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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, $CH_3\ Hg^+$ or dimethylmercury $(CH_3)_2$ 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 Quarternary 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.

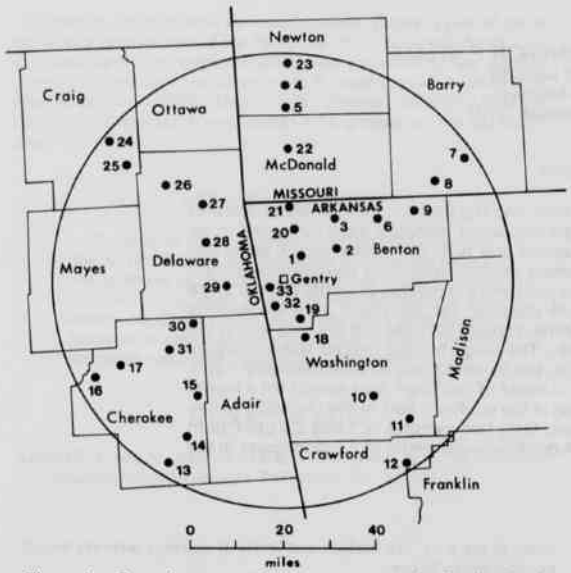

Figure 1. Ground water and stream water sample distribution for the Ozark area. See Table 2 for data.

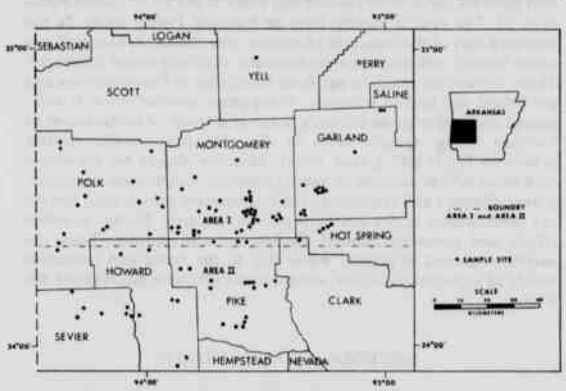

Figure 2. Ground water sample distribution for the Ouachita Mountain area. After Wagner and Steele, 1980.

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 subjected to regular treatment with chlorine bleach and had been treated the day the sample was collected. Therefore mecuric 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).

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

Location	Number of Samples	ppb Range	ppb Mean	ppb Median
Ground Water				
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., AR[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

[a]Coughlin (1971)
[b]Wagner et al. (1980)
[c]Proctor et al. (1976)
[d]Klusman (1977)
[e]Abernathy (1979)
[f]Buller (1950)
[g]Wershaw (1970)

