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Arsenic in Groundwater in the Tolono Region

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Illinois State Water Survey
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Introduction

In November 2010, a well water sample from a home near Tolono (labeled as well TOL-1 for this study) was sent to the Illinois State Water Survey's (ISWS) Public Service Laboratory (PSL) in Champaign. The total arsenic (As) concentration was determined to be 344 micrograms per liter (µg/L), more than 30 times the maximum contaminant level (MCL) of 10 µg/L allowed for public water supplies. This was the highest As concentration ever measured by the PSL. Several neighbors of this well owner subsequently sent in well samples to the PSL, and some of them had As concentrations above the MCL, although considerably lower than TOL-1.

An article appeared in the local newspaper in the spring of 2011 about the elevated As concentrations in the Tolono area, and a number of additional well owners contacted the PSL to have their well water tested. Normally the PSL mails sampling kits to well owners with instructions on how to collect samples. In order to collect samples for additional chemical analyses that are not routinely done by the PSL and ensure sample integrity, it was decided that ISWS personnel should collect the samples. The main advantages of having ISWS personnel collect samples were that field parameters, such as pH and specific conductance, could be measured on-site, and samples could be filtered and preserved in the field and delivered to the PSL the day they were collected.

Arsenic in Groundwater

Arsenic is well known for its acute toxicity, and chronic consumption of As in drinking water can also cause serious dermatological conditions and affect the respiratory, gastrointestinal, cardiovascular, and nervous systems (Leonard, 1991; Lu et al., 1991; Jain and Ali, 2000). In 2006, the U.S. Environmental Protection Agency (USEPA) lowered the As MCL in drinking water from 50 to 10 µg/L for public water supplies; there is no standard for private wells. Arsenic is a minor constituent of some common minerals, and dissolved As concentrations greater than 1 µg/L are common in groundwater. Much greater As concentrations can be found in many aquifers, and concentrations above 10 µg/L are common. Focazio et al. (2000) reviewed analyses of 2,262 public groundwater supply sources, and Welch et al. (2000) reviewed analyses of 30,000 groundwater samples from throughout the U.S. They found that about 8 percent and 10 percent of them, respectively, had As concentrations greater than 10 µg/L.

Most As in aquifer material in Illinois is associated with iron (Fe) oxyhydroxides (e.g., FeOOH). Arsenic may be released from these minerals by desorption or dissolution. The most common cause of widespread As contamination in the U.S. and the world is thought to be the reduction of Fe oxyhydroxides in the presence of organic carbon and the release of adsorbed As (Welch et al., 2000; Smedley and Kinniburgh, 2002), a conclusion that was reached by Kelly et al. (2005) concerning the Mahomet and Glasford Aquifers of central Illinois.

Arsenic in groundwater occurs in two oxidation states, As(III) (arsenite) and As(V) (arsenate). As(III) is usually present in solution as the uncharged species (chemical form) H_3AsO_3, while As(V) usually exists as an oxyanion, $H_2AsO_4^-$ or $HAsO_4^{2-}$, depending on the pH ($pK_a = 6.98$, i.e., $H_2AsO_4^-$ dominates at $pH < 6.98$ and $HAsO_4^{2-}$ dominates at $pH > 6.98$) (Smedley and

Kinniburgh, 2002). Arsenic(III) is the predominant As species in groundwater in Illinois (Kelly et al., 2005; Warner, 2001; Holm et al., 2008; Holm and Curtiss, 1989) and other Midwestern states (Kim et al., 2002; Erickson, 2005; Korte, 1991). Methylated As species are sometimes found in groundwater, but they usually comprise a small fraction (<1%) of dissolved As (Shraim et al., 2002; Kondo et al., 1999; Watt and Le, 2003), except in groundwater that has been contaminated by methylated As-containing herbicides (Holm et al., 1980; Wallschlger and London, 2008). Kelly et al. (2005) found no methylated As species in Illinois groundwater.

Both As(III) and As(V) sorb to many common aquifer materials, such as metal oxides and clays (Pierce and Moore, 1982; Manning and Goldberg, 1996, 1997; Goldberg, 2002), a process which is thought to limit the mobility of As in aquifer systems. Metal oxides, especially Fe oxides, are common in sand and gravel aquifers as coatings on particles. Iron oxide can be reduced under anoxic conditions, and the sorbed As may be re-released into solution. Aqueous carbonate, ferrous iron, silica (Si), phosphate, pH, and organic matter in groundwater can influence the sorption and possibly the desorption of As (Manning and Goldberg, 1996; Meng et al., 2000; Appelo et al., 2002; Holm, 2002; Redman et al., 2002; O'Day et al., 2004). High concentrations of free sulfide produced by sulfate (SO_4^{2-}) reduction may remove As from solution through precipitation of sulfide minerals, such as As_2S_3 or FeAsS (Rittle et al., 1995; Smedley and Kinniburgh, 2002) or adsorption of As(III) to FeS and FeS_2 (Bostick and Fendorf, 2003).

Arsenic concentrations in groundwater have been observed to be related to other chemical parameters, especially redox-sensitive ones, depending on hydrogeological and geochemical conditions. The most extensive studies on the source and fate of As in groundwater have been conducted in the shallow aquifers in Bangladesh and eastern India. In these regions, the As-polluted groundwater comes from organic-rich deltaic sediments, with the highest concentrations in the more reduced sections of the aquifers. Arsenic and Fe have been found to be associated in the solid phase (Nickson et al., 1998, 2000; McArthur et al., 2001; Harvey et al., 2002). In groundwater, however, As and Fe are sometimes correlated (Nickson et al., 1998; Dowling et al., 2002) but sometimes not (Nickson et al., 2000; McArthur et al., 2001). Arsenic was not found where dissolved oxygen (DO) or nitrate (NO_3^-) were present, but has been observed to be positively correlated with bicarbonate (HCO_3^-), ammonium-nitrogen (NH_4-N), dissolved organic carbon (DOC), and methane (CH_4), although the correlations are often weak (Nickson et al., 1998, 2000; McArthur et al., 2001; McArthur et al., 2004; Dowling et al., 2002; Harvey et al., 2002). Ravenscroft et al. (2001), Harvey et al. (2002), and McArthur et al. (2004) observed that As and SO_4^{2-} tended to be mutually exclusive, and SO_4^{2-} was absent from the high-As samples collected by Dowling et al. (2002). Many of these relationships have been observed in Illinois groundwater (Kelly et al., 2005; Kirk et al., 2004). The observed chemical relationships are hypothesized to result from reductive dissolution of Fe oxyhydroxides coupled with oxidation of abundant organic matter in the sediments, releasing As, either adsorbed to or co-precipitated with FeOOH, into solution.

Hydrogeological Setting

The aquifers in the Tolono area are glacial sand and gravel deposited during the Illinois Episode, specifically the Glasford and Pearl Formations (Figure 1) (Stumpf and Dey, in press). These deposits of sand and gravel are interlayered with glacial tills of the Illinois and pre-Illinois Episodes. Although these sand and gravel units are generally less than 25 feet thick, they are an important source of water for domestic wells and some communities. The Glasford and Pearl Aquifers are laterally discontinuous, and their boundaries are not well defined. In most places, an organic-rich paleosol (Sangamon Geosol) is developed in the upper part of deposits correlated to the Glasford Formation (Herzog et al., 2003). Glacial sediments deposited during the Wisconsin Episode, primarily tills, overlie the Glasford Formation and are the surficial material in most of the study area. In addition to wells drilled into the Glasford or Pearl Aquifers, there are also a number of large-diameter dug and bored wells completed in deposits of the Wisconsin Episode. These wells are shallow (almost always < 100 feet deep) and do not penetrate the Glasford Formation, but collect shallow groundwater from phreatic (water table) sources.

