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Comparison of Dissolved and Acid-Extractable Metal Concentrations in Groundwater, Eastern Arkansas

Burmshik Kim
University of Arkansas, Fayetteville

Kenneth F. Steele
University of Arkansas, Fayetteville

Todd Fugitt
Arkansas Soil and Water Conservation Commission

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Burmshik Kim* and **Kenneth F. Steele**
Environmental Dynamics Program
113 Ozark Hall
University of Arkansas
Fayetteville, AR72701

Todd Fugitt
Arkansas Soil and Water Conservation Commission
101 East Capitol, Suite 350
Little Rock, AR 72201

*Corresponding Author

Standard Methods for the Examination of Water and Wastewater (Clescerl et al., 1999) and Environmental Protection Agency Analytical Methods (EPA, 1994) recommend that all water samples should be filtered through a $0.45\mu m$ pore-size membrane immediately after sample collection and acidification of the sample. These recommendations are needed in order to provide the "dissolved" metal concentrations, which are used for most monitoring projects (Lussier et al., 1999). Most domestic water supplies and irrigation waters are not filtered prior to use; thus, the suspended solids concentrations may supply ions that are environmentally available to people, animals and plants (Pohlmann et al., 1994). In many wells, the water at depth is a reducing environment, however Fe may precipitate in the well as it is mixed with more oxygenated water. Filtration of this well water removes the precipitated Fe, resulting in underestimation of the amount of Fe in many aquifers. Iron concentrations can be used to determine the likelihood of iron oxides clogging well screens or damaging pumps, but if the samples are filtered, the Fe concentration in water at depth will be underestimated and the potential damage also underestimated. Iron and Mn maximum concentration levels are set for esthetic reasons– to avoid precipitation in sinks, toilets and tubs. The potential for staining porcelain also may be underestimated if the sample is filtered (Pohlmann et al., 1994). Toxic metals, such as As, Pb, Cr are often associated with suspended solids--clays and iron oxides. Once ingested, metals from these suspended solids may become bioavailable.

The objective of this study was to determine the effect of filtration on metal analyses of groundwater from the Mississippi River Valley Alluvial aquifer (Alluvial aquifer) and the Sparta aquifer. Because of the high concentration of Fe and the importance of precipitated iron oxides, Fe was the focus of the study.

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 (Fig. 1). This area is dominated by agricultural production of rice, soybeans, cotton, milo, and in recent years, aquaculture of catfish and game fish fingerlings. The Alluvial aquifer is the most intensively used aquifer in Arkansas. In the late 1990's, withdrawals from the Alluvial aquifer were 20.1 million m^3/day (Czarnecki et al., 2003), with 1 million m^3/day being withdrawn from Sparta aquifer (McKee et al., 2004). Use of Sparta aquifer has increased rapidly since the mid-1980s. Sands and gravels of the Alluvial and Sparta aquifers coarsen northward and with depth. The gravel is mostly chert and is overlain by medium - to fine - grained sand. Discontinuous lenses of clay, silt or sandy silt occur at many places (Cooper, 2002).

Fifty-two domestic, agriculture, and monitoring wells in the Alluvial and Sparta aquifers were investigated. The well locations are shown in Fig. 1. The wells were sampled during spring and summer 2002 and 2003. All wells were sampled as near to the wellhead as possible through available outlets. Most wells were in use at the time of sample collection. Typical well depths for the alluvial aquifer range from 30 m (98 ft) to 45 m (148 ft), and wells in the Sparta aquifer ranged from 120 m (390 ft) to 170 m (552 ft) in depth. Samples for dissolved metals were filtered through a $0.45\mu m$ pore-size membrane immediately after sample collection. All samples 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 Water Quality Laboratory of the University of Arkansas, Fayetteville. The sample pretreatment methodology followed EPA Analytical Methods Manual, Method 200.15 (EPA, 1994), for total recoverable metals in groundwater with the exception that samples were not heated. That is the acid-extractable sample pre-treatment for this project consists of only the addition of nitric and hydrochloric acids prior to analyses. Samples were analyzed for major and some trace metals (Ca, Mg, Na, K, Fe, Mn, Cu, Pb, and Zn) and total suspended solids. Analytical methods followed Standard Methods for the Examination of Water and Wastewater (Clescerl et al., 1999) i.e. inductively coupled plasma (ICP) instrumental analyses method for metals. The differences between dissolved and acid-extractable concentrations were assessed by the Paired Student-t test.

