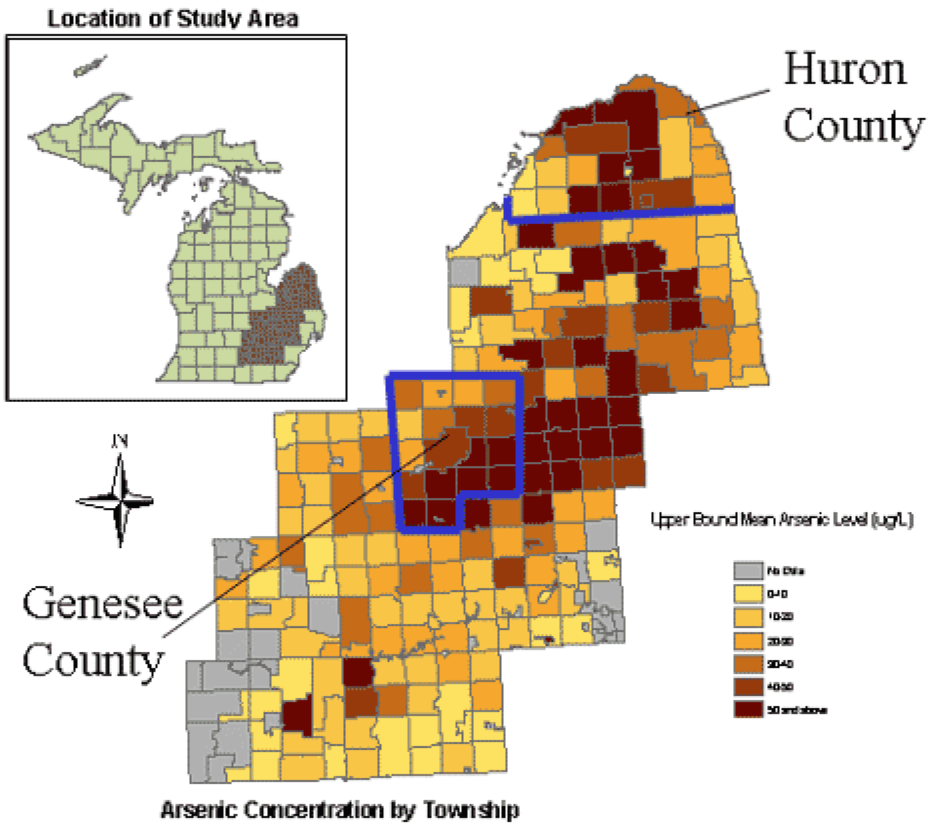

Figure 3: The 288 townships in the 11 county study area in the Michigan Thumb region. The arsenic values for each township represent the mean township value + 2 standard deviations; a rough estimate of the maximum arsenic concentration for each township. Regional spatial pattern is evident, as indicated by the cluster of dark townships and the Moran's I, first order neighbors, of 0.47.

Analogous to the spread of arsenic across all aquifers, elevated arsenic is identified in most types of surficial geologic formations in Huron (Figure 4a) and Genesee (Figure 4b) counties. The darker points in the figures represent higher concentrations of arsenic. As can be seen from Figures 4a and 4b, there are high levels of arsenic associated with almost all of the surficial material types in Huron and Genesee County. Data on surficial geologic formations were used as input to the USGS-developed recharge model. In Huron County, almost all of the elevated arsenic values are above the Marshall Sandstone subcrop (Figure 5a). In Genesee County, many of the high arsenic values are above both the Marshall Sandstone and Michigan Formation

Table 1: Genesee County Arsenic Value (µg/L) by Aquifer Type

	Count	Mean	Min	Max
A1	3	11.33	ND	23
A2	18	20.30	ND	43
A3	4	11.00	ND	29
A4	6	13.50	ND	23
Drift	20	16.40	ND	39
Unclassified Drift	11	22.36	ND	46
Coldwater	9	19.30	ND	42
Marshall	25	23.48	ND	55
Michigan	17	19.00	ND	45
Saginaw	219	10.96	ND	69
Total	332	13.60	ND	69