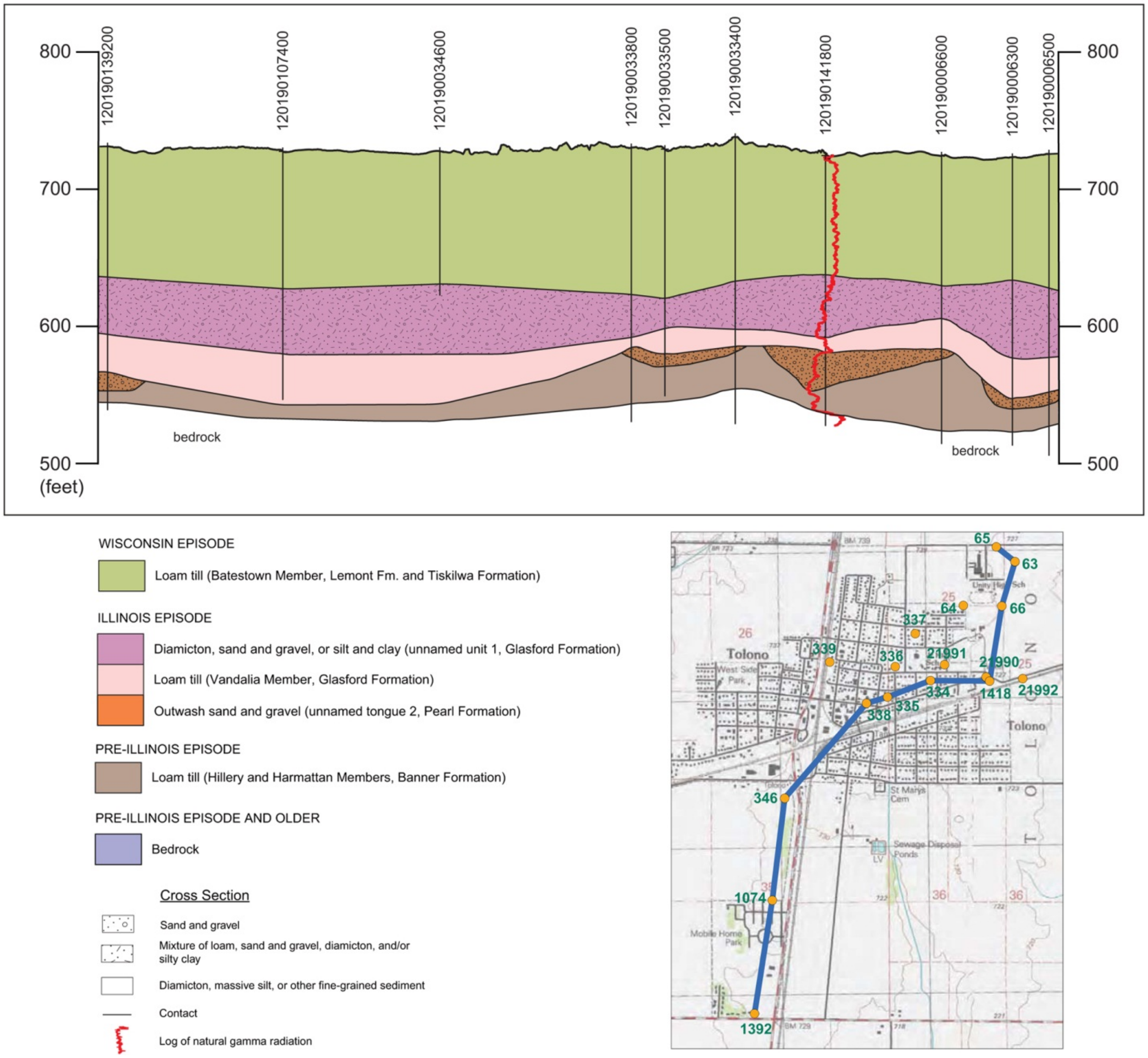

Figure 1. Geologic cross section running roughly southwest-northeast through Tolono. Vertical axis in feet above sea level. Discontinuous sand and gravel layers are found in the Glasford (rose colored) and Pearl (dark orange) Formations, sources of drinking water in this area (Stumpf and Dey, in press)

Procedures

Sample Collection

A total of 17 wells were selected for sampling by ISWS personnel (Table 1). Construction records containing the driller's log were found for ten wells, and the authors identified possible records for six others (identified with a question mark after the P number). A well log was not found for TOL-3. Water samples were collected from 13 of the wells on March 30, 2011, and from the other four on April 7, 2011.

A multi-probe instrument was used for measuring temperature, specific conductance (SpC), pH, platinum-electrode oxidation-reduction potential (ORP), and dissolved oxygen (DO). The instrument was calibrated according to the manufacturer's directions (Hydrolab Mini-Sonde®, Hach Hydromet, Loveland, CO) before each sampling trip.

Wells were generally sampled from outside taps indicated by the home owners to be upstream of any water treatment device (e.g., softener). A flow splitter was attached to the tap. A garden hose was connected to one branch of the connector, and a Hydrolab® flow cell was connected to the other branch. The tap was turned to the maximum flow, and most of the flow went through the hose. Temperature, pH, and the other variables were monitored until the readings stabilized. Readings were considered stable if the change in 60 seconds was less than a temperature of 0.1°C, SpC of 5 percent of the initial value, pH of 0.02, and ORP of 5 millivolts (mV). Readings typically stabilized within 5 to 10 minutes.

The flow cell was disconnected from the sampling line to collect samples. The sample tube was connected to a 0.45 micrometer (µm) filter capsule (Environ-Tech, Martinez, CA), and filtered samples were collected to measure metals, anions, alkalinity, ammonium-nitrogen (NH_4-N), and dissolved organic carbon (DOC). The preservatives for the various samples were metals 0.2% (by volume) HNO_3, NH_4-N 0.5% H_2SO_4, DOC 0.5% H_3PO_4, As species 63 mM acetic acid + 1 mM EDTA (Karori et al., 2006; Samanta and Clifford, 2006).

Water samples were collected inside the house, generally from a cold water tap in the kitchen, to determine if any water treatment devices affected As concentrations. These samples were not filtered. After all samples were collected, bottles were stored in a cooler with ice for transport back to the PSL.

Duplicate raw samples were collected from two wells on March 30 and one well on April 7 to test for combined sampling and analytical replicability. For each sampling trip, a set of blanks containing deionized water was collected prior to departure and analyzed with the samples. These sample blanks were prepared to check if the sampling procedures (i.e., acidification and storage) introduced solutes. Chain-of-custody sheets were completed at the end of each sampling day to track the samples during the analytical process and ensure that sample holding times were not exceeded.

Table 1. Wells sampled in this study. P numbers are unique Water Survey well identifiers. NA = not available. "?" indicates uncertain P number.

Study ID	P Number	Depth (ft)	Well type	Latitude	Longitude	Land Elevation (ft)
TOL-1	5919	179	drilled	39.96626	-88.27557	732.541
TOL-2	10627?	117	drilled	39.99599	-88.34855	606.870
TOL-3	NA	NA	NA	39.96008	-88.27536	656.506
TOL-4	10767	148	drilled	40.01077	-88.23154	733.842
TOL-5	293482	113	drilled	39.99690	-88.23749	614.486
TOL-6	10834?	100	drilled	39.99583	-88.20777	617.629
TOL-7	10844	142	drilled	39.98475	-88.23697	668.472
TOL-8	9973	80	drilled	39.92246	-88.21123	674.624
TOL-9	9573	147	drilled	39.93230	-88.27512	624.248
TOL-10	9517?	178	drilled	39.95876	-88.27560	693.135
TOL-11	9549	92	drilled	39.93856	-88.32574	637.331
TOL-12	10409?	116	drilled	39.98128	-88.38174	624.057
TOL-13	10610?	127	drilled	39.99290	-88.31361	643.266
TOL-14	10814?	94	bored?	40.00978	-88.23857	679.646
TOL-15	10639	95	bored	39.97286	-88.27535	714.501
TOL-16	374208	118	drilled	39.97713	-88.30596	633.888
TOL-17	10526	170	drilled	40.01297	-88.27490	659.496

Chemical Analyses

Chemical analyses were done by the PSL, using standard analytical methods (www.sws.uiuc.edu/chem/ias/). Anions were analyzed by ion chromatography, metals by inductively coupled plasma-atomic emission spectrometry, alkalinity by titration, NH_4-N by colorimetry, and DOC by carbon analyzer. Arsenic was determined by graphite furnace atomic absorption spectrometry with Zeeman background correction. The method specifies sample digestion, adding 1% HNO_3 and heating at 95°C to fully dissolve any colloidal As before analysis. All samples were analyzed both digested and undigested.

The As species As(III) and As(V) were separated by anion exchange (Ficklin, 1983; Edwards et al., 1998). In this method, the resin column retains any As(V) and As(III) that passes through. The column effluent is analyzed for As by atomic absorption. The As(V) concentration can be estimated from the difference in As concentrations between column effluent (As(III)) and total dissolved As.

ISWS Groundwater Quality Database

Sample data collected in this study were supplemented with data from the ISWS Groundwater Quality Database (GWQDB), which contains historical water quality data. The GWQDB was searched for data in the Tolono area (17N 08-09E, 18N 07-09E) dating back to 2004, when As was added to the PSL suite of analytes. Because the elevated As concentrations are found in the Glasford or Pearl Aquifers, samples from shallow wells (< 75 feet) were not considered because they are not completed in these aquifers. Wells less than 75 feet deep are generally bored and dug wells, which all had As concentrations below the detection limit. A total of 39 samples from sand aquifers were found in the GWQDB. These samples were generally collected by the well owner following PSL instructions. They were not filtered or preserved during collection, thus the quality of the data may not be as great as for the samples the authors collected.

