TRACE METALS IN WATER AND SEDIMENTS OF WETLANDS IN THE RAINWATER BASIN AREA OF NEBRASKA

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ABSTRACT

Water column and sediment samples, collected from 55 sites in the rainwater basin area of Nebraska during Spring 1988, were analyzed for total concentrations of 20 metal constituents. The survey was designed to quantify the concentrations of metal constituents in wetlands in an area of intensive agriculture. These wetlands are particularly important to migratory waterfowl and other wetland birds. Trace metals in water column samples were compared with U.S. Environmental Protection Agency (EPA) national criteria for freshwater aquatic organisms. Iron (Fe) and mercury commonly exceeded EPA criteria in study wetlands. Copper (Cu), lead (Pb), and zinc (Zn) EPA criteria depend on water hardness; these elements exceeded EPA criteria in some wetlands for which hardness data were available. EPA criteria for Aluminum (Al), molybdenum (Mo), and strontium (Sr) in water were not available; EPA criteria for trace metals in sediments were not available. Metal concentrations in sediment samples were compared with published crustal abundances from untilled prairie soils in Missouri. Beryllium (Be), mercury (Hg), and zinc (Zn) were in higher concentrations in sediments than in Missouri soils. None of the elements in the sediments were markedly elevated in comparison with background levels reported in the literature.

INTRODUCTION

Intensive agricultural development in Nebraska has prompted concern for possible environmental contamination of wetland areas with concentrations of trace elements resulting from the extensive and intensive use of pesticides, fertilizers, and other agricultural chemicals. Metals may have toxic, sublethal, and latent effects on wildlife if found in sufficient concentrations (Eisler, 1985). In 1983, elevated levels of selenium on the Kesterson National Wildlife Refuge in Central California caused selenium teratogenesis in natural populations of
aquatic birds (Hoffman et al., 1988). Blus et al. (1987) reported that declines in certain mammal populations in highly contaminated areas near smelters in northern Idaho were attributed to direct and secondary effects of toxic metals, such as lead and cadmium. Since 1970, sport and commercial fishing have been banned in mercury contaminated waters in 26 of the contiguous 48 states (Eisler, 1987).

The rainwater basin area of Nebraska (Fig. 1) serves as a major staging area for migratory waterfowl. Each spring since 1975, thousands of migrating waterfowl have succumbed to avian cholera as a result of the bacterium Pasteurella multocida. Researchers have suggested that the micro-environment of a wetland may be a critical factor involved in the transmission of the disease, the lifespan of the disease organism, or the increased susceptibility of waterfowl to a disease (Friend, 1981; Franson, 1986).

The objectives of this study were (1) to determine the concentrations of 20 trace metals in the water columns and sediments of wetland areas in south-central Nebraska; (2) to compare water column concentrations with U. S. Environmental Protection Agency (EPA) national criteria for freshwater aquatic organisms; (3) to compare metal concentrations in sediments with crustal concentrations in untilled soils characteristic of nonglaciated prairie in Missouri (standards are not available for sediments); and (4) to compare water column and sediment concentrations with values from published studies as available.

STUDY AREA

The rainwater basin area, which is located in south-central Nebraska, occupies approximately 10.8 thousand square km of land area. The basin formations characteristic of the area are thought to have been caused by irregular loess deposits, as controlled by topography and modified by wind (Evans and Wolfe, 1967). Although the wetland basins occur as a continuum, the rain-

Figure 1. Location of the eastern and western regions of the study area in the rainwater basin of Nebraska.
water basin area is administratively divided into an eastern and western region. The main differences between the eastern and western basin areas are that the topography is more rolling and rainfall is greater in the east, allowing for deeper and more permanent wetland basins due to more runoff.

