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Dissolved Metal Concentrations in Surface Waters from West-Central Indiana Contaminated with Acidic Mine Drainage

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A significant amount of coal mining activity in the west-central region of Indiana, has resulted in a large number of sites where surface waters are contaminated with acidic mine drainage (AMD) (Harper, 1981). Contamination of drinking and irrigation water supplies is of concern mainly due to elevated levels of toxic metals. Abandoned mine sites are frequently located near occupied houses and farms in rural areas. Consequently, constituents of surface waters contaminated by AMD have the potential to be transported into sub-surface drinking water wells and irrigation water supplies. The extent of surface water contamination in west-central Indiana by AMD is not well characterized. For this reason, samples of surface waters that are contaminated with AMD were collected from a wide variety of locations in west-central Indiana and subjected to metals analysis.

Acid mine drainage is formed as a result of the oxidation of FeS_2 (pyrite). This process can be represented by the following reaction sequence (Lowson et al. 1993):

$$2FeS_2(s) + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \quad (1)$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (2)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (3)$$

Where step (1) represents the initiation reaction while steps (2) and (3) represent propagation reactions. The Fe^{2+} formed in step (3) is cycled back to Fe^{3+} in step (2). The Fe^{3+} may also be photoreduced by sunlight absorption (McKnight et al., 1988). As the AMD is transported away from the mine site, it typically undergoes an increase in pH due to dissolution of alkaline minerals such as limestone. At pH values above 3, the Fe(III) precipitates as yellow hydrated Fe(III) oxide:

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3(s) + 3H^+ \quad (4)$$

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giving streams beds and surface-water lagoons that are contaminated with AMD their characteristic appearance (Manahan, 1994). The impact of AMD upon the chemistry of streams and other natural waters has been previously documented (Herlihy et al., 1990 and Short et al., 1990).

Surface waters typically have pH values that range from 6 to 8, and contain relatively low concentrations (< 1 mg L^{-1}) of dissolved iron and other metals and metal complexes. Surface waters that receive AMD typically have pH values in the range of about 1.5 to 4, and high concentrations (100-1000 mg L^{-1}) of dissolved iron and elevated levels of other metals. Of particular concern, are elevated levels of toxic heavy metals and metalloids such as lead, mercury, cadmium, and arsenic.

MATERIALS AND METHODS

Surface water samples contaminated with acidic mine drainage (AMD) were collected from twelve different locations in west-central Indiana. All samples were collected in the vicinity of abandoned coal mines. Samples 94-2, 94-3, and 94-4 were collected April 24, 1994 from a stream approximately 3 km west of Brazil, Indiana. Samples 94-5 and 94-6 were collected November 12, 1994 approximately 1 km north of Terre Haute, Indiana near Clinton, Indiana from a stream feeding into the Wabash River. Samples 7 and 8 were collected December 11, 1994 from a pond in Clay county, Indiana approximately 1 km northwest of Howesville, Indiana (Indiana Division of Reclamation Site # 269). Samples 9 and 10 were collected December 11, 1994 approximately 2 km north of Dugger, Indiana (Indiana Division of Reclamation Site # 287). Samples 11, 12, and 13 were collected December 11, 1994 from a stream in Knox County, Indiana approximately 1 km southeast of Bicknell, Indiana (Indiana Division of Reclamation Site # 292). Samples were collected in high density polyethylene bottles and were stored in the dark at 5°C until used. All samples were filtered prior to analysis using an all-glass filtration apparatus (Schleicher and Schuell) and 0.47 µm Teflon filters.

The pH value for each sample was measured using an Orion Model 710 pH meter with a Ross combination pH electrode. A three point calibration using NIST traceable buffers (Fisher) was used for all pH measurements.

Metals were determined in samples by inductively coupled plasma spectroscopy (ICP) using a Spectra Analytical Instruments Spectroflame Model FPM-M5 instrument. The instrument was zeroed using a 10% solution of high purity HNO_3 (Baker). Calibration plots for each metal were constructed using data acquired by determination of standard solutions containing Fe, Cu, Mn, and other metals. Reported results represent an average of three measurements.

RESULTS AND DISCUSSION

The results of pH and metals analysis are reported in Table 1. As can be seen by an examination of the data, there appears to be no clear relationship between pH and metals concentrations.

Table 1. Total dissolved metal concentrations in surface water samples contaminated with AMD (mg L^{-1})

Sample	pH	Fe	Al	Cu	Mg	Mn	Ti	V	Pb
94-2	3.2	8.1		0.51		41			8.2
94-3	2.9	6.0		0.96		7.2			6.6
94-4	2.3	47		0.63		8.6			47
94-5	2.5	606		0.39		5.5			668
94-6	2.6	770		0.48		5.8			811
94-7	3.1	6.8	6.0	0.32	8.0	8.0	0.03	0.17	7.0
94-8	3.4	205	171	0.68	41	37	0.07	0.33	9.0
94-9	3.0	361	80	0.83	17	15	0.07	0.36	40
94-10	3.1	368	81	0.91	16	14	0.08	0.38	46
94-11	2.6	112	52	0.72	9.0	9.0	0.07	0.34	20
94-12	2.4	852	269	1.2	27	25	0.13	0.61	90
94-13	2.1	1203	217	1.2	0.9	31	0.40	0.66	113

A blank entry in the table indicates that the quantity is not available.

Based upon an examination of Equations 1-3, it might be expected that pH and iron concentrations would exhibit some form of inverse relationship. However, samples were collected from different locations where sources of alkalinity (e.g. dissolution of $CaCO_3$) are likely to vary considerably. This variable input of alkalinity to the AMD samples would undoubtedly cause variations in the measured pH values. Metals found at high concentrations included iron as expected but also included aluminum and lead. These metals as well as the other meatals listed in Table 1 have markedly higher aqueous solubility at reduced pH. Elevated levels of aluminum and lead are of concern due to their toxicity.

The levels of lead contamination in the AMD samples examined are particularly alarming. In many samples, the dissolved lead concentration exceeded 100 mg/L and, in the most contaminated sample, lead was found at a concentration of 811 mg/L. Typical surface water lead concentrations are approximately 3 µg/L

(Friedman, 1995). The measured lead concentrations are thus four to five orders of magnitude greater than typical surface water lead concentrations.

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REFERENCES

Friedman, B (1995) Environmental Ecology, Academic Press, New York, pp. 64-65.

Harper, D (1981) Trends in Underground Coal Mining in Indiana, Indiana Deptartment of Natural Resources Geological Survey, Occaisional Paper 33, Bloomington, IN.

Herlihy, AT, Kaufman, PB, and ME Mitch (1990) Regional estimates of acid mine drainage impact on streams in the mid-Atlantic and southeastern United States. Water Air Soil Pollut. 50: 91-107.

Lowson, RT, BJ Reedy and JK Beattie (1993) The chemistry of acid mine drainage. Chem. Australia. 60: 389-391.

Manahan, S Environmental Chemistry, 6th Ed. (1994) CRC Press, Boca Raton, Fla. pp. 172-173.

McKnight, DM, BA Kimball and KE Bencala. (1988) Iron photoreduction in an acidic mountain stream. Science. 240: 637-639.

Short, TM, Black, JA, and WJ Birge (1990) Effects of acid mine drainage on the chemical and biological character of an alkaline headwater stream. Arch Environ Contam and Toxicol 19: 241.