Results and Discussion

Two of the wells sampled were determined to be bored wells (TOL-14 and TOL-15), and these samples were discarded from further consideration. One of the samples collected from an outside tap (TOL-10) and two of the samples from the GWQDB were determined to have passed through a water softener (identified by anomalously low hardness and dissolved iron concentrations). Because water softening does not appear to significantly affect As concentrations in these samples, they were included in mapping of As concentrations but their water chemistries were not considered in data analysis.

Complete analytical results for the raw well water samples collected are given in Tables 2 and 3, and from the GWQDB in Table 4. Of the 54 samples (15 sampled and 39 from the GWQDB), 24 had As concentrations > 10 µg/L, and eight had concentrations > 50 µg/L, the old drinking water standard (Table 4). Six of the samples with concentrations > 50 µg/L, including the four samples with concentrations > 100 µg/L, were less than one mile from TOL-1 (Figure 2). This also happened to be the most densely sampled part of the study area. Other than this area, there does not appear to be any discernible spatial pattern for elevated As levels. This is in agreement with other studies in sand and gravel aquifers in Illinois and the Midwest, where considerable spatial heterogeneity in As concentrations was observed (Kelly et al., 2005; Holm, 1995; Holm et al., 2009; Erickson and Barnes, 2005; Goovaerts et al., 2005).

One of the most striking results is the relationship between As concentrations and well depth (Figure 3). For both the samples we collected and those from the GWQDB, the samples with the highest As concentrations (> 40 µg/L) were from wells between about 165 and 180 feet deep, which corresponds to the discontinuous Pearl Formation (Figure 1). The available well logs for these wells indicated no significant water-bearing sand deposits at shallower depths. These results suggest that the Pearl Formation contains the highest As concentrations. Wells screened in the shallower sand layers of the Glasford Formation sometimes have As concentrations greater than the MCL, but rarely > 30 µg/L. It should also be noted that not all wells screened in the Pearl Formation have high As concentrations. Other wells in the Glasford or Pearl Formations previously sampled in Champaign County did not show this depth relationship (Figure 3).

One unexpected result was the change in As concentrations in the well that initially triggered this study, i.e., TOL-1. The sample collected by the homeowner in November of 2010 had an As concentration of 344 µg/L, while the sample collected in March 2011 had an As concentration of 137 µg/L. While this is still a very high As concentration, it was surprising that it was about 60 percent lower. In previous studies, some natural variability in As concentrations has been observed (Holm et al., 2006), but such a large difference is unprecedented in the authors' experience. One difference between the two analyses is that the study sample was filtered while the homeowner's was unfiltered, but in previous studies the authors generally did not find significant amounts of As in the suspended fraction (unfiltered minus filtered concentrations) (Holm et al., 2004, 2008). This is probably why the As concentrations in undigested and digested samples were essentially the same.

Table 2. Results for field parameters for samples collected by ISWS personnel

Study ID	Date	Time	T	pH	SpC	ORP	DO	Comments
			C		µS/cm	mV	mg/L	
TOL-1	3/30/2011	9:25	12.8	7.40	696	56	0.28	
TOL-2	3/30/2011	8:50	11.8	6.99	714	83	0.17	
TOL-3	3/30/2011	9:55	12.9	7.34	673	58	0.18	
TOL-4	3/30/2011	10:25	12.2	6.92	559	113	0.70	
TOL-5	3/30/2011	11:05	12.9	6.60	706	94	0.20	H_2S odor; S bacteria in toilet
TOL-6	3/30/2011	11:50	13.1	7.06	568	94	0.17	
TOL-7	3/30/2011	12:10	12.7	7.06	634	90	0.16	
TOL-8	3/30/2011	13:00	12.8	6.59	1062	104	0.17	Gassy water
TOL-9	3/30/2011	13:25	12.8	7.11	673	86	0.20	Gassy water
TOL-10	3/30/2011	13:50	12.3	7.16	794	195	0.15	Gassy water
TOL-11	3/30/2011	14:20	11.6	7.03	741	76	0.17	Gassy water?
TOL-12	3/30/2011	14:50	12.8	7.08	693	91	0.18	Gassy water
TOL-13	3/30/2011	15:15	12.2	6.77	991	100	0.17	Gassy water
TOL-14	4/7/2011	12:40	12.6	6.85	635	411	7.3	Bored well?
TOL-15	4/7/2011	13:15	12.3	6.91	628	419	7.4	Bored well
TOL-16	4/7/2011	13:35	12.4	6.81	933	117	0.30	H_2S odor
TOL-17	4/7/2011	14:10	13.0	6.54	1235	135	0.20	Gassy water

Table 3. Complete chemical analysis for samples collected by ISWS personnel. Duplicate samples were collected for TOL-9, TOL-11, and TOL-17. A duplicate sample for As(III) analysis was collected for TOL-2. Al, Be, Cd, Co, Cr, Li, Ni, Sb, Se, Sn, Ti, Tl, and V were below detection limits in all samples. Alkalinity reported as $CaCO_3$.

Study ID	PSL #	As*	As**	As(III)	NH_3-N	DOC	Ca	K	Mg	Na	Alkalinity	TDS	F^-	Cl^-	NO_3-N	SO_4
		µg/L	µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
TOL-1	236725	131	137	131	1.34	7.36	41.8	1.31	20.8	101	374	394	0.73	9.45	<0.07	<0.31
TOL-2	236724	3.74	3.95	3.66	1.70	8.90	56.0	1.86	23.2	80.7	396	414	0.58	5.33	<0.07	<0.31
TOL-2†				3.77												
TOL-3	236727	38.2	35.7	33.2	1.04	6.69	39.3	1.01	17.1	102	361	385	0.85	7.16	<0.07	<0.31
TOL-4	236729	3.16	3.10	2.66	1.18	5.62	53.5	1.39	17.0	50.4	299	313	0.42	2.08	<0.07	<0.31
TOL-5	236731	5.86	6.73	6.70	10.2	10.3	70.0	2.64	22.2	40.3	377	366	0.44	1.40	<0.07	<0.31
TOL-6	236733	6.59	6.48	7.21	0.59	5.40	48.9	1.03	16.3	62.0	306	321	0.67	2.56	<0.07	<0.31
TOL-7	236735	15.2	14.7	15.4	0.59	5.44	52.8	1.37	21.2	60.6	334	354	0.66	7.88	<0.07	<0.31
TOL-8	236737	21.8	21.8	24.8	17.6	23.4	74.0	3.54	31.3	111	568	552	0.41	6.71	<0.07	<0.31
TOL-9	236739	7.16	7.04	7.65	0.87	7.41	38.1	1.10	15.2	107	364	399	0.69	3.95	<0.07	<0.31
TOL-9†	236741	7.62	7.31	8.23	0.85	7.59	38.1	1.12	14.8	107	366	388	0.67	4.00	<0.07	<0.31
TOL-10	236742	11.7	11.7	13.1	0.06	13.8	0.140	0.155	0.029	216	430	504	0.64	3.08	<0.07	<0.31
TOL-11	236744	1.16	1.10	1.02	0.87	10.6	62.6	1.01	26.7	79.9	409	423	0.41	4.86	<0.07	<0.31
TOL-11†	236746	<0.95	0.96	<0.95	0.86	10.1	63.4	1.01	27.0	79.7	407	419	0.40	4.86	<0.07	<0.31
TOL-12	236747	<0.95	<0.95	<0.95	1.22	8.63	51.7	1.68	20.6	83.4	358	388	0.65	13.9	<0.07	<0.31
TOL-13	236748	3.46	3.58	3.83	3.82	15.8	94.7	2.22	34.4	94.9	550	560	0.40	4.55	<0.07	<0.31
TOL-14	236764	<0.95	<0.95	<0.95	0.05	2.37	82.8	2.50	30.5	8.41	272	363	0.17	14.9	1.92	43.0
TOL-15	236765	<0.95	<0.95	<0.95	0.08	1.36	79.6	0.754	34.5	6.92	250	358	0.34	9.07	6.35	49.0
TOL-16	236767	6.08	6.11	5.97	2.43	14.2	85.7	1.93	30.8	97.7	521	549	0.46	5.70	<0.07	<0.31
TOL-17	236768	66.4	64.6	62.7	21.3	16.0	105	4.32	50.2	92.9	698	639	0.19	3.25	<0.07	<0.31
TOL-17†	236769	67.2	65.5	62.1	19.5	15.7	104	4.36	51.1	94.2	691	646	0.20	3.17	<0.07	<0.31