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	NE¼ SE¼, Sec. 23, T21N R33W	GW	0.8
2	Arkansas	Benton	NE¼ SW¼, Sec. 11, T21N R32W	GW	0.6
3	Arkansas	Benton	SW¼ SE¼, Sec. 3, T22N R32W	GW	0.3
4	Missouri	Newton	SW¼ SW¼, Sec. 20, T29N R31W	SW	0.7
5	Missouri	Newton	NE¼ NE¼, Sec. 29, T27N R32W	GW	0.4
6	Arkansas	Benton	NE¼ NW¼, Sec. 26, T22N R31W	SW	0.5
7	Missouri	Barry	NW¼ NW¼, Sec. 25, T25N R28W	GW	0.3
8	Missouri	Barry	SW¼ SW¼, Sec. 22, T24N R28W	SW	0.5
9	Arkansas	Benton	NE¼ SE¼, Sec. 21, T23N R29W	GW	0.3
10	Arkansas	Washington	SE¼ SW¼, Sec. 6, T16N R30W	SW	0.5
11	Arkansas	Washington	NE¼ SW¼, Sec. 3, T15N R29W	GW	<0.2
12	Arkansas	Crawford	SW¼ SE¼, Sec. 13, T14N R29W	SW	0.3
13	Oklahoma	Cherokee	NE¼ SW¼, Sec. 28, T/4N R22E	SW	0.2
14	Oklahoma	Cherokee	NW¼ SW¼, Sec. 22, T15N R23E	GW	0.4
15	Oklahoma	Cherokee	SW¼ NE¼, Sec. 27, T17N R23E	SW	0.2
16	Oklahoma	Cherokee	NW¼ SW¼, Sec. 8, T17N R20E	GW	0.8
17	Oklahoma	Cherokee	NW¼ NE¼, Sec. 16, T17N R20E	SW	0.4
18	Arkansas	Washington	NW¼ NW¼, Sec. 6, T18N R32W	GW	<0.2
19	Arkansas	Benton	NE¼ SW¼, Sec. 7, T19N R32W	SW	0.5
20	Arkansas	Benton	SW¼ NE¼, Sec. 24, T22N R33W	SW	0.2
21	Arkansas	Benton	NE¼ SE¼, Sec. 23, T23N R33W	GW	<0.2
22	Missouri	McDonald	NW¼ SE¼, Sec. 19, T26N R32W	SW	0.8
23	Missouri	Newton	NW¼ SE¼, Sec. 7, T29N R31W	GW	<0.2
24	Oklahoma	Craig	SE¼ NW¼, Sec. 7, T26N R21E	SW	0.4
25	Oklahoma	Craig	SE¼ SE¼, Sec. 27, T26N R21E	GW	0.2
26	Oklahoma	Delaware	SE¼ NW¼, Sec. 22, T25N R22E	SW	0.2
27	Oklahoma	Delaware	NE¼ SW¼, Sec. 19, T23N R24E	GW	<0.2
28	Oklahoma	Delaware	SE¼ NW¼, Sec. 24, T22N R23E	SW	<0.2
29	Oklahoma	Delaware	SW¼ NW¼, Sec. 9, T20N R24E	GW	0.7
30	Oklahoma	Cherokee	NW¼ SE¼, Sec. 14, T19N R23E	SW	<0.2
31	Oklahoma	Cherokee	SE¼ NW¼, Sec. 7, T18N R23E	GW	0.2
32	Arkansas	Benton	NW¼ SE¼, Sec. 6, T20N R33W	GW	0.3
33	Arkansas	Benton	NW¼ SW¼, Sec. 24, T20N R34W	SW	<0.2

LITERATURE CITED

ABERNATHY, A. R. 1979. Heavy metal contamination of surface waters and fish flesh in South Carolina. Clemson Univ., Water Resour. Res. Inst., Rep. No. 74, 119 p.

BULLER, W. 1972. Natural background concentration of mercury in surface water of the Adirondack Region, New York. *In* Geological research 1972: U.S. Geol. Survey Prof. Paper 800-C, p. C223-238.

COUGHLIN, T. L. 1975. Geologic and environmental factors affecting groundwater in the Boone Limestone of northcentral Washington County, Arkansas. M.S. Thesis, University of Arkansas, Fayetteville, 98 p.

ENVIRONMENTAL PROTECTION AGENCY. 1976. Quality criteria for water. U.S. Environmental Protection Agency, Washington, D.C., 256 p.

HEM, J. D. 1970. Chemical behavior of mercury in aqueous media, *In* Mercury in the environment. U.S. Geological Survey Prof. Paper 173, p. 19-24.

HINKLE, M. E. and R. E. LEARNED. 1969. Determination of mercury in natural waters by collection on silver screens. *In* Geological survey research 1969. U.S. Geol. Survey Prof. Paper 650-D, p. D251-254 (1970).

JENNE, E. A. 1970. Atmospheric and fluvial transport of mercury. *In* mercury in the environment. U.S. Geol. Survey Prof. Paper 713, p. 40-45.

KLUSMAN, R. W. and K. W. EDWARDS. 1977. Toxic metals in ground water of the Front Range, Colorado. Ground Water, 15:160-169.

PROCTOR, P. D., G. KISVARSANYI, E. GARRISON and R. R. DILAMARTER. 1976. Heavy metal additions to waters of the Joplin area, Tri-state mining district, Missouri. *In* Csallany, S.C. (ed.) hydrologic problems in karst regions.

U.S. GEOLOGICAL SURVEY. 1970. Mercury in the environment. U.S. Geol. Survey Prof. Paper 713, p. 1-5.

TUREKIAN, K. K. 1972. Chemistry of the earth. Holt, Rinehart and Winston, Inc., New York, 131 p.

WAGNER, G. H., K. F. STEELE and J. B. SHARP. 1980. Chemistry of the spring water of the Ouachita Mountains, excluding Hot Springs, Arkansas. Office of Water Resources Research, University of Arkansas, Fayetteville, in press.

WERSHAW, R. L. 1970. Sources and behavior of mercury in surface waters. *In* Mercury in the environment. U.S. Geol. Survey Prof. Paper 713, p. 29-31.