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Heavy Metals in Mammals from Two Unmined Copper-Zinc Deposits in Wisconsin

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This paper describes concentrations of zinc, copper, cadmium, lead, nickel, mercury and arsenic from eight species of mammals collected at two areas in northern Wisconsin where zinc and copper deposits have been discovered and mines will be developed. The purposes of these analyses were: (1) to determine if differences existed in heavy metal concentrations in mammals between the two areas with different ore compositions and with the different amounts of glacial deposits over the ore bodies; and (2) to provide background levels which can be used for comparison of concentrations of these metals in mammals from other areas and from these same areas after the mines have been developed.

Both study areas are sulfide deposits, one located near Ladysmith, Wisconsin and the other 160 km east near Crandon, Wisconsin. The Ladysmith deposit is essentially a vertically-oriented, lens-shaped pod 15 m wide, 730 m long and 250 m deep and averages 3.5 to 4.0% copper and trace amounts of gold and silver. Small amounts of zinc are found in lower areas but not in sufficient amounts to warrant recovery (DUTTON & WHITE 1977, MUDREY & OSTROM 1977). The deposit is overlain by 3 to 9 m of glacial material. MAY (1977) concluded that the deposit is continually reacting with the environment, and contributes significant quantities of acid and heavy metal ions to the surface via capillary action from the oxidizing deposit into the groundwater. Surveys have shown that groundwater, soils and vegetation over the deposit and down the hydraulic gradient have high levels of heavy metal ions (MAY 1977).

The Crandon ore-body is about 1.5 km long, approximately 38 m wide and 720 m deep and averages 5% zinc, 1.1% copper, 0.4% lead and smaller amounts of silver and gold (DUTTON & WHITE 1977, EXXON MINERALS CO. 1980, MUDREY & OSTROM 1977). This deposit is overlain with about 30 m of glacial material which probably reduces any reaction between the ore-body and the surface environment.

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METHODS

Small mammals were captured with mouse-size snap-traps. At Ladysmith, traps were placed on a 10 m grid that covered, and also extended on both sides of the 15 m wide ore deposit. Most animals were trapped on the west end of the deposit where the glacial material was only 3 m thick.

At Crandon, small mammals were not trapped over the deposit but adjacent to the area. No small mammals were caught over 1.6 km from the ore body. Since this area was covered by 30 m of glacial deposits, we did not feel that the trapping location was as critical as at Ladysmith where heavy metal levels in vegetation showed sharp declines on either side of the narrow deposit.

The two snowshoe hares (*Lepus americanus*) that we analyzed were trapped in live-traps near the Crandon site but not directly over the deposit.

Coyote (*Canis latrans*) carcasses were collected from local trappers. The 10 coyotes that were analyzed for heavy metals (2 composite samples of 5 each) were all killed within 16 km of the Crandon ore deposits.

All specimens were labeled and stored frozen until they were prepared for shipment to the analytical lab. To reduce variability and the cost of analysis, we pooled 5 individuals of the same species, sex, age, and locality of capture (only the two snowshoe hares were individual samples). The 5 individuals were simultaneously homogenized in a commercial Waring blender, frozen in a sealed metal-free jar, and later packed in dry ice for shipment to the Analytical Biochemistry Laboratories, Columbia, Mo.

Since trappers skinned the coyotes and because of their large size, whole body analyses of heavy metals in coyotes were not feasible. We therefore selected hair, liver and kidneys for analysis because of possible heavy metal concentrations in these tissues. Hair was removed from the distal portion of the leg of the coyote which was usually not skinned by the trapper.

All glassware and instruments were double-washed in reagent grade nitric acid and rinsed with metal-free deionized water.

Since analysis of initial samples from Crandon yielded low levels of mercury and arsenic, we did not have later Crandon samples and none of the Ladysmith samples analyzed for these metals.

At the Analytical Biochemistry Laboratories, samples were digested in double-distilled nitric acid and brought to volume with deionized water. Samples were analyzed by atomic absorption spectrophotometry with background correction. Zinc, copper, and cadmium analyses were performed by flame atomic absorption. Nickel and lead analyses were performed by flameless atomic absorption using a graphite furnace for ashing. Arsenic analyses were done by flame A.A. in conjunction with a Perkin-Elmer MHS-10 hydride generation system. Mercury concentrations were determined using a cold vapor method. Results are reported as wet weight concentrations (ug g^{-1}).

RESULTS AND DISCUSSION

There is little difference (between Crandon and Ladysmith), in levels of any of the metals that we analyzed, for the five species that we compared (Table 1). All values appear to be within the variability that likely exist within one area.

Three of the pooled samples of red-backed voles (Clethrionomys gapperi) from Ladysmith were animals that were caught directly over the ore body and two of the samples were from just off the ore body on the upper side of the hydraulic gradient. Although the animals from directly over the ore body had higher zinc and copper levels (33 vs. 32 ug g^{-1} for zinc and 4.5 vs. 3.5 ug g^{-1} for copper), they were probably not significantly different.

The metal values for the five species of small mammals and the snowshoe hare samples probably represent background levels for much of northern Wisconsin and do not reflect any increases due to the ore deposit. SMITH (1980) reported values for 5 pooled samples of Peromyscus maniculatus collected from an area 80 km north of Ladysmith which had comparable values.

