

Comparison of Dissolved and Acid-Extractable Metal Concentrations of Ground Water, Eastern Arkansas, USA

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ABSTRACT. The objective of this project was to compare dissolved and acid-extractable metal concentrations in ground water in the alluvial and Sparta aquifers in eastern Arkansas, USA. Typically, water samples for metal analyses are filtered through a 0.45 µm pore-size membrane immediately after sample collection, yielding “dissolved” concentrations. In some situations, acid-extractable metal concentrations (unfiltered samples but acidified) may better represent potential metal “availability”, e.g., from cation exchange or from dissolution of Fe hydroxyoxides. For this project, 41 wells were sampled in the Mississippi River Valley Alluvial and Sparta aquifers. The paired student-T test was used to determine differences in the dissolved and acid-extractable concentrations for Fe, Mn, Cu, Pb, Zn, Ca, Mg, Na and K. The test indicated that there are significant differences between dissolved and acid-extractable concentrations for Fe, Mn, Pb and Ca at the 95% confidence level. The test indicated no differences for Mg, K, Na, Cu, and Zn (confidence level < 95%). In most cases the difference ratios for dissolved and acid-extractable concentrations were less than 25% but in about one third of samples the difference ratios were greater than 90%. Highly turbid samples had the highest difference ratios. The results indicate that acid-extractable concentrations can be important in determining metal availability for Mn, Pb, Ca and especially Fe. The Fe concentrations show spatial variation that is related to variations in lithology, ground water flow and/or geochemical processes.

Keywords: Acid-extractable concentration, alluvial, cation concentrations, dissolved concentration, eastern Arkansas USA, field Measurements, flow modeling, ground water, heavy metals velocity, overbank flow, Sparta aquifer, spatial variation, turbulence

1. Introduction

U.S. Environmental Protection Agency (EPA) recommends use of dissolved metal concentrations to set water quality standards (Lussier et al., 1999). In order to measure dissolved metal concentrations, Standard Methods for Examination of Water and Wastewater (Clesceri et al., 1999) and EPA Analytical Methods (1994) recommend that water samples be filtered through a 0.45 µm pore-size membrane immediately after sample collection and before acidifying the samples. However, most domestic water supplies and irrigation waters are not filtered; thus, the suspended sediments concentration may supply ions that are environmentally available to human beings, animals and plants. According to EPA (Pohlmann et al., 1994), the field filtration of samples can affect trace metal concentration. For example, during sample collection, Fe in the well water likely existed as Fe hydroxyoxide particles, and the Fe sorbed to particle surfaces due to the oxic conditions caused by pumping. In this paper the term hydroxyoxide includes oxides. Removal of the particles from the water by filtration therefore greatly reduces Fe concentrations in the filtered samples. Other metals likely exist as the aqueous species sorbed to particle surfaces, or as elemental components of particles originating as aquifer solids, and these concentrations

were similarly reduced by filtration (Pohlmann et al., 1994). Herczeg et al. (2004) show that the interactions between soil and ground water and geochemical processes such as aerobic CO₂ production, carbonate mineral dissolution, and sulfide oxidation control the ground-water quality. In many wells the water at depth is in a reducing environment (Pyne, 1994; Fitts, 2002), and thus heavy metals may be present mainly as ions, but these ions can precipitate in the well as the groundwater is mixed with more oxygenated water during sample collection (Pohlmann et al., 1994). This precipitation could cause underestimation of metal concentrations by using dissolved concentrations for the ground-water quality assessment. This underestimation of metal concentrations, such as Fe, Mn, Pb, and As, can be important in protection of well screens and pumps, as well as human health. The iron-oxides can clog pump filters and damage pumps (Pyne, 1994). Fe and Mn Secondary Maximum Concentration Levels (SMCL) are set for aesthetic reasons -- precipitation of hydroxyoxide minerals in sinks, toilets tubs and on clothes (EPA, 1992). The potential for staining porcelain and clothes also will be under estimated if the sample is filtered. Toxic metals are often associated with suspended sediments, clays and Fe hydroxyoxide particles. Once ingested these metals may become bioavailable. Because of the potential association of the metal ions on the sediments, including clay minerals as well as the chemical processes like precipitation, dissolved metal concentrations cannot represent

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the ground-water quality for these situations (Lussier et al., 1999).

The objective of this study was to determine the effect of filtration on metal concentrations in ground water from the Mississippi River Valley Alluvial and Sparta aquifers and any spatial variability in Arkansas. Fe is the focus of this study because it is one of the most abundant and important metal ions in the study site, and because some of the other metal ion concentrations are too low to be investigated, or there are no data for some wells.