* undigested sample

** digested sample

† duplicate sample

Table 3. Continued

Study ID	PSL #	*o*PO_4-P	B	Ba	Cu	Fe	Mn	Mo	P	Pb	S	SiO_2	Sr	Zn	Color	Turbidity	Hardness
			µg/L	µg/L	µg/L	mg/L	µg/L	µg/L	mg/L	µg/L	mg/L	mg/L	µg/L	µg/L	PCU	NTU	mg/L
TOL-1	236725	0.099	415	338	<0.79	1.14	22.3	39	0.459	<41	<0.22	11.8	322	27.9	9	4.1	190
TOL-2	236724	0.023	547	201	<0.79	1.11	11.0	<22	0.243	<41	<0.22	18.8	331	15.8	14	6.1	236
TOL-3	236727	0.106	186	218	<0.79	0.968	36.1	43	0.439	<41	<0.22	13.5	306	64.1	15	4.5	169
TOL-4	236729	0.018	772	120	<0.79	1.40	53.6	<22	0.217	<41	<0.22	21.5	128	<9.7	10	7.6	204
TOL-5	236731	0.020	738	209	0.81	4.07	39.4	<22	0.721	<41	<0.22	27.1	310	<9.7	14	48.6	266
TOL-6	236733	0.021	815	132	1.13	0.924	44.4	<22	0.223	<41	<0.22	18.4	161	<9.7	6	5.9	189
TOL-7	236735	0.015	137	224	<0.79	1.25	77.7	<22	0.224	<41	<0.22	17.9	251	10.3	<5	11.9	219
TOL-8	236737	0.019	771	318	<0.79	5.58	35.9	<22	1.14	<41	0.37	23.0	462	13.7	21	63.9	314
TOL-9	236739	0.053	1449	172	<0.79	0.836	11.4	<22	0.238	48	<0.22	18.4	203	<9.7	11	2.0	158
TOL-9†	236741	0.054	1445	173	<0.79	0.826	11.4	<22	0.242	<41	<0.22	18.3	203	<9.7	22	3.8	156
TOL-10	236742	0.187	2123	<0.85	1.69	0.041	<1.5	<22	0.256	<41	<0.22	19.0	0.53	34.5	33	0.2	0.47
TOL-11	236744	0.020	392	186	<0.79	1.51	20.6	<22	0.319	<41	<0.22	19.6	189	24.0	22	10.5	266
TOL-11†	236746	0.020	395	186	<0.79	1.52	20.3	<22	0.304	<41	<0.22	19.8	189	22.0	20	12.8	270
TOL-12	236747	0.025	443	228	<0.79	1.09	9.5	<22	0.275	<41	<0.22	21.3	306	<9.7	18	5.7	214
TOL-13	236748	0.020	610	315	<0.79	3.71	16.1	<22	0.333	<41	0.25	28.9	294	14.7	21	37.6	378
TOL-14	236764	0.014	137	73.0	5.28	<0.024	18.2	<22	0.119	<41	14.8	11.6	286	<9.7	14	0.2	332
TOL-15	236765	0.017	106	48.7	9.24	<0.024	<1.5	<22	0.078	<41	17.0	11.0	305	<9.7	6	<0.1	341
TOL-16	236767	0.035	582	335	<0.79	2.38	12.7	<22	0.332	<41	0.23	24.7	279	<9.7	83	24.2	341
TOL-17	236768	0.042	429	527	1.56	3.41	5.5	<22	0.244	<41	0.32	30.6	370	<9.7	151	40.1	468
TOL-17†	236769	0.062	431	535	1.42	3.40	5.7	<22	0.273	<41	0.33	30.6	372	<9.7	164	39.1	470

† duplicate sample

Table 4. Results from GWQDB. P No. is ISWS well identification. Results are for total (unfiltered) samples except where indicated (d = dissolved). Blank fields indicate parameter not analyzed for or unknown (depth). Arsenic results are for digested samples. Alkalinity reported as $CaCO_3$.

P No.	Location	Date	Lab No.	Depth	As	Ca	Cl^-, d	F^-, d	K	Mg	Na	Alkalinity	SO_4, d	NO_3-N, d	NPOC
				ft	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
9637	01917N08E268B	11/30/2004	234004	104	< 0.71	42.6	3.13	0.69		13.1	112	376	< 0.31	< 0.07	8.51
	01918N09E13	3/9/2011	236609		< 0.95	47.8	2.34	0.686	1.56	20.4	65.8	335	0.321	< 0.07	
9634	01917N08E252H	3/14/2011	236630	91	< 0.95	45.1	1.94	0.462	1.02	16.9	78.4	365	< 0.31	< 0.07	
9641	01917N08E275A	7/7/2006	234817	94	< 0.95	37.8	1.19	0.46		19.4	68.4	326	< 0.31	< 0.07	
242476	01918N09E027A	3/3/2011	236551	111	< 0.95	41.9	1.87	0.644	1.07	17	75.9	318	1.15	< 0.07	
314209	01918N09E038A	4/26/2011	236790	210	< 0.95	42.6	1.67	0.454	0.847	11.6	74.5	304	< 0.31	< 0.07	
	01918N08E051H	10/24/2005	234477		1.03	64.9	3.83	0.17		31.8	52.2	406	< 0.31	< 0.07	
	01918N09E19	3/11/2011	236610	98	1.16	83.8	2.48	0.344	3.21	30.9	72.6	541	< 0.31	< 0.07	
	01918N09E343H	12/28/2005	234562	89	2.71	42.6	2.56	0.74		16.1	84.2	327	< 0.31	< 0.07	5.1
266295	01918N09E281C	12/26/2005	234560	180	2.95	135	24.9	0.26		50.9	176	1006	< 0.31	< 0.07	> 20
360153	01918N07E256A	9/25/2007	235296	180	3.56	57.4	10.2	0.54	1.74	23.1	86.5	389	< 0.31	< 0.07	
9516	01917N08E031C	2/14/2011	236521	185	3.7	40.4	7.49	0.78	1.28	18.2	96.7	371	< 0.31	< 0.07	
303275	01917N09E078H	8/17/2010	236303	149	4.89	41	19.4	0.849	1.14	20.3	115	381	< 0.31	< 0.07	
	01918N08E327G	3/17/2011	236658		5.2	61.5	4.18	0.395	0.958	28.4	48	365	< 0.31	< 0.07	
9588	01917N08E195A	4/15/2011	236779	90	6.84	56.9	4.95	0.399	1.23	26.3	65.8	372	< 0.31	< 0.07	
242472	01917N09E278G	8/15/2008	235650	226	6.99	42.6	404	< 0.08	2.99	19.7	307	291	< 0.31	< 0.07	
	01918N07E16	3/16/2011	236655	120	7.64	63.1	7.69	0.501	1.78	30	52.7	395	< 0.31	< 0.07	
358724	01918N08E202G	12/9/2004	234016	124	8.71	84	4.19	0.35		31.3	90.4	513	< 0.31	< 0.07	11.3
9614	01917N08E227D	3/3/2011	236539	138	9.41	51.9	6.69	0.625	1.8	16.7	89.5	362	< 0.31	< 0.07	
339322	01918N09E108F	3/10/2011	236599	175	10.1	40.2	1.95	0.269	1.42	15.2	85	314	5.8	< 0.07	
260721	01918N09E265D	3/12/2008	235465	132	14.0	46.4	1.95	0.765	1.66	17.7	68.7	324	1.98	< 0.07	
10715	01918N09E084H	6/3/2004	233782	103	15.4	56	0.76	0.35		27.5	36.9	308	< 0.31	< 0.07	
360155	01918N07E021A	5/3/2004	233754	143	17.5	55.1	4.6	0.33		26.2	77.8	374	0.48	< 0.07	
383936	01918N07E361H	8/6/2008	235638	110	19.2	55.5	10.7	0.54	1.43	25.2	79.7	398	< 0.31	< 0.07	
10449	01918N08E026H	3/6/2011	236563	186	19.3	75.6	3.37	0.211	2.46	37.4	53.4	434	< 0.31	< 0.07	
266004	01918N08E227A	4/25/2005	234099	126	20.1	95.4	4.45	0.35		40.5	117	573	< 0.31	< 0.07	
453475	01917N09E196A	3/25/2011	236705		20.5	36.2	4.69	0.947	1.26	17.1	95.8	351	< 0.31	< 0.07	
354600	01918N08E188C	1/14/2004	233611	102	29.3	43.4	3.95	0.84		24.6	87.8	372	< 0.31	< 0.07	18.6
	01917N08E187G	3/17/2011	236660	130	30.4	63.5	6.89	0.494	1.47	26.5	83.7	431	< 0.31	< 0.07	
349173	01918N07E361H	2/7/2006	234638	133	36.2	52.9	11.6	0.53		24.4	85.1	375	0.86	< 0.07	
242475	01918N08E151B	7/26/2005	234293	165	40.0	94.6	3.17	0.16		44.2	80.2	604	< 0.31	< 0.07	
	01917N08E293A	10/18/2006	234910		75.7	65.4	6.47	0.46		21.8	89.5	418	< 0.31	< 0.07	
9518	01917N08E031F	1/30/2011	236494	175	82.0	38.4	9.02	0.801	1.16	17.5	103	373	< 0.31	< 0.07	
	01917N08E03	1/1/2050	236522		90.3	38.6	6.76	0.822	1.14	18.3	106	371	< 0.31	< 0.07	
	01917N08E03	2/1/2011	236497	180	103.7	36.6	9.87	0.77	1.18	17.8	96.9	362	< 0.31	< 0.07	
	01917N08E03	4/11/2011	236773	300	105.0	36.8	7.85	0.991	1.2	16.8	109	360	< 0.31	< 0.07	
9517	01917N08E031D	2/20/2011	236529	178	118.9	36.4	7.21	0.896	1.13	17.5	104	370	< 0.31	< 0.07	