Water levels are generally dependent upon direct precipitation, runoff from snowmelt, and irrigation systems. In addition, deep percolation of water from the Tri-County Canal System and from irrigation runoff from row crops has raised the water table 3 m or more in some areas (Spalding, 1981). The uplands surrounding most wetland basins experience intensive agricultural practices and deep well irrigation, primarily by center-pivot systems. Agriculture was the primary land use within all watersheds. The extent of idle lands separating study wetlands from adjacent agricultural activities varied from approximately 100% native prairie to 100% cultivated farm land (Gordon, 1989).

METHODS

Samples were collected in both the eastern and western regions during March and May of 1988. Forty-nine water column samples and 53 sediment samples were collected from 55 collection sites that included 36 wetland basins, 2 irrigation canals, 11 re-use pits, 2 intensive cattle-use areas, 3 rivers (Platte, Big Blue, Little Blue), and 1 area that was directly affected by an irrigation pivot. One sample collected from a cattle-use area was taken from a dry basin just below a feedlot, and another was collected from a livestock watering area. About 1/3 of the sample sites were in the western region and 2/3 in the eastern region of the rainwater basin (Fig. 1).

Water samples were collected in acid-washed, 125-ml, polyethylene bottles which were submerged 5-10 cm below the water surface, and later preserved with nitric acid to a pH of 2. Sediment samples were collected using an epoxy-coated core sampler. A minimum of 30 g of sediment were placed in acid-washed, Qorpak, 118-ml, glass jars with Teflon-lined lids. Each sample was a composite of different layers of a single core sample. Sediment samples were kept frozen until analysis.

All water column and sediment samples were analyzed for 20 trace metals at the Environmental Trace Substances Research Center, at the University of Missouri, Columbia. At the center, sediment samples were dried, weighed, and further homogenized using a blender. Approximately 0.5 g of sediment or 50 ml of water were digested by one of 2 methods: mercury was analyzed on nitric reflux digestates, while the remaining elements were analyzed on nitric-perchloric acid digestates. Concentrations were determined using 3 methods: mercury concentrations were analyzed by cold vapor atomic absorption; arsenic and selenium concentrations were determined using a hydride method; and the other 18 trace metals (Ag, Al, B, Ba, Be, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, Ti, V, Zn) were analyzed using an inductively coupled plasma (ICP) scan. Instrumentation included a Perkin-Elmer 403AA, Varian VGA-76 hydride generator, Perkin-Elmer Model 603AA or 3030AA, and a Jarrell-Ash Model 1100 Mark III.
Trace metal concentrations in water column samples were compared with EPA national criteria where available for freshwater aquatic organisms (EPA, 1986; EPA, 1987). To date, EPA has not developed a set of sediment quality criteria; therefore, concentrations were compared with the crustal abundances reported by Erdman et al. (1976A) and Erdman et al. (1976B).

RESULTS

Water column elemental concentrations were lower than EPA national criteria for freshwater aquatic organisms with the exception of Cu, Fe, Hg, Pb, and Zn (EPA, 1986; EPA, 1987) (Table 1). Criteria for Cu, Pb, and Zn require knowledge of water hardness. Although these data were not collected as part of this study, information pertaining to water hardness was obtained for 7 of the 56 study areas (Gordon, 1989) and it was determined that Cu, Pb, and Zn exceeded the EPA criteria. Water hardness ranged from 33 mg/L at County Line Marsh to 439 mg/L at Funk Lagoon. Generally, water hardness increases from the eastern region to the western region of the rainwater basin area (Spalding, 1981; Windingstad et al., 1984; Gordon, 1989). Copper was found to be elevated in 2 of the 7 wetlands for which water hardness data were available. Excessive amounts of lead were found in 2 of the 7 wetlands. Zinc concentrations were high in 3 of the 7 wetlands for which water hardness data were available. Water column concentrations for Ag, Be, Cd, Cr, Hg, Mo, Ni, and Tl were found near or below detection limits. National criteria were not available for aluminum, strontium, and vanadium.

Most of the elements in sediment samples were in lower concentrations than those reported for unglaciated soils in Missouri. Trace metal concentrations were not unusual for loess and soils on silt deposits (Kabata-Pendias and Pendias, 1984).