2. Site Description

The study site is in the Grand Prairie region of eastern Arkansas (part of the Mississippi River Alluvial Plain), which includes Arkansas, Lonoke, Monroe, Prairie, and Pulaski counties (Figure 1). Agriculture production is dominated by rice, soybeans, cotton, sorghum, and in recent years, aquaculture (catfish and game fish fingerlings), which rely on the ground water. The alluvial aquifer is the most intensively used aquifer in Arkansas. In 1965, withdrawals from alluvial and Sparta aquifer were 4.66 million m³/day, and it increased to 25.32 million m³/day in 2000 (Holland, 2004). The use of the Sparta has increased rapidly (150%) since the mid-1960s until 2000 (McKee et al., 2003). Sands and gravels of the alluvial and Sparta aquifer coarsen northward and with depth (Czarnecki et al., 2003; McKee et al., 2003). The gravel is mostly chert, and overlain by medium- to fine-grained sand. Discontinuous lenses of clay, silt or sandy silt are common throughout the region (Cooper, 2002). Water samples from the shallow (< 10 m) monitoring wells (Pulaski and Monroe counties) were very turbid, however, most other ground water samples were clear. The shallow wells were turbid at all times because of poor development related to larger amounts of clay in these wells. The deeper wells were completed in sand and gravel, and thus clear.

3. Methodology

3.1. Sampling

Forty-one domestic, agricultural irrigation and monitoring wells (52 samples) in the alluvial and Sparta aquifers were used in this project. The wells were sampled during the spring and summer in 2002 and 2003. All wells were sampled near the bottom of the well.

In order to collect samples, submerged pumps and bailers were used. After 2 to 3 hours pumping at a rate of 76 L/min, samples were collected from newly installed deep monitoring wells in both aquifers. The existing shallow monitoring wells were sampled using bailers for purging three well volumes of water and for sample collection. Domestic wells were flushed and three well volumes were purged prior to sampling. After purging three well volumes, pH, conductance and temperature were stable and the representative aquifer water was collected from the monitoring and domestic wells (Rounds and Wilde, 2005). Irrigation wells were in use at the time of collection

(see Table 1), therefore no purging was necessary. The typical well depths for the alluvial aquifer range from 30 to 46 m, and 122 to 168 m for wells in the Sparta aquifer. The samples for the dissolved metals were filtered through a 0.45 µm pore-size membrane immediately after sample collection. The samples for dissolved metals and total metals were collected in clean polypropylene bottles and were preserved with nitric acid to a pH of 2.0. All samples were stored on ice and delivered to the Arkansas Water Resources Water Quality Laboratory at the University of Arkansas, Fayetteville, for analyses.

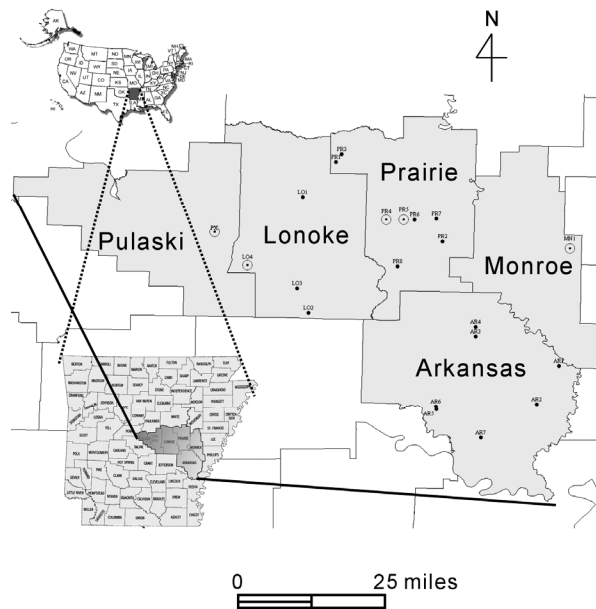


Figure 1. Map of research sites in Arkansas, Lonoke, Monroe, Prairie, and Pulaski counties (Dots are single monitoring wells, and circled points include several irrigation and/or monitoring wells within a 1 mi. diameter of recently installed monitoring wells).

3.2. Sample Analysis

Samples were analyzed for major and some trace cations (Fe, Mn, Cu, Pb, Zn, Ca, Mg, Na, and K), several anions (alkalinity [HCO₃], SO₄, Cl), total suspended solids (TSS), and turbidity. Trace cations (Fe, Mn, Cu, Pb, Zn, Ca, Mg, Na, and K) were analyzed by inductively coupled plasma atomic emission spectrophotometry (ICP-AES) instrumental analysis method. The alkalinity was analyzed using the acid titration method on raw water samples, and HCO₃ concentration was calculated from alkalinity and pH values. The anions (SO₄, Cl) were analyzed through ion-exchange chromatography (IC/MS) instrumental analysis method. TSS was analyzed by using the drying oven method. The turbidity, pH, and temperature were analyzed by meters in the field or laboratory. All analytical methods followed Standard Methods for Examination of Water and Wastewater (Clesceri et al., 1999), and EPA Analytical Method (EPA, 1992). The differences between dissolved and acid-extractable cation concentrations were assessed by paired

Table 1. Specifications for Wells Used in this Study

Well Type	Well Diameter (cm)	Number of wells	Well Depth (m)		Sampling Method
			Alluvial	Sparta	
Monitoring Well	5	7	30 – 46	122 – 168	Bailer (Sampling after flushing)
	10	9	30 – 46	122 – 168	Submerged pump (Sampling after 2 to 3 hours pumping with 76 L/min pumping rate for newly installed wells)
Irrigation Well	40	19	30 – 46	122 – 168	On-site-Installed Submerged pump (Sampling in use)
Domestic Well	20	6	30 – 46	122 – 168	Submerged pump (Sampling after flushing)

