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MERCURY CONTENT OF WATERS IN THE MIDCONTINENT REGION

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ABSTRACT

Two major areas of the midcontinent region were investigated for their aqueous mercury concentrations. Sixteen surface water and 17 ground water samples were collected in an eleven county area of N.W. Arkansas, S.W. Missouri and N.E. Oklahoma (Ozark area) and analyzed for total dissolved mercury by the flameless atomic absorption spectrophotometric method. The range (<0.2 to 0.8 ppb), the mean (0.4 ppb) and the median (0.4 ppb) are the same for both ground water and surface water. Values obtained for the Ozark area are slightly greater than those reported for surface water by others (about 0.1 ppb), but are well within the range reported for surface waters (0.1 to 17.0 ppb). The range for 102 ground water samples from the Ouachita Mountain area is <0.1 to 2.3 ppb, the mean 0.3 ppb and the median 0.1 ppb. Thus, the mercury values for this area are similar to those of the Ozark area except for a higher upper range. The mercury mineralization (cinnabar) in the southern part of the Ouachita Mountain area, in part, is the cause of the higher values. Only two samples (2.1 and 2.3 ppb), both from the Ouachita Mountain area, exceed the EPA drinking water limits of 2 ppb mercury in the western Arkansas region.

INTRODUCTION

Eh-pH diagrams for aqueous inorganic mercury under natural surface conditions indicate that the only significantly abundant form of mercury is undissociated metallic mercury which has a solubility of about 25 ppb. In waters with a high chloride concentration the solubility of mercury may be greatly increased by the formation of chloride complexes. In addition, much of the mercury in natural waters occurs as soluble organic complexes such as methylmercury, CH_3Hg^+ or dimethylmercury ($\text{CH}_3)_2\text{Hg}$. Under reducing conditions, mercury may be precipitated as the insoluble sulfide, HgS_2 , lowering mercury concentration in solutions (Hem, 1970). The affinity of mercury for sorption and complexing reactions with suspended particulate material results in the metal being effectively removed from solution (Hinkle and Learned, 1969). Because of these reactions, natural waters generally contain extremely low concentrations of mercury (Wershaw, 1970; Jenne, 1970). Surface waters, except where they have been influenced by special geological conditions or man-made pollution, generally contain less than 0.1 ppb mercury but concentrations can range much higher. Higher concentrations are likely to occur in underground waters because of the longer and more intimate contact with mineral grains and other environmental factors (U.S.G.S., 1970).

GEOLOGIC SETTING

Two areas of the midcontinent region, the Ozark study area and the Ouachita Mountain area, have been investigated to determine background aqueous mercury concentrations. The Ozark study area includes most of the northwestern corner of Arkansas, and small parts of southwestern Missouri and northeastern Oklahoma (Fig. 1). Agriculture and forestry are the major industries of the Ozark area, which is located primarily within the Boston Mountains, and the more gentle relief Springfield and Salem Plateaus. The predominant rocks of this area are limestone, sandstone and shale which are primarily of Mississippian and Pennsylvanian age with only a small amount of Ordovician strata. Sedimentary rocks generally average less than 100 ppb mercury and seldom exceed 200 ppb except for certain organic rich shales (U.S.G.S., 1970). Localized lead and zinc mineralization and several coal deposits in the Ozark area could contain at least 100 ppb of mercury. Based on the mercury content of the

rocks of the area, the background levels of aqueous mercury would be expected to be low.

The Ouachita Mountain area is 135×103 km. The northern part encompasses the core of the Ouachita Mountains and the southern part includes the Athens Plateau and some of the Gulf Coastal Plains (Fig. 2). The area is largely farm or National Forest lands. In the northern part of the Ouachita Mountain area shales, Arkansas Novaculite (chert), and sandstone predominate with only minor limestone. These formations range in age from Cambrian to Carboniferous and are folded and faulted intensely. Manganese mineralization is widespread and major barite deposits occur as a result of replacement or fracture filling. Quartz veins in the area occasionally contain sphalerite (ZnS) and galena (PbS). Mercury should be associated with these sulfide deposits in minute amounts. Cretaceous limestone, gravel, siltstone and sandstone, and Quaternary gravel, sand and silt are predominate in the southern part of the area. Barite, cinnabar (HgS), and antimony mineral districts are also present. Thus, the mercury content of ground water due to the rocks and sediments would be expected to be low, except in the cinnabar mineralized district.

METHODS AND MATERIALS

Thirty-three samples, including 16 surface water and 17 ground water samples, were collected in the Ozark study area during the period from June, 1978 to June, 1979 (Table 1). The distribution of the sample sites is shown in Fig. 1. The samples were collected within a 50 mile (km) radius of Gentry, Arkansas, to serve as background data for further studies concerned with the coal-fired electric plant located there. The distribution of the 102 ground water samples of the Ouachita Mountain area are shown in Fig. 2. Wagner et al., (1980) have reported on the water chemistry of these samples.

