

Assessment of the Sensitivity of Missouri Reservoirs to Acidification

Glenn D. Wylie and John R. Jones

School of Natural Resources

112 Stephens Hall

University of Missouri-Columbia

Columbia, MO 65211

ABSTRACT

We used water quality information from 103 Missouri reservoirs to assess their sensitivity to acidification from acidic atmospheric deposition. Total alkalinity less than 20 mg/L or a Calcite Saturation Index (CSI) of 1.0 or greater were the criteria to classify reservoirs as sensitive to acidification. Most of the reservoirs (83 of 103) would be considered circumneutral, hard water systems with high acid neutralizing capacity. Thirteen reservoirs were sensitive to acidification based on alkalinity or CSI. Four reservoirs with both low alkalinity and high CSI are located in southeast Missouri in areas of igneous rock outcroppings or chert deposits in limestone formations. These reservoirs are small (<40 ha) and have limited watersheds (<600 ha) and site-specific edaphic factors that likely determined their water chemistry. Site-specific factors also influenced water chemistry of acid-sensitive reservoirs that were located in regions expected to yield highly buffered water. No reservoir classified as acid-sensitive presently seems affected by acidification.

INTRODUCTION

Low pH of precipitation, particularly over the eastern half of the United States, and the potential for adverse effects of acidic deposition on aquatic ecosystems have been the impetus for surveys of various regions of the United States to identify the distribution of acid-sensitive water bodies (Canfield 1983, Linthurst et al. 1986, Schnoor et al. 1986, Summers et al. 1986). In Missouri, yearly pH of rainfall (weighted mean) has declined from 5.6 in 1965 to 4.5 at present with some events as low as 3.7 (NADP 1988). Although rainfall has become more acidic in Missouri, carbonate minerals dominate the geology of most areas (USGS 1967, Stout and Hoffman 1973), thereby imparting high acid neutralizing capacity (ANC) to most surface waters and reducing the effects of acidic deposition on these systems.

Southeast Missouri, however, may contain surface waters vulnerable to acidification because of unique geology and edaphic conditions. In the St. Francois Knob and Basin Region within the Ozark Highlands (Fig. 1) remnants of Precambrian orogeny are exposed at the surface (Collier 1955). Soils in the central portion of this region are derived from granitic bedrock and likely have little ANC. Soils in the Mississippi Lowlands also are low in ANC because they are derived from weathered alluvial deposits of the Mississippi River (Allgood and Persinger 1979). Although Missouri has few natural lakes, reservoirs built within these physiographic provinces may be sensitive to acidification.

The purpose of this paper is to identify reservoirs in Missouri that may be vulnerable to acidification, and add to the information base of other regional surveys for acid-sensitive lakes.

MATERIALS AND METHODS

Data for this report are from 103 reservoirs (Fig. 1) located in all major physiographic provinces of Missouri (after Collier 1955, Stout and Hoffman 1973, Thom and Wilson 1980). Individual reservoirs were sampled 3 to 12 times during summer from 1978 to 1984. Most reservoirs are sampled for various research projects not directed to this report (e.g., Hoyer and Jones 1983). Not all reservoirs were sampled each year, and not all variables were measured for each sample. Additional reservoirs in the St. Francois Knob and Basin area within the Ozark Highlands province were sampled once each in summer 1985 and once in spring 1988 specifically for this report. These reservoirs had not been included in previous surveys but were sampled because of their potential to have low ANC. For all reservoirs in this report, we used the mean of individual samples to represent water chemistry.