Table 2. Comparison of Dissolved and Acid-Extractable Metal Concentrations

Species	Acid-extractable (mg/L)			Dissolved (mg/L)			P	Number of samples	R _{diff}
	Mean	±	S.D.	Mean	±	S.D.			
Ca	72.053	±	43.763	70.892	±	41.986	0.044	28	1.611
Cu	0.014	±	0.044	0.005	±	0.004	0.120	33	65.539
Fe	13.233	±	19.400	5.336	±	7.167	0.003	52	59.678
Pb	0.010	±	0.020	0.001	±	0.003	0.014	33	85.127
Mg	17.616	±	10.492	17.564	±	10.193	0.362	28	0.298
Mn	0.768	±	1.026	0.285	±	0.383	0.001	52	62.852
K	2.846	±	1.264	2.855	±	1.225	0.411	28	-0.339
Na	41.616	±	37.764	40.524	±	35.378	0.060	28	2.625
Zn	0.019	±	0.048	0.018	±	0.043	0.441	28	3.933

* S.D. is standard deviation; P is probability for the paired student-T test comparing dissolved and acid-extractable metal concentrations; R_{diff} is difference ratio (see text for equation).

student-T test. Triplicate samples were collected from some of the Pulaski County wells and the student-T test was applied to determine the difference in cation concentrations. The sample pre-treatment methodology followed EPA Analytical Methods, Method 200.15 (EPA, 1992), for the total recoverable metals in ground water with the exception that samples were not heated. That is, the acid-extractable sample pre-treatment for this project consisted of only the addition of the nitric and hydrochloric acids prior to analyses.

4. Results and Discussion

4.1. Comparison of Dissolved and Acid-Extractable Concentrations

Table 2 compares dissolved and acid-extractable sample analyses. Although Ca, Mg and Na dissolved concentrations are relatively high (5 to 150 mg/L), the dissolved cation concentrations are similar to the data for other alluvial aquifer studies (Aremu, 2002; Elbaz-Poulichet et al., 2002; Kresse et

al., 2002). The geochemical environment of the aquifers is such that high dissolved Fe concentrations occur at depth, likely as a result of decomposition of organic matter that produces lower Eh values, i.e., the water is more reducing (Steele et al., 2003).

The difference between dissolved and acid-extractable concentrations can be represented by difference ratio, calculated as:

$$R_{diff} = \frac{(C_{ae} - C_d)}{C_{ae}} \times 100$$

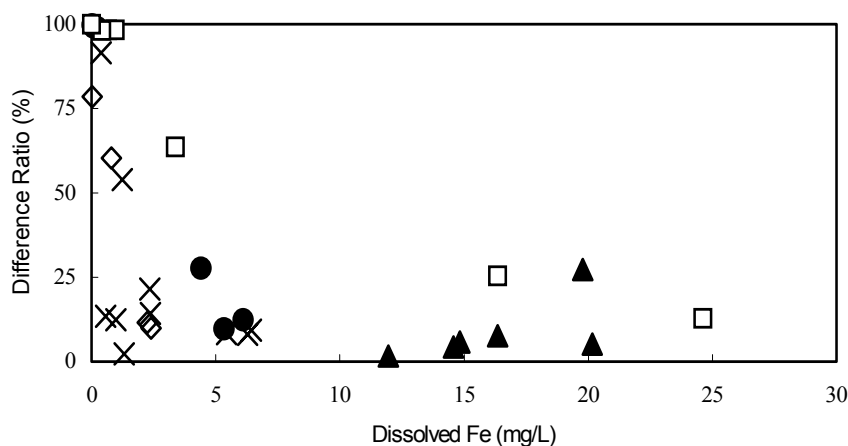
where R_{diff} is the difference ratio, C_{ae} is the acid-extractable concentration in mg/L, and C_d is the dissolved concentration in mg/L.

The paired student-T test indicates that, generally, the acid-extractable samples have higher concentrations of Ca, Fe, Mn and Pb than dissolved concentrations (confidence level >

Table 3. Comparison of Dissolved and Acid-Extractable Metal Concentrations by County