DISCUSSION

Copper is an essential micronutrient for living organisms but it can produce toxic effects at elevated levels. Principal sources of copper include the following: metalliferous mining, smelting, industrial emissions and effluents, traffic, urban development and dumped waste materials, contaminated dusts and rainfall, sewage sludge, pig slurry, composted refuse, fertilizers, ameliorants, and pesticides (Nriagu, 1979). Copper is widely used as an algicide and herbicide for nuisance aquatic plants, but this use is uncommon in the rainwater basin. Potential copper sources in the study area would primarily be pesticides and fertilizers. Water column concentrations of copper in Nebraska wetlands ranged from <0.004-0.079 mg/L. Spalding (1981) reported concentrations in the groundwater in the Tri Basin area of Nebraska as ranging from <0.002-0.011 mg/L. Copper concentrations in sediments were almost identical to those reported by Erdman et al. (1976A) for unglaciated prairie soils.

Mercury from fungicides is a potential source for contamination of rainwater basin wetlands. Although its use as a fungicide has been discontinued in many places, Hg residues may still remain in soils and wetland areas. Mer-
cury concentrations in study wetlands (0.0003 mg/L) exceeded maximum amounts recommended by the EPA for aquatic systems (0.000012 mg/L). Martin and Hartman (1984) found mercury concentrations in sediments to range from 0.02-0.06 mg/kg in the North Central United States. Lake Winnipeg and other Canadian lakes had sediment levels of 0.03-0.28 mg/kg (Allan and Brunskill, 1977). Levels ranging from 0.03-0.62 mg/kg were reported for sediments in Lake Oahe in South Dakota (Walter et al., 1973). Concentrations in soils collected in eastern North Dakota had a mean concentration of 0.2 mg/kg (Houghton and Briel, 1987). Sediment mercury levels in this study (0.02-0.80 mg/kg) were comparable to other studies but may be of concern in some wetlands. Mercury concentrations in sediments appeared to be clearly elevated in relation to prairie soils in Missouri (Erdman et al., 1976A).

Iron is the fourth most abundant element in the make-up of the earth’s crust and it is a major component of clay soils (EPA, 1986). Therefore, it is not surprising to find elevated levels of Fe in Nebraska wetlands, where clay soils are dominant (Evans and Wolfe, 1967). Although Fe levels are elevated in comparison to EPA criteria, concentrations found in rainwater basins are considered to be normal. Sediment concentrations were below those observed by Erdman (1976A) for prairie soil in Missouri.

Lead enters the environment from several sources. Vehicle exhaust has been a major contributor but restriction on lead use in gasoline has reduced