Data provided by Genesee County Health Department, collected in 1987 with a detection limit of 5 µg/L. ND stands for non-detectable levels. Surficial aquifers include A1, A2, A3, A4, Drift, and Unclassified Drift. Bedrock aquifers include Coldwater, Marshall, Michigan, and Saginaw.

subcrops (Figure 5b). Results of the analysis of variance tests for bedrock and surficial geologic formations and aquifer type for Huron and Genesee datasets are shown in Table 2. The ANOVA results indicate that bedrock geology, surficial material, and aquifer type can explain up to 16% of the variance in the arsenic. Investigation of these trends suggests that of all of the aquifers

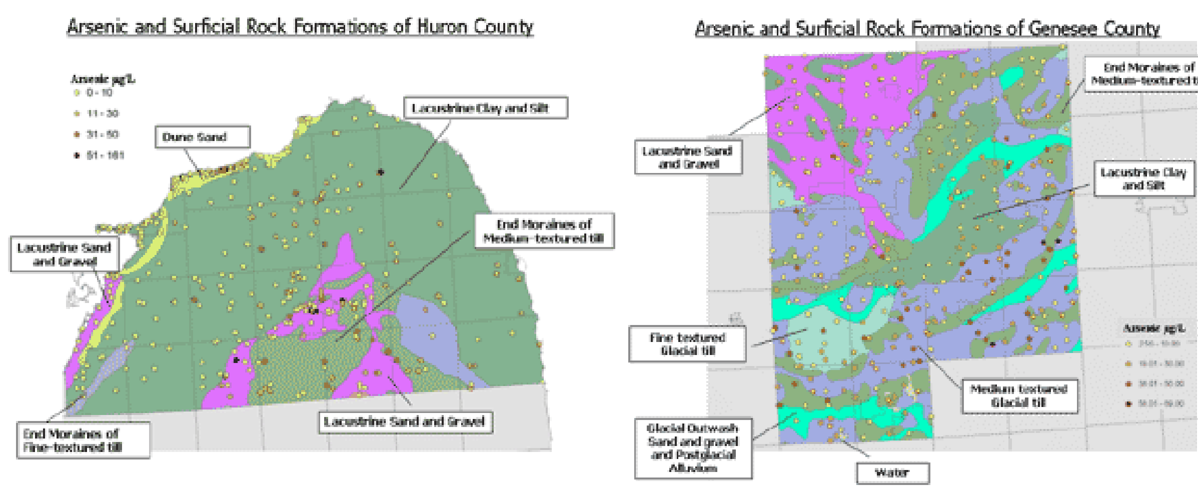

Figure 4: The spatial relationship between upper layer of surficial rock formation (beneath topsoil) and arsenic in groundwater is illustrated for (a) Huron and (b) Genesee counties. No spatial relationship appears to be evident between arsenic and any particular type of surficial material. The depth of the types of surficial material is unknown.