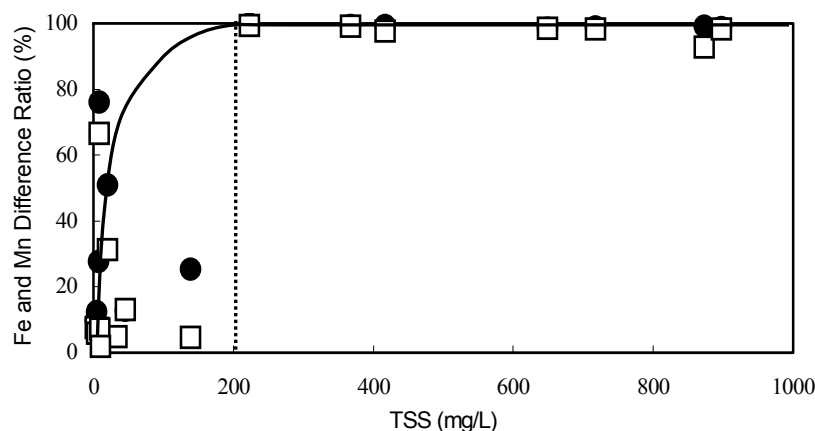
County	Species	Acid-extractable (mg/L)			Dissolved (mg/L)			P	Number of samples	R _{diff}
		Mean	±	S.D.	Mean	±	S.D.			
Arkansas	Ca	62.878	±	44.214	60.479	±	42.394	0.013	6	3.816
	Cu	0.053	±	0.101	0.001	±	0.003	0.132	6	97.484
	Fe	1.249	±	1.292	0.940	±	1.116	0.080	6	24.780
	Pb	0.005	±	0.005	0.004	±	0.003	0.454	6	3.704
	Mg	18.197	±	13.417	17.727	±	13.032	0.016	6	2.587
	Mn	0.145	±	0.102	0.126	±	0.115	0.180	6	13.018
	K	3.240	±	1.334	3.210	±	1.299	0.129	6	0.926
	Na	61.533	±	60.693	60.310	±	59.349	0.042	6	1.988
Monroe - Highly Turbid*	Zn	0.075	±	0.085	0.056	±	0.087	0.181	6	26.106
	Cu	0.007	±	0.009	0.008	±	0.001	0.385	8	-15.094
	Fe	6.961	±	6.455	2.038	±	2.724	0.046	8	70.717
	Pb	< 0.06		-	< 0.06		-	-	-	-
Pulaski - Highly Turbid*	Mn	0.946	±	0.671	0.545	±	0.743	0.027	8	42.393
	Cu	< 0.03		-	< 0.03		-	-	-	-
	Fe	28.407	±	28.458	6.647	±	9.037	0.007	16	76.601
	Pb	0.014	±	0.028	0.001	±	0.003	0.032	16	95.652
Prairie	Mn	1.589	±	1.417	0.242	±	0.306	0.002	16	84.782
	Ca	79.967	±	50.421	78.302	±	48.614	0.059	15	2.083
	Cu	< 0.03		-	< 0.03		-	-	-	-
	Fe	3.299	±	2.845	2.304	±	2.137	0.025	15	30.161
	Pb	< 0.06		-	< 0.06		-	-	-	-
	Mg	18.598	±	11.348	18.500	±	11.131	0.328	15	0.527
	Mn	0.186	±	0.265	0.177	±	0.244	0.097	15	4.485
	K	3.025	±	1.393	3.035	±	1.358	0.447	15	-0.353
	Na	45.731	±	29.837	44.163	±	25.432	0.115	15	3.427
Zn	< 0.09		-	< 0.09		-	-	-	-	
Lonoke	Ca	62.958	±	26.836	63.940	±	24.867	0.210	7	-1.559
	Cu	< 0.03		-	< 0.03		-	-	-	-
	Fe	17.280	±	5.454	16.374	±	2.922	0.270	7	5.243
	Pb	< 0.06		-	< 0.06		-	-	-	-
	Mg	15.014	±	5.850	15.417	±	5.416	0.101	7	-2.685
	Mn	0.470	±	0.206	0.456	±	0.183	0.112	7	3.069
	K	2.124	±	0.582	2.166	±	0.529	0.117	7	-1.950
	Na	15.727	±	7.043	15.764	±	6.926	0.397	7	-0.236
Zn	< 0.09		-	< 0.09		-	-	-	-	

* There are no data for dissolved Ca, Mg, K, Na, and Zn concentrations; S.D. is standard deviation; P is probability for the paired student-T test comparing dissolved and acid-extractable metal concentrations; All “< values” are for the practical quantitation limit; R_{diff} is difference ratio (see text for equation).



Notes: ● = Monroe County - highly turbid sample, □ = Pulaski County - highly turbid sample, ▲ = Lonoke County, ◇ = Arkansas County, and X = Prairie County ground-water samples; the difference ratio is calculated by the equation $R_{diff} = (C_{ae} - C_d) / C_{ae} \times 100$, where R_{diff} is difference ratio, C_{ae} is acid-extractable concentration in mg/L, and C_d is dissolved concentration in mg/L.

Figure 2. Difference ratio for Fe versus dissolved concentration of Fe.



Notes: ● = Fe and □ = Mn; Solid line is the trend and dotted line divides high (> 200 mg/L) and low TSS; the difference ratio is calculated by equation $R_{diff} = (C_{ae} - C_d) / C_{ae} \times 100$, where R_{diff} is difference ratio, C_{ae} is acid-extractable concentration (mg/L), and C_d is dissolved concentration (mg/L).

Figure 3. The difference ratios versus TSS for Monroe and Prairie counties.