<table>
<thead>
<tr>
<th>Trace Metal</th>
<th>Water Column (mg/L)</th>
<th>EPA Criteriaa</th>
<th>Sedimentsb (mg/kg)</th>
<th>Rainwater Basin</th>
<th>Ungle. pr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.02 (+0.02)</td>
<td>0.00012</td>
<td>1.5 (&lt;1.0-2.0)</td>
<td>Unavail.</td>
<td></td>
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<tr>
<td>Al</td>
<td>4.99 (0.04-5.90)</td>
<td>Unavailable</td>
<td>39.742 (4.710-75,500)</td>
<td>47,000</td>
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<tr>
<td>As</td>
<td>0.0069 (0.0001-0.080)</td>
<td>1.9</td>
<td>3.90 (0.07-4.60)</td>
<td>12</td>
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<tr>
<td>B</td>
<td>0.088 (0.040-0.490)</td>
<td>TDS (plants)</td>
<td>11.5 (&lt;3.0-19.0)</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.596 (0.093-2.770)</td>
<td>50</td>
<td>502.7 (75.0-489.0)</td>
<td>490</td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>0.003 (+0.001-0.002)</td>
<td>0.0551-0.13</td>
<td>1.7 (0.2-2.7)</td>
<td>1.3</td>
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<tr>
<td>Cd</td>
<td>0.003 (+0.000-0.006)</td>
<td>g/L (Ag and Au) 0.120</td>
<td>0.5 (&lt;0.2-1.0)</td>
<td>&lt;1</td>
<td></td>
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<tr>
<td>Cr</td>
<td>0.01 (+0.01-0.04)</td>
<td>0.21</td>
<td>22.6 (4.0-40.0)</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.016 (+0.004-0.079)</td>
<td>g/L (Ag and Au) 0.164</td>
<td>17.8 (3.0-33.0)</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>5.61 (0.03-28.20)</td>
<td>1</td>
<td>22.599 (4.390-34.300)</td>
<td>35,000</td>
<td></td>
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<tr>
<td>Mg</td>
<td>0.0002 (&lt;0.0003-0.0007)</td>
<td>0.000012</td>
<td>0.23 (&lt;0.02-0.80)</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.592 (0.017-3.820)</td>
<td>&gt;1.5</td>
<td>303.4 (101.0-810.0)</td>
<td>780</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.01 (+0.01)</td>
<td>Unavailable</td>
<td>2.5 (&lt;1.0-3.0)</td>
<td>&lt;3</td>
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<tr>
<td>Ni</td>
<td>0.019 (&lt;0.010-0.110)</td>
<td>g/L (Ag and Au) 0.151</td>
<td>17.3 (3.3-27.0)</td>
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<tr>
<td>Pb</td>
<td>0.05 (&lt;0.04-0.17)</td>
<td>g/L (Ag and Au) 0.160</td>
<td>19.4 (&lt;4.0-35.0)</td>
<td>24</td>
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<tr>
<td>Se</td>
<td>0.161 (&lt;0.0003-0.0060)</td>
<td>0.35</td>
<td>0.45 (&lt;0.10-1.50)</td>
<td>&lt;67</td>
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<tr>
<td>Sr</td>
<td>0.210 (0.036-0.979)</td>
<td>Unavailable</td>
<td>51.8 (15.5-73.6)</td>
<td>95</td>
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<tr>
<td>Ti</td>
<td>0.05 (&lt;0.04-0.05)</td>
<td>0.840-1.400</td>
<td>7.0 (&lt;5.0-8.0)</td>
<td>Unavail.</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.030 (&lt;0.000-0.200)</td>
<td>Unavailable</td>
<td>49.9 (11.0-74.0)</td>
<td>92</td>
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</tr>
<tr>
<td>Zn</td>
<td>0.124 (&lt;0.005-0.940)</td>
<td>g/L (Ag and Au) 0.164</td>
<td>87.3 (14.0-171.0)</td>
<td>51</td>
<td></td>
</tr>
</tbody>
</table>

* Environmental Protection Agency (EPA) criteria (maximum allowable levels) for freshwater aquatic organisms.

* Sediment criteria have not been established by the EPA. Erdman et al. (1976) reported concentrations of trace metals for soils in unglaciated Missouri Prairie and these are presented for comparison with our sediment samples. Erdman et al. (1976A) present the geometric mean instead of the arithmetic mean as in our study — these means should still be roughly comparable.

* Sediment criteria for Cu was taken from till, soil in Missouri (Erdman et al. 1976A) because no value was given for till soil in Erdman et al. (1976A).
this source. Pesticides and lead shot are also sources of Pb (May and McKinney, 1981). Oates (1989) examined the incidence of lead shot in 8 rainwater basin wetlands and found an average of 47,217 pellets/ha; steel shot has been required for waterfowl hunting on these areas since 1980. Thus, lead shot may provide a source of contamination for many years. Levels of Pb in the water in rainwater basin wetlands ranged between <0.04-0.17 mg/L. EPA criteria for lead in the water are influenced by water hardness and, in some study wetlands of known hardness, exceeded recommended criteria for aquatic ecosystems; further monitoring of lead concentrations in rainwater basin wetlands is recommended. Sediment concentrations of lead do not appear excessive.