Calcium, Mg, and Na concentrations are relatively high (Table 1), but similar to data for other alluvial aquifer studies (Aremu et al., 2002; Elbaz-Poulichet et al., 2002; Kresse and Fazio, 2002). The geochemical environment of the aquifers is such that high Fe concentrations occur in these aquifers

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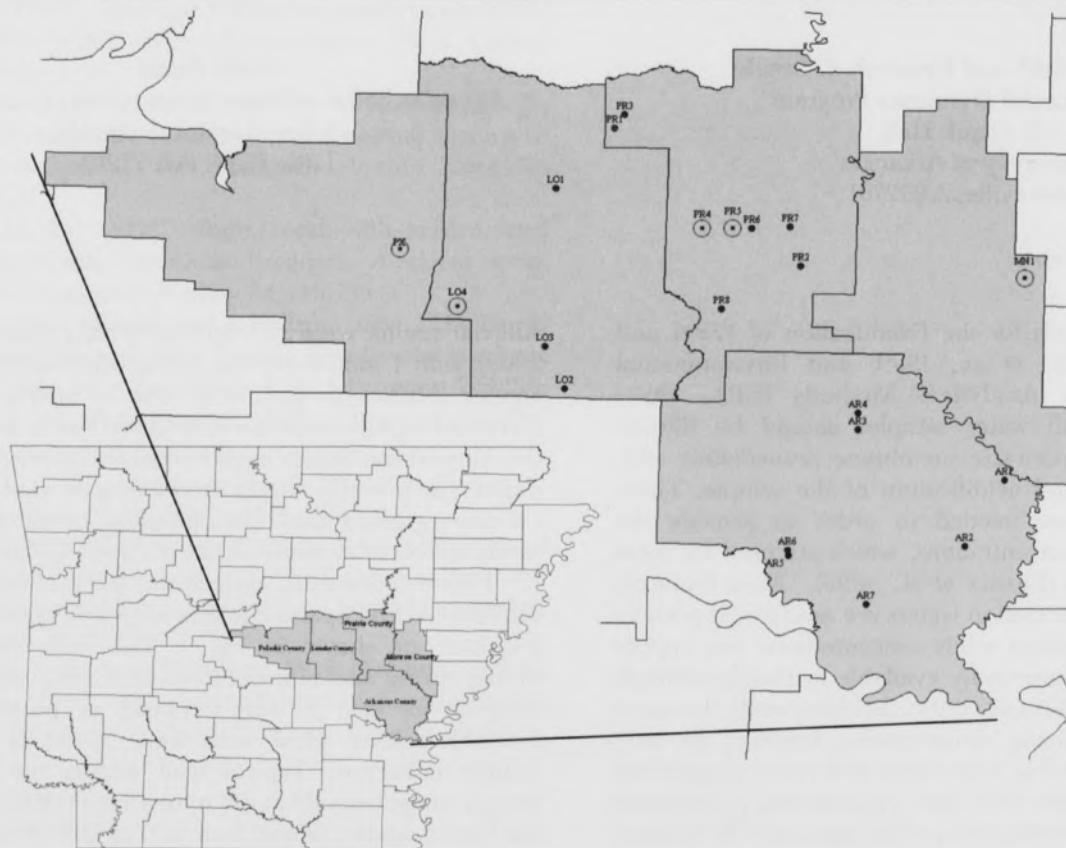

Fig. 1. The map of research site and well locations. Note that around the well named LO4, MN1, PR4, PR5 and PX, several irrigation wells were sampled within 1-mile from the monitoring well. Around LO4 and PR4 each, six wells are sampled. Around PX, seven wells were sampled, and around MN1, six wells were collected.