At the laboratory, pH was measured with a Radiometer CDM2e meter, a total alkalinity was determined by titration with 0.02 N sulfuric acid to pH 4.5 (APHA 1985). Because the alkalinity endpoint is higher than pH 4.5 for water with low alkalinity, determinations of total alkalinity might be slight overestimates in some cases. Calcium content was determined by titration with a chelating reagent and a color indicator (Hach Chemical Co., 1978) or by atomic absorption (APHA 1985). The calcite saturation index (CSI) was calculated for each lake using the equation from Conroy et al. (1974):

$$\text{CSI} = \text{p}(\text{Ca}^{++}) + \text{p}(\text{ALK}) - \text{pH} + \text{pK},$$

where $\text{p}(x) = -\log(x)$, $(\text{Ca}^{++}) = \text{mol/L}$, $(\text{ALK}) = \text{eq/L}$, and $\text{pK} = +2$. Values of CSI of one or greater or total alkalinity less than 20 mg/L (400 $\mu\text{eq/L}$) generally indicate sensitivity to acidification (Glass and Loucks 1980, Haines 1982). We used these criteria in classifying reservoirs as acid-sensitive.

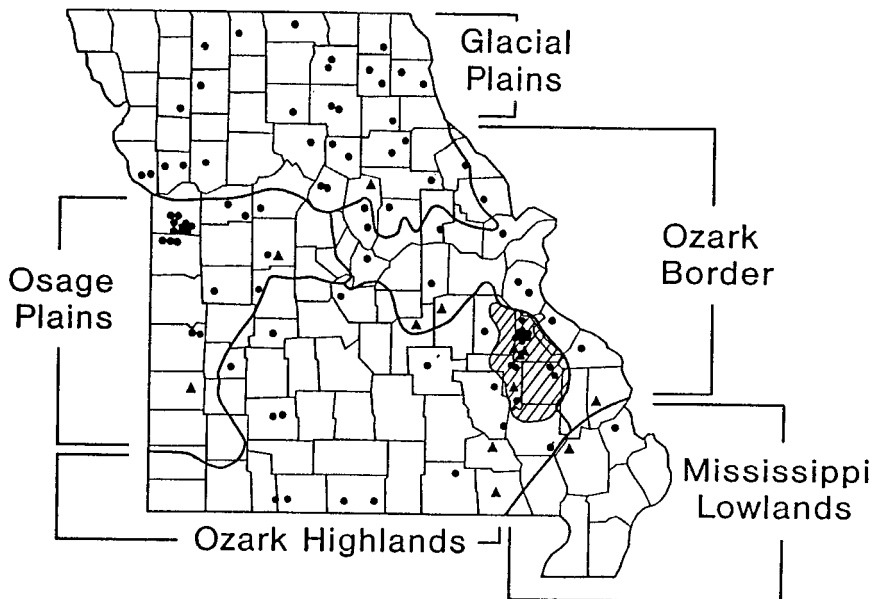


Figure 1. Map of Missouri showing the location of the reservoirs included in this assessment of sensitivity to acidification. The circles indicate reservoirs that are not sensitive and the triangles indicate reservoirs that are considered sensitive to acidification. The hatched area represents the St. Francois Knob and Basin region within the Ozark Highlands.

RESULTS

Most reservoirs in our survey (83 of 103) would be considered circumneutral, hard water systems with high ANC. Among these waterbodies values for pH averaged about 8.0, alkalinity was 70-100 mg/L CaCO₃, calcium was 20-37 mg/L, and CSI was 0.0-0.3 (Table 1). These values are similar to an earlier survey (Jones 1977) and characterize the mineral chemistry of most reservoirs in major physiographic provinces of the state. Reservoirs in the Mississippi Lowlands, however, have higher pH values and lower alkalinity and calcium concentrations than elsewhere (Table 1).

Thirteen reservoirs were judged sensitive to acidification (Table 2), and had CSI values from 1.0-4.0. Four of these reservoirs also had low total alkalinity concentrations of less than 20 mg/L. Two reservoirs with both high CSI and low alkalinity values were Holiday Shores and Crane Lakes located in the St. Francois area. These characteristics together with relatively low specific conductance values (EC, Table 2) suggest that their water chemistry is directly affected by the igneous minerals in their catchments (<600 ha).