Table 4. Comparison of Dissolved and Acid-extractable Metal Concentrations for Triplicate Field Samples from Wells in the Pulaski County

Species	Wells	Acid-extractable (mg/L)		Dissolved (mg/L)		P	R_{diff}
		Mean ±	S.D.	Mean ±	S.D.		
Fe	X	66.39 ±	53.70	0.94 ±	0.60	0.05	98.58
	Z	23.50 ±	6.06	0.41 ±	0.09	0.05	98.24
Mn	X	3.22 ±	2.59	0.05 ±	0.02	0.001	98.57
	Z	1.60 ±	0.37	0.02 ±	0.001	0.001	98.92

* S. D. is standard deviation; P is probability for the student-T test comparing dissolved and acid-extractable metal concentrations; R_{diff} is difference ratio (see text for equation).

95%). The Mg, K and Zn do not have significant differences (the confidence level > 65%) between the dissolved and the acid-extractable concentrations. Although differences in Na dissolved and acid-extractable concentrations are significant (the confidence level > 90%), the difference ratio is small ($R_{\text{diff}} < 3\%$). The Cu has a large difference ratio ($R_{\text{diff}} > 65\%$) but a low confidence level (the confidence level < 88%). The differences are interpreted to be caused primarily by precipitation of Fe and the other transition metals and cation exchange of Ca, Mg, Na and K on clay mineral surfaces (Table 2).

Spatial variation of dissolved Fe is shown by the differences in concentrations for well water by county (Table 3). Lonoke County has relatively low difference ratios for Fe and Mn, whereas Pulaski County, where the ground water is from shallow depth and is highly turbid, has relatively high Fe and Mn difference ratios and significant differences between dissolved and acid extractable concentrations.

In Pulaski County, triplicate samples were collected from some wells to determine the analytical variations due to sample collection. The analytical results are presented in Table 4, which includes difference ratio and student-T test results. The probability values from student-T test indicate that there are significant differences (the confidence level > 95%) between the dissolved and acid-extractable Fe and Mn concentrations. Because the suspended solids can be composed of Fe and Mn hydroxyoxides and may sorb dissolved metal ions, the difference ratios between dissolved and acid-extractable metals can be quite large (> 98%) for the shallow monitoring wells. Although, two shallow wells are separated by less than 100 m, mean acid-extractable Fe and Mn concentrations for these two wells differ by 42.89 and 1.62 mg/L resulting in large difference ratios of 64.6 and 50.3% respectively.

4.2. Spatial Distributions of Fe Concentrations

Table 3 and the plot of dissolved Fe concentration versus R_{diff} (Figure 2) by county reveal spatial variability of Fe. Other metal ions do not have significant spatial distributions. Monroe, Prairie, and Arkansas counties have relatively low dissolved Fe concentrations (< 10 mg/L) and large variations in R_{diff} (2.4 to 99.7%). Lonoke County has relatively high Fe concentration (> 12 mg/L) and small variations in R_{diff} (2 to 27%), whereas Pulaski County has relatively larger variations of dissolved Fe concentration (0.4 to 25 mg/L) and relatively high R_{diff} (> 50%). These observations indicate that the R_{diff} is related to spatial variability of lithology, ground-water flow, and/or geochemical processes. It is hypothesized that more homogeneous distributions of minerals and organic matter yields less variation of the concentrations in Lonoke County.

The lithology of the research area is Holocene alluvium (parts of Pulaski and Prairie counties), and Pleistocene valley trains (parts of Monroe and Arkansas counties). A complex of these two geological units is present in parts of Lonoke, Prairie, and Arkansas counties. The Pleistocene valley trains generally have coarser grains than the Holocene alluvium, whereas the Holocene alluvium has a thicker clay and silt surficial unit. Kleiss et al. (2000) noted that SO_4 , pH, and Cl

were present in higher values in water from wells in the Pleistocene valley trains, whereas Fe, NH_4 , F, K, HCO_3 , Mg, Ca, and dissolved solids were present in higher concentrations in water from wells in the Holocene alluvium. The spatial distribution of Fe concentrations in this study is consistent with the interpretations of Kleiss et al. (2000).

The part of Pulaski County covered by Holocene alluvium has higher Fe concentration and TSS, but the other part of Pulaski County covered by Pleistocene valley trains and the complex unit has lower Fe concentrations, resulting in large spatial variation of the Fe concentrations in the county. Most of Monroe County is covered by Pleistocene valley trains which have coarser grains allowing more ground water flow. The faster flow rate decreases the retention time of ground water in the aquifer which reduces the sediment-water interaction. This decreased sediment-water interaction yields lower ion concentrations. Slower ground water flow in the Holocene alluvium increases water interaction with lenses of clay, silt and organic matter. Organic matter produces a reducing environment that increases the solubility of heavy metals (Kleiss et al., 2000).

4.3. TSS and Metal Concentration Variations

Figure 3 shows a positive logarithmic relationship between TSS and the R_{diff} for Fe and Mn, i.e., the larger the TSS concentrations the greater the differences of dissolved and acid-extractable concentrations. Figure 3 also indicates that if TSS concentrations are greater than 200 mg/L, then most of metal exists in the acid-extractable form.