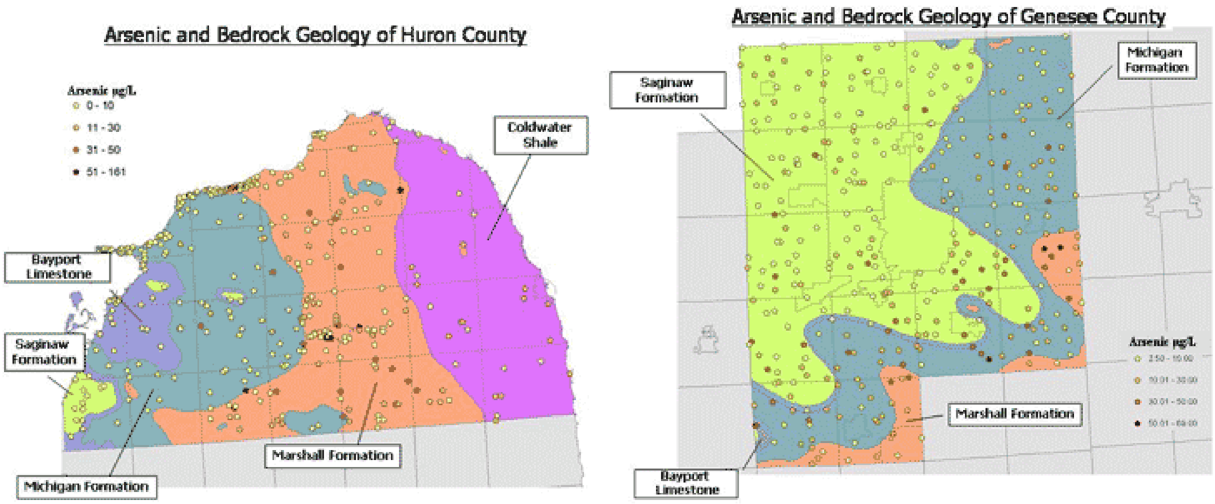

Figure 5: The spatial relationship between upper layer of the bedrock geology and arsenic in groundwater is illustrated for (a) Huron and (b) Genesee counties. There does appear to be an association between arsenic and the Marshall Sandstone in Huron County. In Genesee County, the Michigan formation and Marshall Sandstone appear to have the strongest relationship with arsenic. The depth of the bedrock geology types is unknown.

and geology types, Marshall Sandstone is most strongly associated with the arsenic (Figures 5a and 5b).

The proposition that arsenic is introduced into the bedrock aquifers during recharge was evaluated in separate regression models using the Genesee, Huron, and USGS 9 County

Table 2: Analysis of Variance Results

County	Well Type	Predictor Variable	F-Value	R^2	p-value
Genesee	Surficial and Bedrock	Aquifer	5.43	0.13	<.0001
Genesee	Bedrock	Surficial Material	2.45	0.05	0.0251
Genesee	Bedrock	Bedrock Geology	17.41	0.16	<.0001
Genesee	Surficial	Surficial Material	1.34	0.13	0.2548
Huron	Bedrock	Surficial Material	3.39	0.05	0.0028
Huron	Bedrock	Bedrock Geology	8.15	0.07	<.0001

Surficial Material was not a predictor of arsenic levels in surficial wells. All other ANOVA analyses were significant at $p<0.05$. Bedrock geology (principally Marshall Sandstone) is a predictor of arsenic levels in bedrock wells.

databases. Different measures of recharge, bedrock and surficial rock formations, and well characteristics were evaluated in stepwise linear regression and the following four variables were most often found to be significant: proximity to highest recharge zone (kilometers), proximity to Marshall Sandstone subcrop (kilometers), surface elevation (meters), and casing depth minus bedrock-surficial interface (meters). The best models in Huron, Genesee and USGS 9 Counties are shown in Table 3. In Genesee and Huron County models, the direction of the parameters was consistent and most of the estimates of the parameters were significant. The negative parameter estimate of casing depth minus interface indicates that higher arsenic is associated with a shorter distance between casing depth and bedrock-surficial interface. Higher levels of arsenic are associated with higher surface elevation. A negative parameter estimate for proximity to Marshall Sandstone subcrop, indicates that observations closer to this subcrop are associated with higher levels of arsenic. Similarly, observations closer to recharge zones are associated with higher levels of arsenic, as indicated by the negative parameter estimate. In Genesee County, the exponential model did a better job of capturing the variability in the data, compared with the linear model. A plot of predicted compared with observed is shown in Figure 6a for the exponential model in Genesee County. The R^2 value for the exponential model is calculated by dividing the sum of squares due to regression (SSR) by the sum of squares total (SST). A corresponding plot for the results of the linear model in Huron County can be seen in Figure 6b. These plots indicate that both models capture some of the variance in the datasets. The wide prediction interval, however, suggests that there is still uncertainty associated with using the model for prediction purposes. The low R^2 value of the counties in the USGS 9 database (Table 3) supports this assessment.