The other two lakes judged acid-sensitive by both CSI and alkalinity values were Miller and Ripley Lakes located south of the St. Francois area in the Ozark Highlands (Table 2). They are the most dilute of any reservoirs in our survey with conductivities from 35-41 uS/cm. Both lakes are small (<15 ha) and have limited watersheds (<150 ha), and their water chemistry is likely influenced by local chert outcrops associated with the carbonate formations in this region (USGS 1967). Anion composition of these reservoirs provides additional evidence that non-carbonate minerals influence their water chemistry: the alkalinity complex accounted for 27% of the negative equivalents in Miller Lake and 60% in Ripley Lake. Typically for reservoirs in the Ozark Highlands province, alkalinity accounts for more than 80% of the anions.

Miller Lake is noteworthy because it had the highest mean CSI (4.0), lowest alkalinity (5 mg/L), and lowest pH (6.1) of any reservoir in this survey (Table 2). It is the only reservoir of those classified as acid-sensitive where individual pH values were consistently below neutrality. At present, however, this lake supports a viable fishery (R. Legler, personal communication) and shows no problem with the biota because of relatively low pH and ANC.

In contrast, Lake Girardeau in the Ozark Border province had relatively low alkalinity (28 mg/L) in conjunction with a relatively high pH (8.3) (Table 2). Algal chlorophyll during summer was greater than 35 ug/L (unpublished data, University of Missouri), making it likely that photosynthetic uptake of carbon dioxide elevated the pH of this poorly-buffered system. Pool 1, a reservoir in the Mississippi Lowlands with similarly low alkalinity, has demonstrated large (nearly three unit) diel shifts in pH caused by photosynthesis and respiration (Wylie and Jones 1987).

Reservoirs on the Glacial Plains (n=1), Osage Plains (n=2), St. Francois area (n=2) and Ozark Border (n=3) were judged acid-sensitive based on CSI but not alkalinity values (Table 2). Specific conductance values of these lakes ranged from 61-134 uS/cm (Table 2), and were lower than others in this survey (Table 1). Many of these waterbodies are located in regions where dolomite is common (Collier 1955); thus, magnesium carbonate would be an important component of their buffering chemistry and would not be reflected in the CSI. In addition, lakes located in the Glacial Plains and Osage Plains may be influenced by coal and shale deposits in those regions (USGS 1967).

Table 1. Statistical summary of some limnological variables by physiographic region for Missouri Reservoirs based on mean values of individual summers.

Measurement	Mean	Median	Range	N
Glacial Plains				
pH	8.0	8.1	7.2 - 8.4	32
Alkalinity (mg/L)	75.0	74.0	33 - 110	31
Calcium (mg/L)	28.0	28.0	12 - 43	26
CSI	0.1	0.1	-0.6 - +1.1	26
EC (uS/cm @ 25°C)	208.0	191.0	97 - 328	31
Osage Plains				
pH	7.8	7.8	7.2 - 8.3	22
Alkalinity (mg/L)	80.0	80.0	42 - 107	21
Calcium (mg/L)	34.0	35.0	14 - 84	17
CSI	0.2	-0.1	-0.5 - +1.2	17
EC (uS/cm @ 25°C)	255.0	240.0	128 - 630	21
Ozark Border				
pH	8.1	8.2	7.5 - 8.6	14
Alkalinity	77.0	86.0	27 - 127	14
Calcium (mg/L)	23.0	26.0	9 - 33	12
CSI	0.1	0.0	-1.0 - +1.3	12
EC (uS/cm @ 25°C)	197.0	208.0	71 - 347	14
Ozark Highlands				
pH	8.0	8.1	6.2 - 8.7	25
Alkalinity (mg/L)	98.0	97.0	6 - 186	24
Calcium (mg/L)	27.0	27.0	4 - 40	21
CSI	0.0	-0.4	-0.8 - +4.0	21
EC (uS/cm @ 25°C)	210.0	226.0	35 - 306	24
St. Francois Knob and Basin*				
pH	8.0	7.9	7.4 - 8.6	9
Alkalinity (mg/L)	69.0	62.0	13 - 132	9
Calcium (mg/L)	20.0	18.0	6 - 40	9
CSI	0.3	0.2	-0.7 - +2.1	9
EC (uS/cm @ 25°C)	132.0	125.0	50 - 315	9
Mississippi Lowlands				
pH	8.2	8.2	7.5 - 9.0	2
Alkalinity (mg/L)	26.0	26.0	24 - 28	2
Calcium (mg/L)	8.0	8.0	6 - 9	2
CSI	0.8	0.8	-0.2 - +1.19	2
EC (uS/cm @ 25°C)	71.0	71.0	61 - 80	2