There are large variations in turbidity (95 - 320 NTU) and TSS concentration (368 - 4562 mg/L) in the shallow wells located in Pulaski and Monroe counties. Figure 4 indicates that turbidity and TSS have a positive relationship for samples with less than 1000 mg/L TSS. It is hypothesized that high TSS concentrations (> 1000 mg/L) include coarser grains that do not contribute to the turbidity measurement as the coarser grains rapidly settle out of the water in the sample cell used to determine turbidity, yielding values that are too low. There is no relationship between turbidity and the R_{diff} , however, TSS concentrations and the difference ratios have a logarithmic relationship. These relationships indicate that a large amount of Fe and Mn concentrations are related to TSS concentrations (Figure 3).

4.4. Assessment of Water Quality

Ground water samples, other than from Monroe and Pulaski counties, have low TSS concentrations. These shallow monitoring wells were completed in sediment enriched in clay and silt compared to the deeper wells completed in sand and gravel. The large differences between the dissolved and the acid-extractable metal concentrations are attributed to dissolution of suspended Fe and Mn hydroxyoxides and/or cation exchange on suspended sediments. However, Figure 5 indicates that there are differences between dissolved and acid-extractable Fe concentrations in the ground water even at low TSS concentrations. There is no significant trend, but the

plot indicates that differences greater than 2 mg/L can result in appreciable precipitation of Fe hydroxyoxides which can clog well screens and pumps, and cause aesthetic problems, e.g., staining, taste and color. Mn behaves similarly as Fe. Because of these problems, U.S. EPA (1992) has set SMCLs of 0.3 mg/L for dissolved Fe, and 0.05 mg/L for dissolved Mn.

Most highly turbid wells and some low turbid wells have high acid-extractable Fe concentration (> 5 mg/L), but the dissolved Fe concentration is low (< 0.3 mg/L). This means that the difference between dissolved and acid-extractable concentrations can be related to precipitation of Fe, and that acid-extractable concentrations indicate the potential amount of metal that may result in problems. Although in some areas, like Prairie County, where the dissolved Fe concentration may be lower than the SMCL; it is therefore necessary to use the acid-extractable concentrations for proper assessment of the ground-water quality. About 88% of unfiltered samples exceed SMCL for Fe, whereas about 77% of filtered samples exceed SMCL for Fe. This indicates the underestimation of filtered samples. Mn also has significant differences between dissolved and acid-extractable concentrations with more than 75% of samples exceeding the SMCL concentration of 50 μ g/L for dissolved Mn (U.S. EPA, 1992). The R_{diff} is less than 20% for Mn concentrations in Arkansas, Lonoke, and Prairie counties that have low TSS concentrations (< 30 mg/L). The Cu, Pb and Zn have lower concentrations, resulting in lower confidence levels for differences between dissolved and acid-extractable concentrations.

Champ et al. (1979) showed that the ground water oxidation-reduction condition was influenced by the variation of lithological differences in the aquifer. Sorbed As and other toxic metals including Pb to Fe hydroxyoxides might be released by oxidation-reduction conditions and microbiological reactions. These could result in ground water contamination and health problems (Kumaresan and Riyazuddin, 2001). The observations of this project indicate that sample filtration alone is not adequate to evaluate the impact of ground-water quality.

The conceptual model for Fe concentrations in ground water is that the reducing conditions within the aquifer allow dissolution of large quantities of the Fe and other transition metals. During pumping, the water becomes oxygenated and significant amounts of these metals are precipitated. Thus, the amount of Fe in solution is not representative of the Fe within most of the aquifer. The Fe concentration of the aquifer water is underestimated and not a useful predictor of Fe hydroxyoxide clogging problems with well screens or pumps.

4.5. Cation Exchange and Ion Balances

In general, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , SO_4^{2-} , and Cl^- are the major ions, which control the ion balance in the ground water, and most ground water is of the Ca- HCO_3 type (Fitts, 2002). Calcite, and to some extent gypsum are the sources for Ca, and Mg, and calcite is the source for HCO_3^- . Na and K are

derived mainly from halite. If Ca+Mg and Na+K cation exchange occurs in Ca- HCO_3 type water, it is expected that the (Na + K)/Cl ratio will increase and the (Ca + Mg - SO_4)/ HCO_3 ratio will decrease because the +2 cations will replace the +1 cations on the exchange sites of the clays (Figure 6). The SO_4 represents the Ca from gypsum which must be subtracted from the total Ca concentration for the "carbonate mineral" ratio, (Ca + Mg - SO_4)/ HCO_3 , to be correctly interpreted.

Figure 6 shows that both high and low TSS samples exhibit Ca+Mg and Na+K cation exchange, but there is imbalance of ions for high TSS samples because the (Ca + Mg - SO_4)/ HCO_3 ratios increase. As previously described, the alkalinity which was used to calculate the HCO_3^- level was measured for unfiltered samples without any preservative; whereas metals were analyzed from acidified unfiltered and filtered samples. For unfiltered acidified samples the acid preservative, nitric acid, will release the cations including Ca, Mg, Na and K from the suspended sediments, which means the measured cation milli-equivalent concentrations, will be larger than observed alkalinity milli-equivalent concentrations.