Table 3: Exponential and Linear Regression Results

					Parameters				Model	
Data Set	**Observations Included**	**Model Type**	**Dependent Variable**	**N▪**	**Casing Depth Minus Interface□**	**Elevation**	**Proximity to Marshall Sandstone Subcrop**	**Proximity to Recharge Zones**	**Adj. $R^{2◊}$**	**F****
Genesee County (GCHD)	Bedrock Wells	Linear	Log (As)	134	-.0029	.0035*	-.013*	.0049	0.18	8.26
	All Detects (≥5 µg/L)	Expon -ential	As	134	-.032*	.021*	-.030*	-.040*	0.76	104.68
Huron County	Bedrock Wells	Linear	Log (As)	271	-.011*	.0073*	-.0063	-.0099	0.34	35.22
	All Detects (≥1 µg/L)	Expon -ential	As	271	-.044*	.058*	-.17	-.36*	0.15	11.79
USGS 9 Counties	All Wells	Linear	Log (As)	1763		.0019*	-.036*	.011*	0.10	67.81
	All Detects (≥1 µg/L)	Expon -ential	As	1763		.032*	-.25*	.12*	0.088	56.48

▪ Number of Samples

* $p<.05$

**$p<.0001$; All Models are significant at this level.

□ Wells logs were only available for Huron County from the USGS dataset so the casing depth minus interface variable could not be included in the USGS 9 Counties analyses.

◊ For the exponential models, the R^2 was calculated by SSR/SST (sum of squares due to regression / sum of squares total

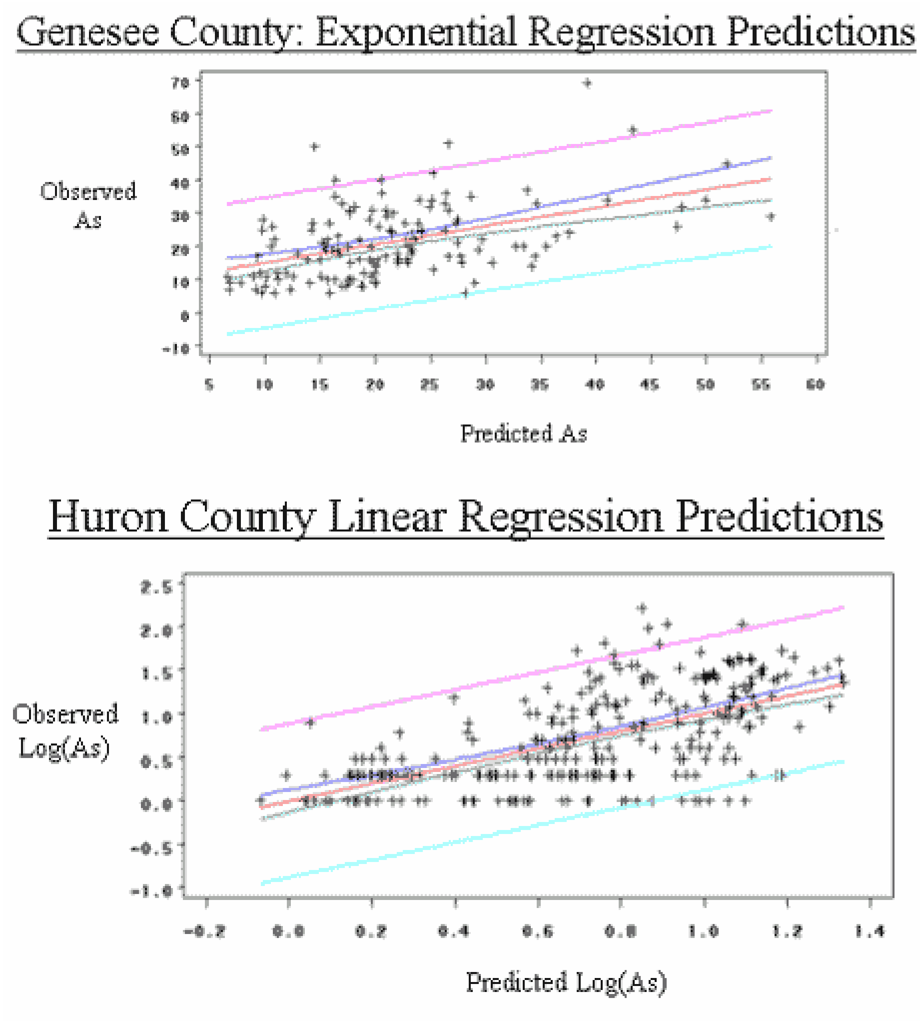

Figure 6: Regression results for (a) Genesee and (b) Huron counties. Results in Genesee are from exponential regression model in Table 3, and show predicted arsenic and observed arsenic. Results in Huron County are from linear regression model in Table 3, and show predicted log(arsenic) and observed log(arsenic). In both plots, the middle line is the estimation. The set of curves around the estimation is the confidence interval. The farther set of lines is the prediction interval. Most of the data fall within the prediction interval.