Table 4. Continued

Lab No.	Al	B	Ba	Zn	Co	Cr	Cu	Fe	Mn	Ni	P	S	SiO_2	Sn	Sr	TDS
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L	µg/L	µg/L	mg/L	mg/L	mg/L	µg/L	µg/L	mg/L
234004	< 134	2854	104	687		< 12	< 11	2.72	28	< 30						416
236609	< 37	2448	139	518	< 13	< 5.8	1.61	1.54	27.6	< 43	0.214	< 0.22	18.4	< 86	557	348
236630	< 37	2813	104	31.8	< 13	< 5.8	4.91	0.814	12.2	< 43	0.209	< 0.22	18.2	< 86	313	388
234817		2570	81	15		< 12	< 11	0.802	16	< 30						338
236551	< 37	2898	110	15.4	< 13	< 5.8	7.74	0.726	14	< 14	< 0.073	0.481	19.7	< 86	440	338
236790	< 37	2219	139	< 9.7	< 13	< 5.8	0.97	0.822	15.7	< 43	0.21	< 0.22	19.9	< 86	116	334
234477		505	215	27		< 12	33	2.16	16	< 30						391
236610	< 37	823	313	53.3	< 13	< 5.8	6.11	4.11	16.9	< 43	0.441	0.36	27.6	< 86	368	508
234562	< 134	2440	79	21		< 12	< 11	1.39	46	< 30						337
234560	437	650	833	34		< 12	< 11	9.11	85	< 30						932
235296	12	707	200	17		< 5.8	37	1.14	11	< 14			19.1			418
236521	< 37	306	257	722	< 13	< 5.8	2.6	2.42	23	< 14	0.227	< 0.22	15.0	< 86	301	383
236303	< 37	322	233	61.7	< 13	< 5.8	< 0.79	0.736	50.8	< 14	0.12	< 0.22	14.2	< 86	390	441
236658	< 37	597	150	37.7	< 13	< 5.8	773	1.65	19.1	< 43	0.092	< 0.22	18.8	< 86	221	377
236779	< 37	771	239	63.3	< 13	< 5.8	4.45	2.22	16.8	< 43	0.221	< 0.22	18.9	< 86	309	378
235650	40	203	125	36		< 5.8	< 0.79	0.655	24	< 14			10.8			978
236655	< 37	959	119	236	< 13	< 5.8	4.72	3.3	22.1	< 43	0.325	< 0.22	18.2	< 86	333	398
234016		631	273	45		< 12	< 11	3.24	38	< 30						515
236539	< 37	863	209	136	< 13	< 5.8	5.76	3.58	29.8	< 14	0.28	< 0.22	23.9	< 86	233	393
236599	< 37	2032	161	40.9	< 13	< 5.8	60.6	0.819	54.1	< 14	0.105	2.09	16.3	< 86	208	339
235465	16.8	2100	69	56.7		< 5.8	13.2	1.75	26	< 14			16.5			341
233782		1294	82	< 3		< 7	< 6	0.596	59	< 13						310
233754		607	209	120		< 7	< 6	1.53	65	< 13						391
235638	44	355	207	< 7.3		< 5.8	2.9	1.44	12	< 14			18.0			416
236563	< 37	381	405	< 7.3	< 13	< 5.8	3	1.85	11	< 14	0.099	< 0.22	21.6	< 86	273	428
234099		914	329	50		< 12	39	5.69	25	< 30						585
236705	< 37	1111	270	79.2	< 13	< 5.8	3.76	1.23	5.2	< 43	0.185	< 0.22	14.3	< 86	396	365
233611		867	128	32		< 7	7	1.21	6	< 13						383
236660	< 37	594	242	< 9.3	< 13	< 5.8	3.28	1.97	13	< 43	0.297	0.23	20.1	< 86	322	462
234638		390	195	189		< 12	< 11	1.66	19	< 30						416
234293		554	368	21		< 12	< 11	3.05	14	< 30						584
234910		811	336	150		< 5.8	1.35	5.15	41.4	< 14						442
236494	< 37	263	242	< 7.3	< 13	< 5.8	<0.79	0.981	77	< 14	0.291	< 0.22	12.8	< 86	321	383
236522	46	474	250	< 7.3	< 13	< 5.8	95	2.07	61	< 14	0.313	< 0.22	13.0	< 86	329	394
236497	< 37	234	260	20.5	< 13	< 5.8	24.6	0.862	26.1	< 14	0.247	< 0.22	12.6	< 86	287	362
236773	< 37	286	216	167	< 13	< 5.8	1.56	1.8	34.6	< 43	0.452	< 0.22	12.0	< 86	290	386
236529	< 37	286	224	< 7.3	< 13	< 5.8	3.1	1.65	56	< 14	0.488	< 0.22	10.0	< 86	300	387

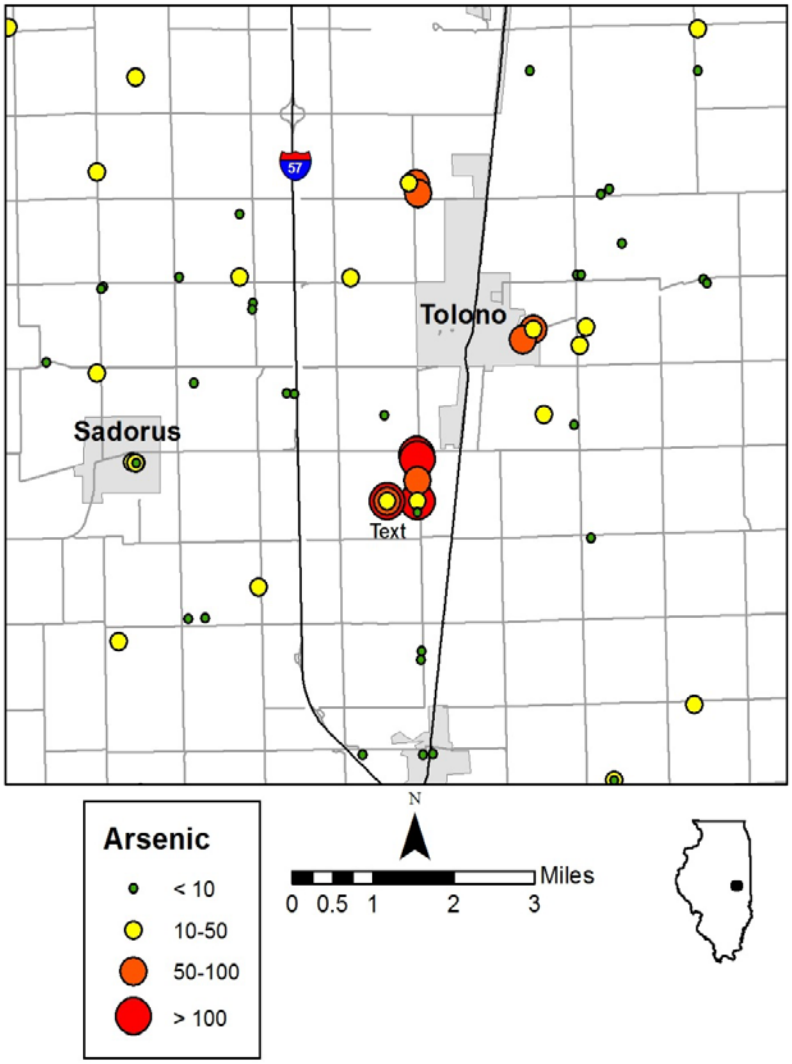

Figure 2. Arsenic concentrations in Glasford and Pearl wells in the Tolono region, including both wells sampled during this study and from the GWQDB. Concentrations in µg/L.