If major cations and anions are balanced, the (Ca + Mg + K + Na - Cl - SO_4 - HCO_3) milli-equivalent value should be zero. However, Figure 7 shows that high TSS concentration (> 250 mg/L) samples are not balanced and the (Ca + Mg + K + Na - Cl - SO_4 - HCO_3) milli-equivalent values increase with the increases of the TSS concentrations. These relationships indicate that higher TSS concentrations will increase the imbalance between total anion and total cation milli-equivalents. Figure 8 shows that higher TSS concentrations (> 900 mg/L) correspond with higher (Ca + Mg)/(Na + K) ratios in milli-equivalent (see trend line in Figure 8), which indicates higher extracted Ca + Mg concentrations. From these observations, we can conclude that cation exchange is occurring between ground water and suspended clay particles. One outlier point on Figure 8 has highest TSS concentrations and is probably an error that was related to sample collection, sample treatment or analysis.

5. Conclusions

Acid-extractable Ca, Fe, Mn, and Pb concentrations are statistically higher than dissolved concentrations. The Monroe, Prairie as well as Arkansas counties have relatively lower Fe concentrations and large variations in the R_{diff} , but the Lonoke County has relatively high Fe concentrations and small variations in R_{diff} . The Pulaski County has a relatively high R_{diff} and larger variations in Fe concentration due to variable lithologies, ground water flow and/or geochemical processes. The R_{diff} for Fe increases with increasing TSS because the Fe ion can be precipitated forming particles or sorbed on suspended sediments. These forms of Fe can be removed from the samples through filtration required for measuring dissolved metal concentrations.

The conceptual model (Figure 9) for the geochemistry of these aquifers is that reducing conditions within the aquifer allows for the dissolution of large quantities of Fe and other

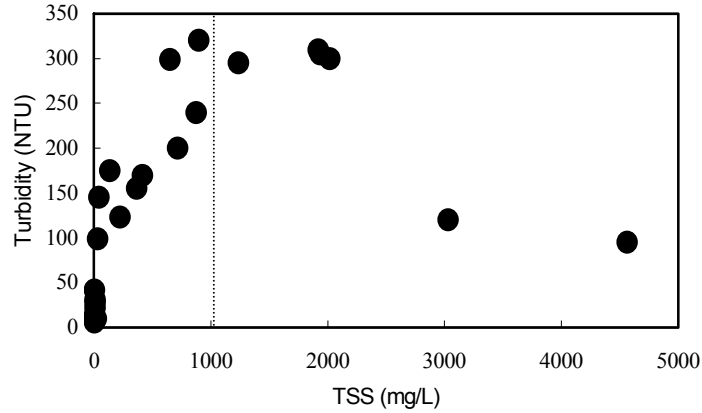
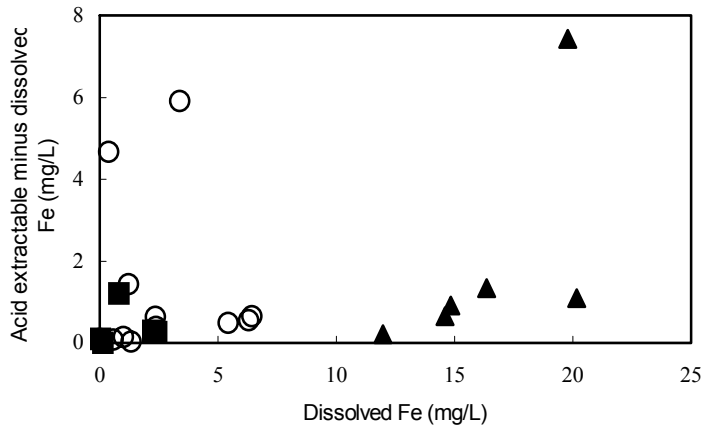
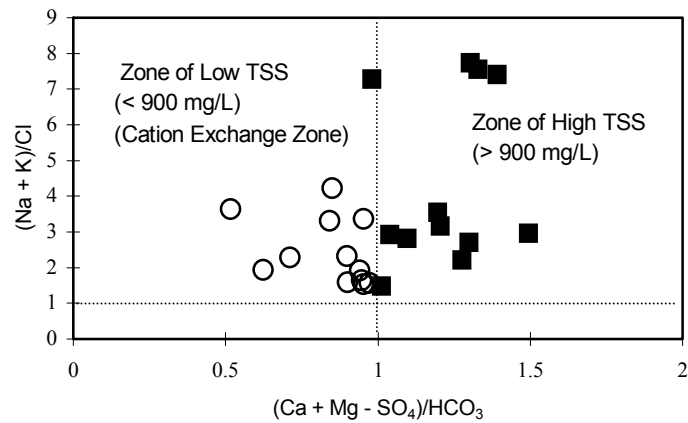


Figure 4. Turbidity versus TSS (the dotted line shows the critical point of change in the relationship between TSS and turbidity).