Normal probability plot of residuals indicated a non-normal error distribution when including the non-detects (assigned a value of one-half the detection limit). This deviation from normality was corrected by eliminating the non-detects (using quantifiable measurements) and by either taking a log transformation of the arsenic values, or using an exponential model. Bedrock wells were evaluated separately from all wells because recharge is hypothesized to influence bedrock wells differently from surficial wells. Interaction terms were evaluated but were not significant; no spatial autocorrelation was found in the residuals.

DISCUSSION

The ultimate aim of this project is to predict arsenic levels in well water at past residences and places of occupation of participants in a bladder cancer case-control study in Michigan (http://epi.grants.cancer.gov/GIS/nriagu.html). A necessary component of the prediction model is an understanding of the hydrogeologic and geochemical mechanisms responsible for the mobilization of arsenic into groundwater. Genesee County provides a unique database for analysis because it includes arsenic measurements, well characteristics, and aquifer categorization. To the authors' knowledge, this is the only database in the 11-county study area that includes all this information. There are elevated levels of arsenic in several different bedrock and surficial aquifers in Genesee County (Table 1). The presence of elevated levels of arsenic in surficial aquifers lends credence to the suggestion that arsenic is released into groundwater from the surficial rock formations. Following mobilization, arsenic is available for infiltration to the bedrock aquifers where there is recharge, and the process may be referred to as the recharge hypothesis.

Several variables proved helpful in predicting arsenic levels in groundwater in the study area: proximity to recharge zones, proximity to Marshall Sandstone subcrop, elevation, and distance between casing depth and bedrock-surficial interface. Surface elevation and proximity to recharge zones represent recharge. In some models both variables are significant, but in other models, only elevation is significant. Higher elevation may indicate regions where there is greater distance for oxidation to occur in the surficial material. Relationship between arsenic and distance between casing depth and bedrock-surficial interface suggests that well intakes closer to the till have higher levels of arsenic. Conversely, well intakes farther from the till have lower arsenic, suggesting the till as a source of arsenic in bedrock aquifers in the study area.

Another observation is that higher levels of arsenic are associated with a close proximity to Marshall Sandstone subcrop. Previous research has demonstrated that although arsenian pyrite is present in Marshall Sandstone bedrock, it is stable in anoxic groundwater and therefore is not a source of arsenic to bedrock aquifers (Kolker et al., 1998). The Marshall Sandstone bedrock, however, may be a proxy for the location of overlying glacial deposits which contain till derived from the Marshall Sandstone. Marshall Sandstone fragments were deposited in the till many years ago, when glaciers retreated. Arseniferrous iron oxy-hydroxides, in addition to arsenian pyrite, have been identified in Marshall Sandstone till fragments (Kolker et al., 2001). Iron oxide reduction in alluvial environments can lead to high-arsenic groundwaters through reductive desorption and/or reductive dissolution, although the precise mechanisms remain uncertain (Smedley and Kinniburgh, 2002). In the deltaic environment of Bangladesh, at least one source of the arsenic in the groundwater appears to be reductive dissolution, driven by microbial degradation of sedimentary organic matter (Nickson et al., 2000). In the high-arsenic region of Michigan, both arsenian pyrite oxidation and reduction of arsenic-rich iron oxy-hydroxides are possible in the zone of fluctuating oxidation and reduction, close to the water table. Both oxidation and reduction mechanisms will release arsenic to solution which would then infiltrate into anoxic bedrock aquifers, through a recharge process. To successfully evaluate the roles of arsenian pyrite oxidation and arseniferrous iron oxy-hydroxide reduction, further research is required in the region of elevated arsenic levels in groundwater in Michigan.