(Steele et al., 2003). Acid-extractable samples have significantly (P = 0.05) higher concentrations of Fe, Mn, Pb, and Ca than dissolved concentrations (Table 1). Sodium differences were marginally significant at the P = 0.06. Magnesium, K, and Zn were not found to be significantly different significant differences (P > 0.05) between dissolved and acid-extractable concentrations (Table 1).

The difference between dissolved and acid-extractable concentrations can be represented by difference ratios,

calculated by $R_{dff} = \dfrac{(C_{a.e.} - C_d)}{C_{a.e.}} \times 100$

where R_{dff} is the difference ratio, $C_{a.e.}$ is the acid-extractable concentration, and C^d is the dissolved concentration. Higher Fe concentration leads to larger R_{dff} value. The R_{dff} for Fe had a positive relationship with total suspended solids concentrations, i.e., the greater the total suspended solids concentrations, the greater the R_{dff} (Fig. 2).

In most cases the difference ratios are small (< 25%), but in about 30% of samples the difference ratios were quite large, more than 90%. Although there are small difference ratios (< 5%) for Ca, Mg, Na, and K, statistical analyses revealed significant differences for Ca, and Na at the 94% confidence level. The differences are interpreted to be primarily the result of precipitation of Fe and the other transition metals and cation exchange of Ca, Mg, Na, and K with clay. Reducing conditions within the well dissolve large quantities of Fe and other transition metals, but during pumping, the water becomes oxygenated and large amounts of these metals are precipitated. Thus, the amount of Fe in solution at the well head is not representative of Fe within most of the aquifer. Filtration of the precipitated iron oxides causes the Fe concentration of the aquifer to be underestimated and not to be a useful predictor of iron oxide 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 solids (e.g.,

Burmshik Kim, Kenneth F. Steele and Todd Fugitt

Table 1. Comparison of dissolved and acid-extractable metal concentrations, difference ratio, and statistical P value. The P value was calculated by the Paired Student-t test where the hypothesis was that the differences between dissolved and acid-extractable metal concentrations were zero. R_{dff} is difference ratio (see text), n is number of samples and SD is standard deviation.

Species	Acid-extractable (mg/L)			Dissolved (mg/L)			P	n	R_{dff}
	Mean	±	SD	Mean	±	SD			
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

iron oxides). The high concentrations of H^+ from the nitric acid added to preserve dissolved metals can cause desorption of Ca, Mg, Na, and K from clay sediment. More Ca (and other ions) may be more environmentally available than indicated by the dissolved concentrations.

The following conclusions can be drawn from this study: 1) Statistical analyses indicate that acid-extractable Fe, Mn, Cu, Pb, Ca and Na concentrations are higher than dissolved concentrations, 2) the difference ratios for Fe increase with increasing total suspended solids and 3) sometimes it may be more meaningful to use acid-extractable metal concentrations rather than the recommended filtered samples to represent environmentally available concentrations.
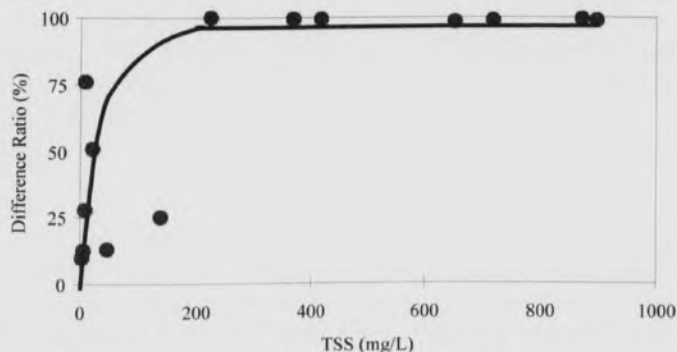
Fig. 2. The difference ratio for dissolved and acid-extractable iron concentrations versus total suspended solids.

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120