SMITH (1980) presented a more detailed comparison of heavy metals in P. maniculatus and Microtus pennsylvanicus by sex and age between Crandon, Wisconsin and Timmins, Ontario where there is an active zinc and copper mine. All levels from Timmins animals were higher than the Crandon animals indicating that the whole body concentration of heavy metals in these species probably reflects environmental exposure.

We do not know why the heavy metals in mammals from Ladysmith did not reflect the high levels that MAY (1977) reported as being in the vegetation, soil, and groundwater. It is possible that our mammal samples were not localized enough or that the vegetation samples reported by MAY (1977) were of deep-rooted species that did not end up in the food chain of any of these mammals.

Table 1. Mean concentrations (ug metal/g wet tissue, 1 s.d. when available) of heavy metals in mammals collected near two unmined copper and zinc deposits in northern Wisconsin. All samples are composits of 5 individuals, except the snowshoe hares which were 2 individuals.

Area/Species	N[1]	Age	Sex	Zn	Cu	Cd	Pb	Ni	Hg	As
Ladysmith										
Microtus pennsylvanicus	1	A + J	♂+♀	32	3.4	<0.1	0.45	0.99	--	--
Peromyscus maniculatus	1	A	♂	33	3.9	<0.1	<0.1	0.77	--	--
Clethrionomys gapperi	5	J	♂+♀	32.3±0.3	4.1±0.6	<0.1	0.48±0.05	0.93±0.20	--	--
Sorex cinereus	2	A	♂+♀	38	5.2	0.22	1.2	2.4	--	--
Blarina brevicauda	1	J	♀	40	7.2	0.32	0.42	2.8	--	--
Crandon										
Microtus pennsylvanicus	7	J	♂	32±2	4.1±0.8	<0.1	0.7±0.4	1.7±0.9	--	--
Peromyscus maniculatus	5	A + J	♂+♀	31±3	3.9±0.6	<0.1	0.9±1.3	1.0±0.2	<0.1	<0.1
Clethrionomys gapperi	2	A	♂+♀	40	4.8	0.2	20	1.3	<0.1	<0.1
Sorex cinereus	7	A + J	♂+♀	36	4.1±0.5	0.2±0.1	0.9±0.2	1.5±0.2	--	--
Blarina brevicauda	2	A	♂+♀	31	3.4	0.28	5.8	1.2	<0.1	<0.1
Lepus americanus	2	A	♀	29	4.2	0.20	1.5	0.23	<0.1	<0.1
Lutra canadensis	1	A + J	♂+♀	14	12	0.98	--	42	9.4	0.20
Canis latrans	1	A	♂							
hair				170	16	0.65	11	0.65	0.1	0.23
liver				43	21	0.44	0.14	0.11	0.1	0.1
kidney				23	5.9	0.91	1.2	0.1	0.1	0.1
Canis latrans	1	A	♀							
hair				150	14	0.55	13	0.68	0.25	0.12
liver				43	20	0.34	1.6	0.1	0.1	0.1
kidney				24	6.3	0.61	0.61	0.1	0.1	0.1

(1) Number of composite samples.

The concentrations of zinc, copper, and cadmium in hair of coyotes and otter (Lutra canadensis) from the Crandon area were higher than whole body concentrations of the small mammals we analyzed. HAMMER et al. (1971) determined that concentrations of arsenic, cadmium, copper, lead, and zinc in human hair reflected environmental exposure to these metals. We do not know how the metal concentrations in the hair of small mammals compared with coyotes. Heavy metal concentrations in hair likely reflect long-term exposure and are likely not regulated as metal levels in soft tissues.

Copper concentrations were higher in coyote livers than in hair and kidneys of these same animals and higher than in any of the whole body small mammals analyzed. The liver has been demonstrated to accumulate copper to a greater extent than other soft tissues (UNDERWOOD 1971). MACPHERSON & HEMINGWAY (1969) determined ranges for dry weight hepatic and renal copper concentrations for sheep with induced chronic copper toxicity. They reported liver concentrations of 970-6300 ug g^{-1} (dry weight) and kidney concentrations of 77-1600 ug g^{-1} (dry weight). Even considering the wet weight conversions for these values, it is clear that copper concentrations we observed in coyote liver and kidney tissues were not close to toxic levels.

Cadmium levels in coyote kidneys were higher than in liver and hair. Rats fed 300 ug g^{-1} cadmium in drinking water over a 12 week period had hair, liver, and kidney cadmium concentrations of 110, 34, and 19 ug g^{-1} (wet weight), respectively (BRANCATO et al. 1976). Again, these levels are much higher than those we observed in coyotes from the proposed mine area (Table 1).

Lead levels were variable and difficult to explain. It may be that this metal is the most easily contaminated during handling and processing of specimens or the most difficult to determine levels in tissues.

The levels of cadmium, nickel and mercury in otter hair were higher than any other samples analyzed. It is probable that this reflects aquatic environmental exposure of a greater magnitude than what we observed in our terrestrial samples. SHEFFY (1977) found that mercury levels were higher in otter fur than in fur of beavers, (Castor canadensis), muskrats (Ondatra zibethica), raccoons (Procyon lotor), red fox (Vulpes fulva), and mink (Mustela vison).

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