The plots of predicted vs. observed arsenic concentrations from Genesee (Figure 6a) and Huron (Figure 6b) counties demonstrate an ability to capture trend in the data. Yet prediction intervals are wide and some variability remains unexplained, as emphasized with the USGS 9 Counties database (Table 3). The parameter estimate for proximity to recharge zones is significantly positive in the USGS 9 counties database, contrary to that observed in Genesee and Huron counties and contrary to the recharge hypothesis. High levels of recharge and low levels of arsenic in the groundwater in the southern region of the study area appear to be driving this association in the USGS 9 Counties database. Possibly, there is less arsenic in the glacial till material in this region of the study area, such that even if there are high levels of recharge, there is less arsenic available to enter the groundwater from the rocks. An alternative explanation is the role of sorption of arsenic back into the till. Under oxidizing conditions, in addition to release of arsenic into solution through the oxidation of arsenian pyrite, there is a counteracting force of sorption of the liberated As(V) species. In waters with a pH of 4-9, as is groundwater in the study area, As(V) occurs as negatively charged $H_2AsO_4^-$ or $HAsO_4^{2-}$ which easily reacts with charged surfaces such as iron, manganese, and aluminum oxides and will become adsorbed. For the recharge hypothesis to hold true, as the groundwater infiltrates deeper into anoxic bedrock aquifers, some As(V) needs to remain in the water and get reduced to As(III) or arsenite, the more soluble form of arsenic and the more prominent form of arsenic in Michigan bedrock aquifers. The adsorption phenomenon has been ignored in the statistical model.

In the Genesee and Huron County/USGS data, sample acquisition goals and protocols were not consistent, thereby resulting in potential sources of error and bias. Huron County/USGS data were collected by MDEQ and represent only those samples requested by homeowners over a 2-year period. The Genesee County dataset, on the other hand, was sampled specifically for the Michigan Groundwater Survey and holds a purposeful uniform geographic spread over the entire county. These differences in data acquisition and sample handling may partially explain why the parameter estimates are different between the models. The high non-detect level (5 µg/L) in the Genesee County dataset is a limitation of the study. By removing the non-detects, the regression model no longer violated normality assumptions, but the model failed to predict arsenic at levels below the non-detect level, as to be expected. In the Huron County database the detection limit was 1 µg/L and therefore is less of a concern. Prediction at low levels may be difficult even if non-detects are included in the model, as subtle differences are likely a result of slight changes in the redox potential/geochemistry.

Within the context of predicting exposure, elevation, proximity to recharge, and proximity to Marshall Sandstone are readily available parameters, given an XY coordinate for one's house and place of employment. Calculation of casing depth minus bedrock-surficial interface and determination of bedrock/surficial well status is obtained from a well log. Collection of well logs for historic locations is both time-intensive and impossible to acquire in a complete fashion. Logs for wells created before 1960 are rarely available and are only sporadically available before the 1980s, when the database was converted to electronic format. Regression results without the information provided by the well log were similar in Genesee and Huron counties (results not shown). In the exponential model in Genesee, the parameter estimates were still significant, the

R^2 dropped to 0.71, and the model F-statistic increased to 107.88. In the linear model in Huron, proximity to Marshall Sandstone subcrop became significant, the R^2 dropped to 0.26, and the model F-statistic fell to 31.83. Removal of the well log information produced larger changes in Huron County results, compared with Genesee County. In both counties, the removal of well log information yielded models that were still significant, demonstrating that information from well logs may not be a necessary component in the present models.

One goal of this research is to incorporate these geospatial predictions in a retrospective exposure assessment component of a bladder cancer case-control study. The township-level analyses provide useful estimates of arsenic concentrations in the low-arsenic, low variability townships. In the townships with higher arsenic levels, the regression results will be applied to aid in predictions of arsenic levels at residences and places of employment. Future research includes repeated sampling of drinking water at selected locations to monitor for arsenic, an examination of temporal variability of arsenic levels in groundwater in the study area, and an evaluation and validation of the models of arsenic distribution in Michigan drinking water. This study demonstrates that spatial pattern analyses, well characteristics, and a geochemical understanding of arsenic mobilization and transport can be combined in a novel way to approximate the site-specific concentrations of arsenic in well water. This information can be used in first-level exposure assessment.

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