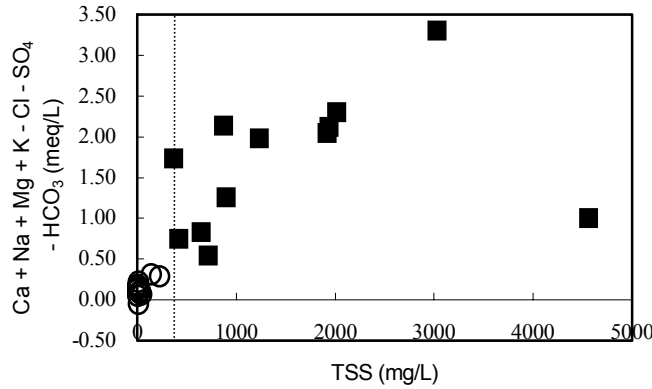
Notes: ■ = Arkansas County, ▲ = Lonoke County, and O = Prairie County.

Figure 5. Difference between dissolved and acid-extractable Fe concentrations versus dissolved Fe concentrations for low TSS (< 30 mg/L) samples.



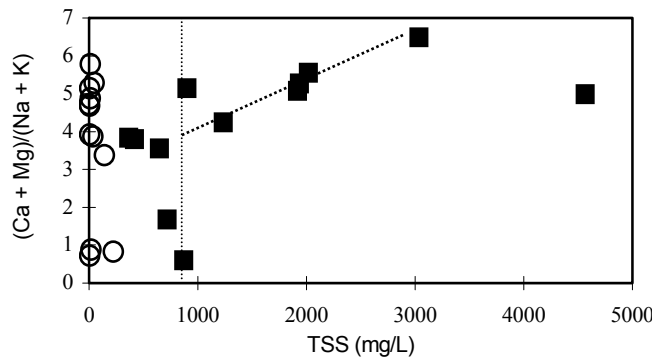
Notes: Ratios are based on acid extractable meq/L concentrations; O = low TSS samples, and ■ = high TSS samples from Monroe and Pulaski counties wells; dotted lines are the theoretical equivalent lines for these ratios.

Figure 6. The ratio of (Na + K)/Cl versus the (Ca + Mg - SO₄)/HCO₃ ratio.



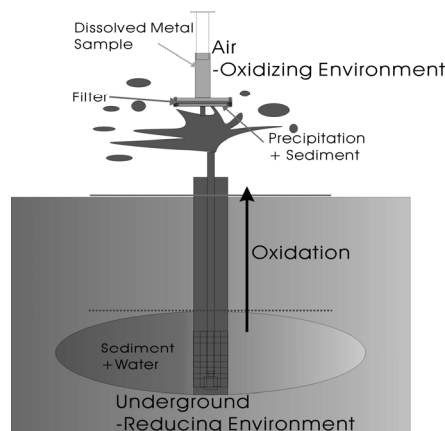
Notes: O = low TSS samples and ■ = high TSS samples from Monroe and Pulaski counties wells; dotted line divides high TSS (> 200 mg/L) and low TSS concentration.

Figure 7. Acid extractable (Ca + Mg + K + Na - Cl - SO₄ - HCO₃) versus TSS.



Notes: O = low TSS samples (< 900 mg/L) and ■ = high TSS samples from Monroe and Pulaski counties wells; ratios are based on acid-extractable cation concentrations (meq/L).

Figure 8. The (Ca + Mg)/(Na + K) ratio versus TSS.



Notes: Reducing condition at depth allows dissolved metal concentrations to increase by dissolution of hydroxyoxide minerals; however, oxidation caused by pumping and sample filtration results in precipitation of the metals, resulting in underestimation of dissolved metal concentrations in aquifer water.

Figure 9. Conceptual model of the effect of filtration on metal concentrations.

transition metals but during pumping, the water will become oxygenated and significant amounts of these metals will be precipitated. Thus, the amount of Fe in solution at the well head is not representative of Fe within the aquifer. Furthermore, sorption of metals on Fe and Mn hydroxyoxide sediment coatings effectively removes some metals from solution. Filtration used to measure the dissolved metal concentration causes the Fe and other heavy metal concentrations of the aquifer to be underestimated and not to be a useful predictor of Fe hydroxyoxide problems with well screens or pumps. Also toxic effects of metals (e.g., Pb) may be underestimated because of the bioavailability of the metal from suspended sediments (e.g., Fe hydroxyoxide). The high concentrations of H⁺ from the nitric acid added as a preservative for metal analyses can cause desorption of Ca, Mg, Na and K from clay sediment. These and other ions may be more environmentally available from clays than indicated by the dissolved concentrations.

Despite the recommendations by the Standard Methods for Examination of Water and Wastewater (Clesceri et al., 1999) and the U.S. EPA Analytical Methods (EPA, 1994) to filter ground-water samples for water-quality investigations, results of this study show that for several cations, especially the Fe, it may be more important to utilize unfiltered acidified samples. The unfiltered samples may better represent environmentally available cation concentrations associated with Fe hydroxyoxide coatings on sediment, sorption on the coatings and/or cation exchange on clays.

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