Zinc ranks fourth among metals of the world in annual consumption (Nriagu, 1980). Fertilizers and fungicides (EPA, 1987) represent the probable sources for contamination of natural wetlands in Nebraska (EPA, 1987). Zinc occurs naturally in freshwater environments, and exposure to elevated concentrations is one to which species of many groups have adapted themselves (Nriagu 1980). Zinc is an essential micronutrient for all living organisms. Zinc levels in groundwater from irrigation wells in the Tri-basin area of Nebraska were 0.004-0.078 mg/L. The mean concentration for water column samples collected in rainwater basin study wetlands was 0.124 mg/L of zinc. Erdman et al. (1976A) reported levels of zinc in unglaciated prairie soils to be 51 mg/kg (geometric mean). Sediments in the rainwater basin study sites averaged 87 mg/kg of zinc, markedly higher than our sediment concentrations.

Selenium is widely distributed in nature and is particularly abundant with sulfide minerals of various metals such as Fe, Pb, and Cu (Eisler, 1985). Selenium should be discussed because of the problems this metal can cause in aquatic ecosystems. The recent discovery of high concentrations at Kesterson Reservoir in California has prompted concerns for excessive Se in the environment. Levels of Se reported in water entering Kesterson Reservoir contained 300 ppb; however, water entering the nearby Volta Wildlife Area contained a more normal level of 1 ppb (Ohlendorf et al., 1986). Spalding (1981) reported Se levels of < 0.2-1.9 ppb in groundwater samples collected in the Tri-basin Natural Resources District in Nebraska. Selenium levels in the water reported for study wetlands in the rainwater basin were 0.3-8.0 ppb. Our findings are consistent with background levels reported in the literature. Sediment concentrations of selenium were also at low levels compared to unglaciated prairie in Missouri (Erdman et al., 1976A).

Allan and Brunskill (1977) examined the presence of element concentrations in bottom sediments of Lake Winnipeg and other Canadian lakes. Results for the analysis of Be were consistent with the findings of this study. Beryllium in Canada was present in concentrations which ranged from 1.0-3.1 mg/kg in sediment samples. Rainwater basin samples contained 0.2-2.7 mg/kg of Be.

Cadmium should be briefly discussed because it has caused environmental problems elsewhere. Runoff from agricultural areas where phosphate fertilizers have been applied may result in a substantial Cd loading to the aquatic environment (May and McKinney, 1981). Background concentrations of Cd reported in the literature demonstrated considerable variation. Martin and Hartman (1984) reported sediment concentrations ranging from 0.13-1.1 mg/kg
in pothole wetlands of the North Central United States, including 2 wetlands which were also sampled in this study. Allan and Brunskill (1977) found sediment concentrations in Lake Winnipeg to range from 1.0-3.0 mg/kg. Cadmi-
num concentrations ranging up to 13.7 mg/kg were considered to be back-
ground levels for Clay and Ball Lakes in Ontario (Jackson, 1978). Based on the concentrations reported in the literature, the findings of this study (<0.2-1.0 mg/kg) did not suggest problems with Cd contamination of water or sediments.

Toxic effects are related to the physical and chemical forms of each element, the toxicity of each form, the degree of interaction among the various forms, and the interrelationship between different trace elements. Tolerance ranges of trace metals, as expected, vary among individuals, species, and larger phylogenetic groups. This study was designed to provide baseline data on trace metal concentrations in a variety of environments within the rainwater basin area of Nebraska. The chemical interactions of an aquatic ecosystem are very complex and dynamic and require a thorough examination. Periodic monitoring of trace metals that were near or above EPA criteria or comparable published data is recommended for the rainwater basin wetlands. Additionally, laboratory studies could examine the effects of trace metals specific to aquatic species which are found in the rainwater basin area. In general, most trace metals in rainwater basin wetlands are not at concentrations that would cause immediate damage to aquatic ecosystems.

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