Each sample was filtered through a 0.45 micron membrane filter, placed in a clean polyethylene container and acidified with 1:1 nitric acid (3 ml of acid per liter of water). The samples were returned to the laboratory and mercury was determined by atomic absorption spectrophotometry using the flameless method.

All collection and analytical methods were those recommended by EPA (1974). This analytical method measures total dissolved mercury (both organic and inorganic species). The limit of detection of mercury based on the above techniques was 0.1 to 0.2 ppb.

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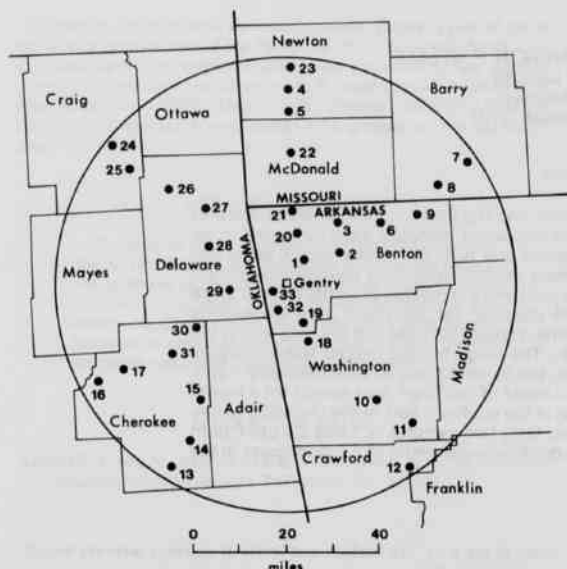


Figure 1. Ground water and stream water sample distribution for the Ozark area. See Table 2 for data.

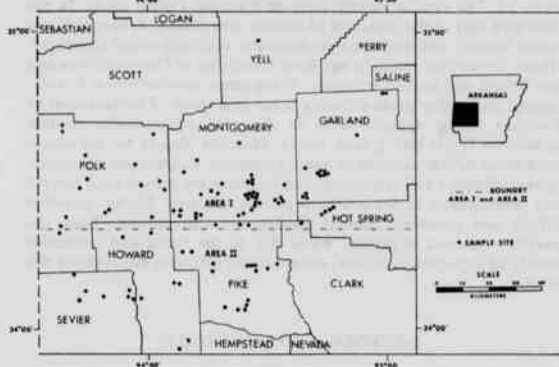


Figure 2. Ground water sample distribution for the Ouachita Mountain area. After Wagner and Steele, 1980.

RESULTS AND CONCLUSIONS

The results of this investigation indicate that the mercury content of waters in the midcontinent region is well below the recommended 2.0 ppb limit set for drinking water by the U.S. Environmental Protection Agency (1976) except for two samples (2.1 and 2.3 ppb) in the Ouachita area. Of the 33 Ozark-area samples, only 6 had concentrations greater than 0.5 ppb mercury. The mean and median values for the groundwater samples were both 0.4 ppb, and the stream water samples had the same values (Table 1). The ranges for the ground water and stream samples were both from less than 0.2 to 0.8 ppb (Table 2). Several of the high values for the Ozark area may be the result of unusual situations or contamination. Sample number 16, a well which had a mercury concentration of 0.8 ppb, had been sub-

jected to regular treatment with chlorine bleach and had been treated the day the sample was collected. Therefore mercuric chloride complexes may have increased the mercury concentration or the bleach may have contaminated the water with mercury because mercury is used in the manufacture of bleach. Another well, sample number 29, had a concentration of 0.7 ppb and contained significant rust. Iron oxide colloids may have sorbed mercury with some having passed through the filter. Stream water sample 22 was collected after a rain from a small stream flowing between a major highway and a railroad track and contained 0.8 ppb mercury.

Although the Ouachita Mountain area has a higher upper range (2.3 ppb) than the Ozark area (0.8 ppb) most of the values of the two areas are similar as indicated by the means and medians (Table 1). Only five samples in the Ouachita Mountain area exceed 1.0 ppb mercury. The generally higher mercury values in the southern part of the Ouachita Mountain area appear to be associated, at least in part, with the mercury mineralization. The four samples collected from the mercury district range from 0.6 to 2.3 ppb mercury, and a greater percentage (42%) of the samples in the southern part of the area exceed 0.5 ppb mercury, than in the northern part (15%). No correlation is readily apparent between mercury concentration and sample areal distribution, well depth, stream flow, rock type or mineralization except for the cinnabar deposits. Finally, all the values fall within the range of normal background concentrations, and are similar to those reported by others (Table 1).