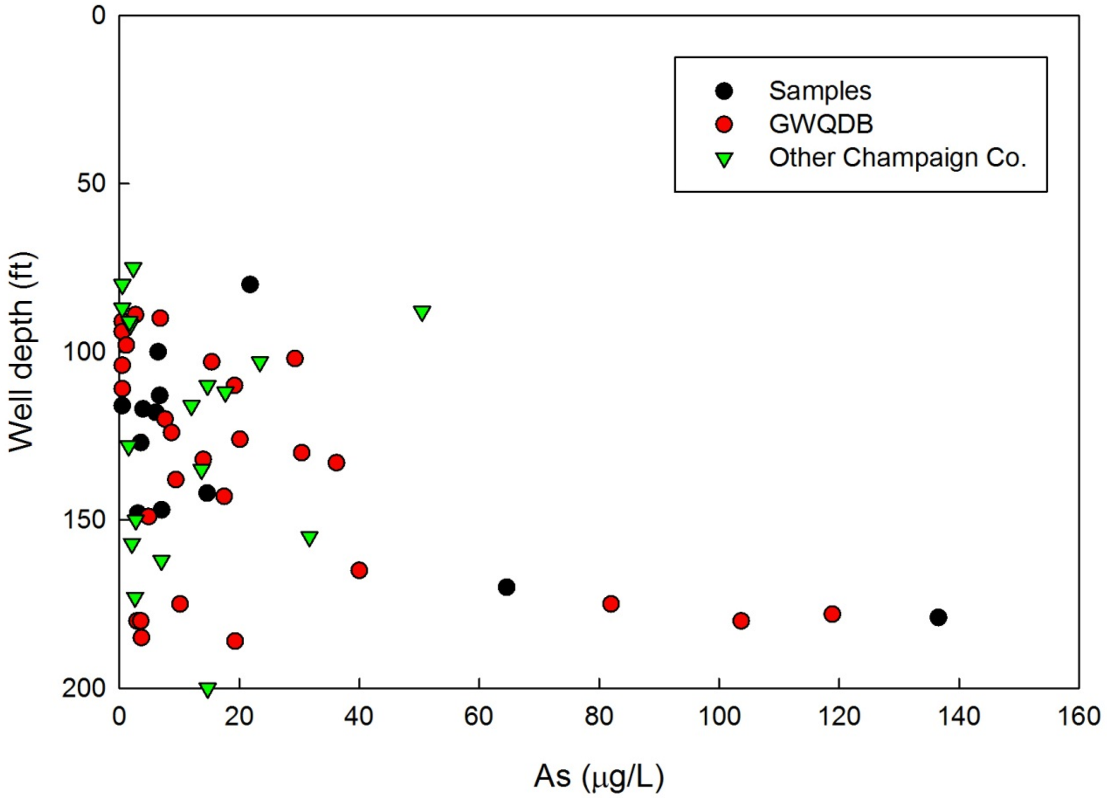

Figure 3. Arsenic concentrations as a function of well depth. Black points are samples collected in this study, red points are from the groundwater quality database, and green triangles are samples collected from wells screened in the Glasford or Pearl Formations in other parts of Champaign County (Holm et al., 2004; Kelly et al., 2005).

Reducing conditions prevailed throughout the aquifer. Dissolved oxygen readings were less than 0.3 mg/L in all samples, which for the multi-probe indicated anoxic conditions. Dissolved Fe is abundant throughout the Glasford and Pearl Aquifers, with most samples having concentrations greater than 1.0 mg/L and more than 20% being greater than 3.0 mg/L, which confirms the water is anoxic. Manganese was detectable in almost all samples. Nitrate-N was below detection (0.07 mg/L) in all of the samples. Sulfate (SO_4^{2-}) was below detection (0.31 mg/L) in all but six of the samples; the largest concentration was 5.8 mg/L. The samples were not analyzed for sulfide, although a H_2S odor was detected in at least two of the samples collected. About half of the samples collected exsolved gas, presumably methane (CH_4). Ammonium-N and DOC are not routinely analyzed by PSL for samples collected by clients, but they were analyzed for the study samples. Ammonium-N was greater than 1.0 mg/L in a majority of samples, and greater than 10 mg/L in three samples. DOC concentrations were very high in the samples collected, greater than 5 mg/L for all samples and > 10 mg/L for seven samples.

The major ion chemistry was primarily a mixed cation (Na-Ca-Mg)-bicarbonate (HCO_3^-) type (Figure 4). This is similar to the major ion chemistry found in other Glasford and Pearl Aquifer samples from Champaign County, although the Tolono area samples tended to have relatively higher Na concentrations, and there were areas in Champaign County with higher SO_4^{2-} values than those found near Tolono. The one outlier from the Tolono area samples is from the GWQDB, and had very high Na and Cl^- concentrations; this suggests it may have been affected by softening and regeneration, although the Ca and Mg concentrations (hardness) were not particularly low, which is the main evidence of softened samples.

Water treatment reduced As by small amounts or had no effect (Table 5). The apparent As removal (fourth column of Table 5) was within the uncertainty of low-level measurements. Lack of As removal was not unexpected. Softening involves cation exchange and the As species are either neutral (As(III)) or anionic (As(V)). The concentrations of Ca, Mg, Fe, Sr, and Ba were much lower and Na was higher in treated water than in raw water. TOL-7, TOL-9, and TOL-17 were exceptions. These were apparently not softened.

Previous studies in the Glasford, Pearl, and Mahomet Aquifers in Central Illinois suggested that oxidation-reduction conditions were the primary control of As concentrations in groundwater (Warner, 2001; Thomas, 2003; Kirk et al., 2004; Kelly et al., 2005). Kelly et al. (2005) observed significant differences in chemistry based on total organic carbon (TOC) concentrations in both aquifers. Arsenic and other redox-sensitive parameters were either significantly greater (As, Fe, NH_4-N, and HCO_3^-) or lower (Mn, SO_4^{2-}, and ORP) in the high-TOC (> 2 mg/L) samples than in the low-TOC samples.

These redox relationships were not as obvious for the Tolono area samples as for the data reported in Kelly et al. (2005) (Figure 5). Redox conditions seemed to be relatively consistent for the Tolono samples. For example, there was little or no SO_4^{2-} in any of the samples, and DOC concentrations were very high (> 5 mg/L) in all samples in which it was measured. These high DOC concentrations are probably promoting very reducing conditions throughout the aquifer. While the authors did not analyze for methane (CH_4), a product of very reducing conditions, they did observe significant amounts of gas in many of the samples, and previous studies suggest the gas fraction is dominated by methane (Hackley et al., 2010). Tolono's public supply wells, which were approximately 180 feet deep but are no longer operational, had reports of methane in them. There were positive relationships among many of the redox parameters, e.g., NH_4-N, DOC, Fe, and HCO_3^-.

Kelly et al. (2005) reported some threshold values for Fe, HCO_3^-, NH_4-N, and TOC below which As was almost always very low. For example, As was not observed in samples with Fe < 1.3 mg/L. There were no obvious Fe, NH_4-N, or DOC thresholds for the Tolono samples. Bicarbonate did appear to have a threshold value of about 350 mg/L. Kelly et al. (2005) also observed that As had “mutually exclusive” associations with SO_4^{2-}, Mn, and Cl^-; i.e., when As was present in appreciable concentrations, SO_4^{2-}, Mn, and Cl^- concentrations were very low, and vice versa. The authors did not observe these relationships in the Tolono samples, in part because $SO_4^{2-}$and Cl^- concentrations were in general low to very low in all samples.

Kelly et al. (2005) did not observe any associations between As and the major cations or trace metals. In the Tolono samples, however, there did appear to be some relationships (Figure 6). For example, the samples with the highest As concentrations tended to have low Ca, Mg, K, and SiO_2 concentrations, and relatively elevated Na and F^- concentrations. There also was a weak positive association between As and phosphate (Figure 5), which Kelly et al. (2005) suggested might exist in their samples. There appears to be a mutually exclusive association between As and boron (B) in the Tolono samples.

While there are some minor differences in chemistry between the Tolono area well water samples and samples collected from other parts of Champaign County, the mechanisms controlling the solubility of As in the Glasford and Pearl Aquifers are likely similar. Namely, it is likely that the primary source of As is reduction of Fe oxyhydroxide minerals in the sand and gravel aquifer deposits. The availability of organic matter appears to be the key factor affecting As solubility. There are organic-rich zones that were deposited with the sands and gravels in the Glasford and Pearl Aquifers, and geochemical conditions are very reducing in these zones. Sulfate is depleted in these zones and thus is no longer available as an electron acceptor, but iron reduction continues even under post SO_4^{2-} reducing conditions, releasing aqueous As into solution. The absence of SO_4^{2-} reduction means no sulfide minerals are being precipitated that could potentially remove As from solution. Arsenic does not appear to be transported large distances, however, and is likely being re-adsorbed to the abundant Fe oxyhydroxide minerals.