*A subdivision within the Ozark Highlands

Table 2. Missouri reservoirs which can be classified as acid-sensitive by mean values of total alkalinity, CSI, or both.

Region/Lake	County	pH	Alkalinity (mg/L CaCO ₃)	Ca (mg/L)	CSI	EC (uS/cm)
Glacial Plains Tri-City	Boone	7.6	33	12	1.1	97
Osage Plains Lamar	Barton	7.3	42	17	1.1	134
Springfork	Pettis	7.2	55	14	1.2	128
Ozark Border Girardeau	Cape Girardeau	8.3	28	9	1.2	71
Indian Hills	Crawford	7.5	33	12	1.3	99
Little Prairie	Phelps	7.6	27	13	1.0	96
Ozark Highlands Miller	Carter	6.2	6	4	4.0	35
Ripley	Ripley	7.7	16	5	1.8	41
St. Francois Knob and Basin Bismark	St. Francois	7.8	36	10	1.2	126
Iron Mountain	St. Francois	7.5	36	10	1.6	102
Crane	Iron	7.2	13	13	2.1	50
Holiday Shores	Washington	8.1	16	6	1.5	70
Mississippi Lowlands Pool 1	Stoddard	7.5	28	8	1.9	80

DISCUSSION

As presumed from regional geology, we located acid-sensitive reservoirs in the St. Francois area (n=4) and the Mississippi Lowlands (n=2) (Figure 1, Table 2). Not all reservoirs sampled in these regions, however, were acid-sensitive. Each physiographic province contained at least one acid-sensitive reservoir -- an unanticipated result, given the predominance of carbonate minerals in Missouri. Collectively our findings suggest that acid sensitivity of reservoirs may be determined by site-specific conditions such as local edaphic factors and lake morphometry (Eilers et al. 1983, Loucks et al. 1986).

All four reservoirs considered acid-sensitive on the basis of both alkalinity and CSI (Table 2) were small (<40 ha), had limited watersheds (<600 ha), and were sited in regions containing non-carbonate mineral deposits. These morphometric traits do not necessarily determine sensitivity to acidification, but they do allow localized edaphic factors to influence chemical characteristics. Large reservoirs in the survey were well-buffered, in part, because their extensive watersheds link their water chemistry to carbonate geology predominant in the state. Because of similar linkage to watersheds, major streams in all physiographic provinces of Missouri would not be considered sensitive to acidification (USGS 1986).

This survey, based on a representative sample of reservoirs located throughout the state, suggests that most Missouri reservoirs are not particularly vulnerable to effects of acidic deposition. And we know of no acid-sensitive reservoir that is presently affected

by acidification. The broad and somewhat unexpected dispersion of acid-sensitive reservoirs suggests, however, that there may be others in the state. Additional studies are needed to identify all acid-sensitive waterbodies in Missouri and assess the effects of acidification.