ACKNOWLEDGEMENTS

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Table 1. Comparison of mercury concentrations of ground and surface waters.

Location	Number of Samples	Ground Water		
		Range	Mean	Median
Ozark Area	17	<0.2-0.8	0.4	0.4
Washington Co., Ark. ^a	5	0.1-0.2	0.1	0.1
Ouachita Mtn. Area ^b	102	<0.1-2.3	0.3	0.1
Joplin, MO ^c	37	<0.1	<0.1	<0.1
Front Range, CO ^d	49	-	1.1*	-
		Surface Water		
Ozark Area	16	<0.2-0.8	0.4	0.4
Washington Co., Ark. ^a	2	0.1-0.3	0.2	-
Joplin, MO ^c	15	<0.1	<0.1	<0.1
S. Carolina ^e	27	<0.2-0.3	<0.2	<0.2
Adirondacks, NY ^f	39	<0.5	<0.5	<0.5
U.S.A. ^g	73	<0.1-17.0	0.9	0.1

*geometric mean for uncontaminated samples

^aCoughlin (1971)

^bWagner et al. (1980)

^cProctor et al. (1976)

^dKlusman (1977)

^eAbernathy (1979)

^fBuller (1950)

^gWershaw (1970)

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Table 2. Sample location, type and mercury concentration for the Ozark Area. GW = ground water and SW = stream water.

Sample	State	County	Description	Type	Concentration, ppb
1	Arkansas	Benton	NEA SEL Sec 22, T21R R33W	GW	0.8
2	Arkansas	Benton	NEA SWL Sec 11, T21R R33W	GW	0.8
3	Arkansas	Benton	SWL SWL Sec 3, T22R R33W	GW	0.3
4	Missouri	Newton	SWL SWL Sec 20, T20R R31W	SW	0.7
5	Missouri	Newton	NEA SEL Sec 29, T21R R31W	GW	2.4
6	Arkansas	Benton	NEA SWL Sec 26, T22R R31W	SW	0.5
7	Missouri	Barry	SWL SWL Sec 28, T23R R28W	GW	0.3
8	Missouri	Barry	SWL SWL Sec 22, T24R R28W	SW	0.6
9	Arkansas	Benton	NEA SEL Sec 22, T23R R28W	GW	0.3
10	Arkansas	Washington	SEL SWL Sec 6, T16R R30W	GW	0.3
11	Arkansas	Washington	NEA SWL Sec 9, T12R R29W	GW	0.2
12	Arkansas	Crawford	SWL SEL Sec 13, T14R R29W	SW	0.3
13	Oklahoma	Cherokee	NEA SWL Sec 38, T14R R22E	SW	0.2
14	Oklahoma	Cherokee	SWL SWL Sec 22, T15R R21E	GW	0.4
15	Oklahoma	Cherokee	SWL SWL Sec 27, T17R R21E	SW	0.2
16	Oklahoma	Cherokee	SWL SWL Sec 8, T17R R20E	GW	0.8
17	Oklahoma	Cherokee	SWL SWL Sec 16, T17R R20E	GW	0.4
18	Arkansas	Washington	SWL SWL Sec 6, T18R R37W	GW	0.2
19	Arkansas	Benton	SWL SWL Sec 24, T22R R33W	SW	0.2
20	Arkansas	Benton	NEA SEL Sec 23, T23R R33W	GW	0.2
21	Missouri	McDonald	SWL SWL Sec 19, T26R R31W	SW	0.8
22	Missouri	Newton	SWL SWL Sec 7, T29R R31W	GW	0.2
23	Oklahoma	Craig	SEL SWL Sec 7, T29R R21E	SW	0.4
24	Oklahoma	Craig	SEL SEL Sec 27, T26R R21E	GW	0.2
25	Oklahoma	Delaware	SEL SWL Sec 22, T25R R22E	SW	0.2
26	Oklahoma	Delaware	NEA SWL Sec 19, T23R R24E	GW	0.2
27	Oklahoma	Delaware	SEL SWL Sec 24, T22R R23E	SW	0.2
28	Oklahoma	Delaware	SWL SWL Sec 9, T20R R24E	GW	0.7
29	Oklahoma	Cherokee	SWL SWL Sec 14, T19R R23E	SW	0.2
30	Oklahoma	Cherokee	SEL SWL Sec 7, T18R R23E	GW	0.7
31	Arkansas	Benton	SWL SWL Sec 6, T20R R33W	GW	0.3
32	Arkansas	Benton	SWL SWL Sec 24, T20N R34W	SW	0.2

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