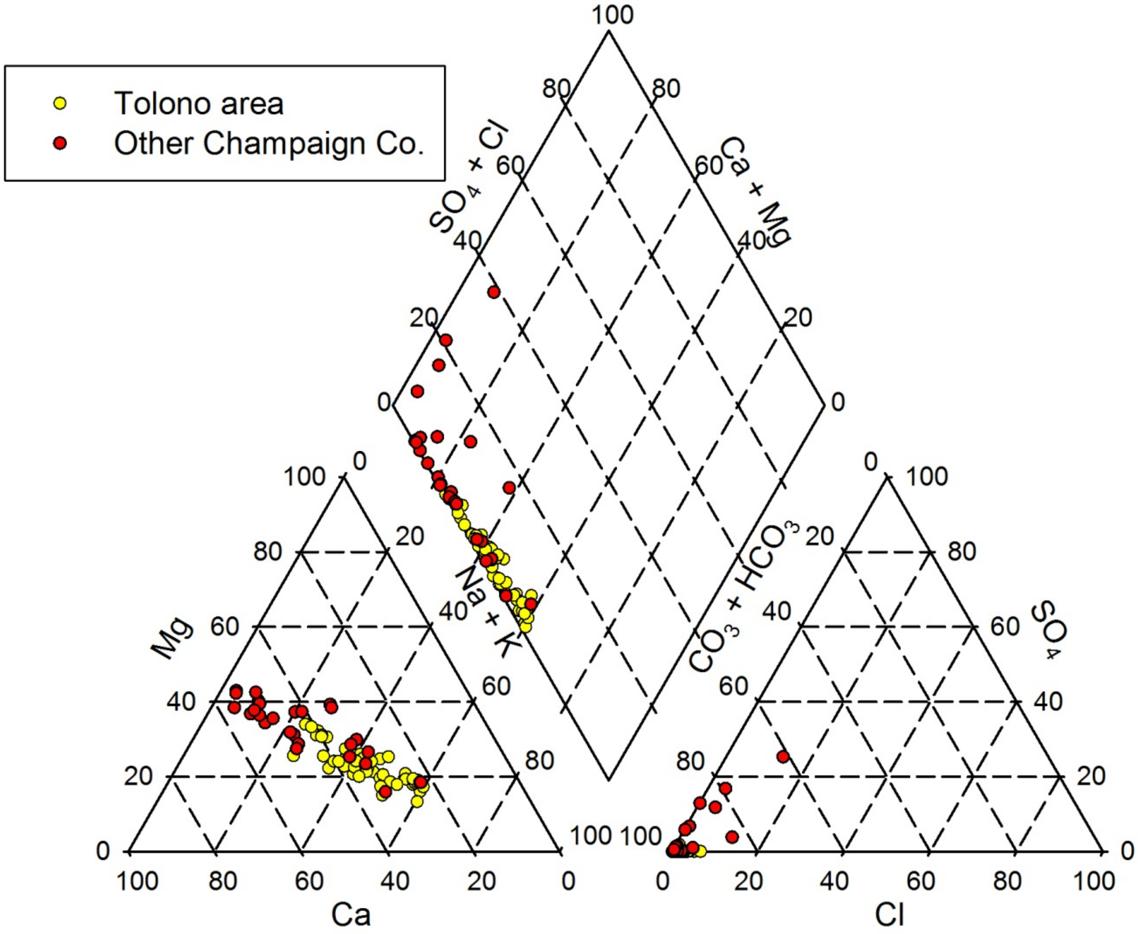

Figure 4. Piper diagram showing major ion chemistry for wells in the Tolono region (yellow points) and for wells screened in the Glasford or Pearl Formations in other parts of Champaign County (Holm et al., 2004; Kelly et al., 2005)

Table 5. Completed analytical results for treated samples. Arsenic results are for digested samples. As removal represents difference between treated and raw As concentrations. NO_3-N, SO_4^{2-}, Al, Cd, Co, Cr, Li, Mo, Ni, Pb, Sb, Se, Sn, Tl, and V were below detection limits in all samples.

Study ID	PSL #	As	As removal	Ca	K	Mg	Na	Alkalinity	TDS	F^-	Cl^-	B	Ba
		µg/L	µg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L
TOL-1	236726	137	-0.86	0.106	0.147	0.033	195	378	437	0.72	9.49	155	416
TOL-3	236728	32.6	3.14	<0.029	0.067	<0.027	183	365	418	0.87	7.14	<110	191
TOL-4	236730	1.63	1.47	0.277	0.226	0.082	150	305	356	0.36	5.73	<110	761
TOL-5	236732	4.75	1.97	0.072	0.098	<0.027	191	392	462	0.43	1.56	<110	753
TOL-6	236734	5.33	1.15	<0.029	0.100	<0.027	155	267	358	0.67	33.4	<110	810
TOL-7	236736	13.8	0.82	54.1	1.36	21.8	63.1	334	352	0.65	7.90	<110	146
TOL-8	236738	19.7	2.11	0.188	0.150	0.070	292	579	684	0.31	6.56	<110	765
TOL-9	236740	7.29	-0.24	37.6	1.07	14.9	104	364	397	0.66	3.99	<110	1415
TOL-10	236743	10.9	0.78	0.033	0.042	<0.027	55.2	111	124	0.20	0.73	<110	1989
TOL-11	236745	<0.95	0.15	0.076	297	0.043	13.8	411	609	0.40	4.83	<110	385
TOL-12	236760	<0.95		0.041	0.079	<0.027	178	364	435	0.65	14.1	<110	430
TOL-13	236749	3.52	0.06	0.151	0.117	0.037	266	548	634	0.43	4.59	<110	606
TOL-16	236766	6.28	-0.17	0.226	0.932	0.082	254	524	608	0.42	5.68	<110	583
TOL-17	236778	66.1	-1.52	58.2	13.6	51.1	92.9	698	639	0.19	3.25	<110	418

Table 5. Continued

Study ID	PSL #	Be	Cu	Fe	Mn	P	S	SiO_2	Sr	Ti	Zn	Color	Turbidity	Hardness
		µg/L	µg/L	mg/L	µg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	PCU	NTU	mg/L
TOL-1	236726	1.26	<0.79	<0.024	<1.5	0.453	<0.22	11.9	0.63	<0.56	<9.7	11	0.2	0.40
TOL-3	236728	<0.85	<0.79	<0.024	<1.5	0.381	<0.22	13.2	<0.37	<0.56	<9.7	7	0.1	<0.18
TOL-4	236730	<0.85	<0.79	0.152	<1.5	0.184	<0.22	20.8	0.50	<0.56	14.5	7	0.3	1.03
TOL-5	236732	<0.85	2.24	<0.024	<1.5	0.669	<0.22	26.1	<0.37	<0.56	<9.7	16	0.2	<0.18
TOL-6	236734	<0.85	<0.79	<0.024	<1.5	0.150	<0.22	18.1	<0.37	<0.56	<9.7	<5	<0.1	<0.18
TOL-7	236736	224	0.84	1.31	78.5	0.203	<0.22	18.4	253	<0.56	<9.7	<5	4.8	225
TOL-8	236738	<0.85	<0.79	0.078	<1.5	1.18	0.38	22.6	0.43	<0.56	<9.7	26	0.3	0.76
TOL-9	236740	168	<0.79	0.840	11.4	0.226	<0.22	18.0	198	<0.56	<9.7	21	1.9	155
TOL-10	236743	<0.85	<0.79	<0.024	<1.5	<0.073	<0.22	4.96	<0.37	<0.56	<9.7	<5	0.1	<0.18
TOL-11	236745	<0.85	<0.79	<0.024	<1.5	0.204	<0.22	18.9	<0.37	<0.56	<9.7	16	0.1	0.36
TOL-12	236760	<0.85	<0.79	<0.024	<1.5	0.152	0.29	20.3	<0.37	0.71	<9.7	22	0.2	<0.18
TOL-13	236749	<0.85	5.27	0.042	<1.5	0.363	0.25	27.9	0.41	<0.56	<9.7	30	0.3	0.53
TOL-16	236766	0.88	<0.79	0.035	<1.5	0.247	0.23	24.3	0.47	<0.56	<9.7	30	0.2	0.90
TOL-17	236778	280	1.15	2.71	10.8	0.255	0.37	29.0	206	<0.56	<9.7	31	35.2	356