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LITERATURE CITED

- Allgood, F. P., and I. D. Persinger. 1979. Missouri general soil map and soil association descriptions. U. S. Dep. Agric. Soil Conserv. Serv. Columbia, MO. 73 pp.
- American Public Health Association. 1985. Standard methods for the examination of water and wastewater, 16th ed., Am. Public Health Assoc., Washington, D.C.
- Canfield, D. E., Jr., 1983. Sensitivity of Florida lakes to acidic precipitation. *Water Resour. Res.* 19:833-839.
- Collier, J. E. 1955. Geographic regions of Missouri. *Ann. Assoc. Am. Geogr.* 45:368-392.
- Conroy, N., D. S. Jeffries, and J. R. Kramer. 1974. Acid shield lakes in Sudbury, Ontario region. *Wat. Pollut. Res. Can.* 9:15-61.
- Eilers, J. M., G. E. Glass, K. E. Webster, and J. A. Rogalla. 1983. Hydrologic control of lake susceptibility to acidification. *Can. J. Fish. Aquat. Sci.* 40:1896.
- Glass, G., and O. Loucks. 1980. Impacts of air pollutants on wilderness areas of northern Minnesota. EPA-600/3-80-044, U. S. Environ. Prot. Agency.
- Hach Chemical Co. 1978. Water and wastewater analysis procedures, 4th ed. Hach Chemical Co. Ames, Iowa.
- Haines, T. A. 1982. Acidic precipitation and its consequences for aquatic ecosystems: a review. *Trans. Am. Fish. Soc.* 110:669-707.
- Hoyer, M. V., and J. R. Jones. 1983. Factors affecting the relation between phosphorus and chlorophyll *a* in midwestern reservoirs. *Can. J. Fish. Aquat. Sci.* 40:192-199.
- Jones, J. R. 1977. Chemical characteristics of some Missouri reservoirs. *Trans. Mo. Acad. Sci.* 10/11:58-71.
- Linthurst, R. A., D. H. Landers, J. M. Eilers, P. E. Kellar, D. F. Brakke, W. S. Overton, R. Crowe, E. P. Meier, P. Kancircuk, and D. S. Jeffries. 1986. Regional chemical characteristics of lakes in North America. Part II: Eastern United States. *Water Air Soil Pollut.* 31:577-591.
- Loucks, O. L., G. E. Glass, J. A. Sorensen, B. W. Liukkonen, J. Allert, and G. Rapp, Jr. 1986. Role of precipitation chemistry versus other watershed properties in Wisconsin lake acidification. *Water Air Soil Pollut.* 31:67-77.
- National Atmospheric Deposition Program. 1988. NADP/NTN annual data summary. Precipitation chemistry in the United States. 1987. Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, Co. 535 pp.
- Schnoor, J. L., N. P. Nikolaidis, and G. E. Glass. 1986. Lake resources at risk to acidic deposition in the upper Midwest. *J. Water Pollut. Control Fed.* 58:139-148.
- Summers, P. W., V. C. Bowersox, and G. J. Stensland. 1986. The geographic distribution and temporal variations of acidic deposition in eastern North America. *Water Air Soil Pollut.* 31:523-535.

- Stout, L. N., and D. Hoffman. 1973. An introduction to Missouri's geological environment. Missouri Geological Survey & Water Resources. Educational Series No. 3. Rolla, Missouri. 44 pp.
- Thom, R. H. and J. H. Wilson. 1980. The natural divisions of Missouri. *Trans. Mo. Acad. Sci.* 14:9-23.
- U. S. Geological Survey. 1967. Mineral and water resources of Missouri. U. S. Geological Survey and the Missouri Geological Survey Water Resources. 90th Congress 1st session, Document No. 19, Washington D.C. 399 pp.
- U. S. Geological Survey. 1986. Water resources data for Missouri. Water Year 1986. U. S. Geological Survey Report MO-86-1. 319 pp.
- Wylie, G. D., and J. R. Jones. 1987. Diel and seasonal variations of dissolved oxygen and pH in relation to community metabolism of a shallow reservoir in southeast Missouri. *J. Freshwater Ecol.* 4:115-127.