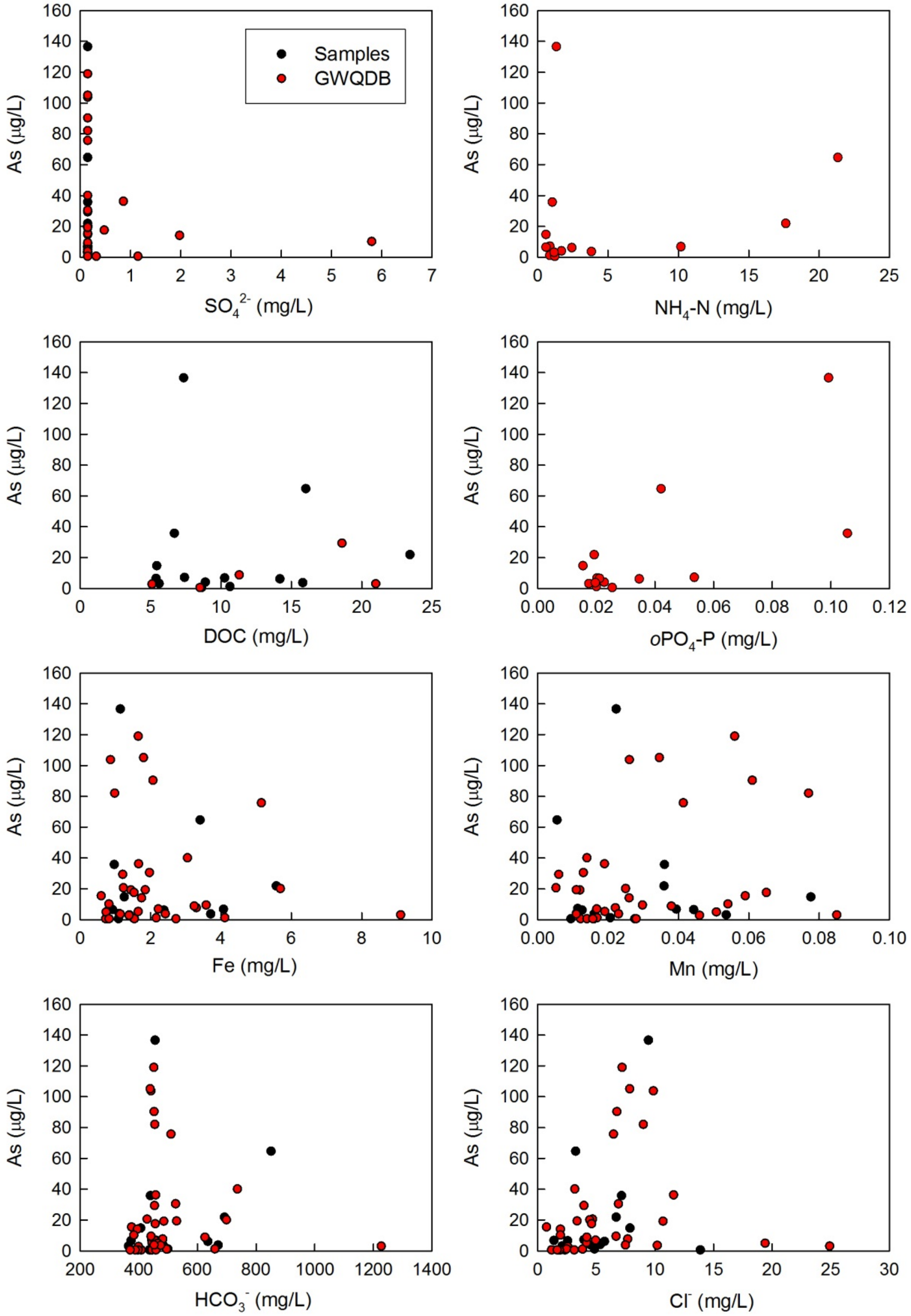

Figure 5. Arsenic concentrations as a function of redox-sensitive species and chloride

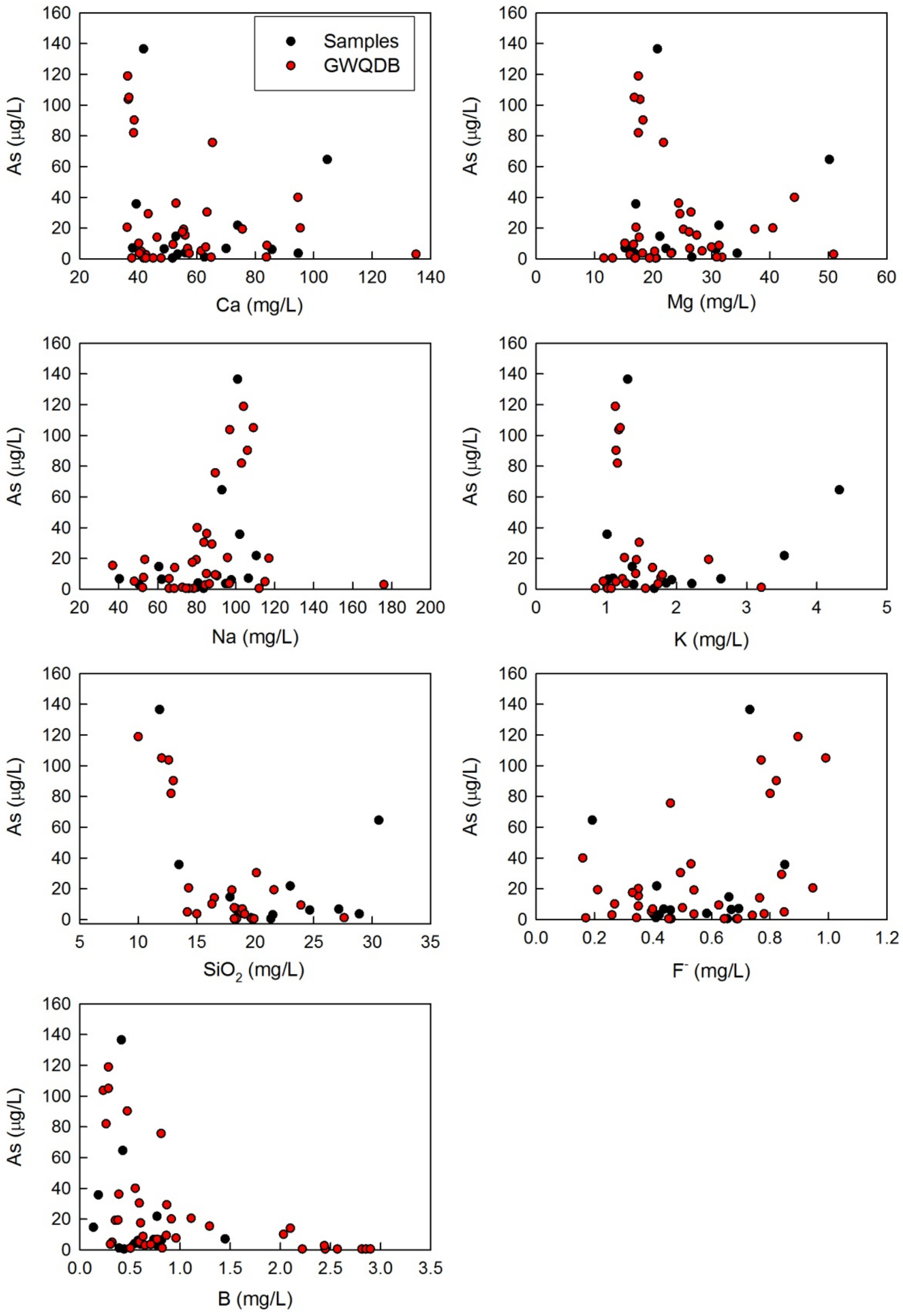

Figure 6. Arsenic concentrations as a function of various aqueous species

Conclusions

Elevated levels of As were found in wells near Tolono, IL. The greatest concentrations (> 40 µg/L) were limited to wells with depths of between 165 and 180 feet, which correspond to the discontinuous Pearl Aquifer. Many shallower wells screened in the Glasford Aquifer do have As concentrations greater than the recommended drinking water standard of 10 µg/L, but these rarely exceed 30 µg/L. The high organic carbon concentrations with strongly reducing conditions in both the Glasford and Pearl Aquifers in this area are consistent with conditions associated with elevated As levels in other aquifers in Illinois. The fact that wells in the Pearl Aquifer have significantly higher As levels than those in the Glasford Aquifer suggests that there may be a larger source of As in the Pearl Formation sediments. It should be noted, however, that not all wells in the Pearl (or Glasford) Aquifer have elevated As levels, and there appears to be no discernible geographic pattern for the elevated As. It is recommended that well owners in this area have their wells tested for As.

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