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Zinc, Iron, Manganese, and Magnesium Accumulation in Crayfish Populations Near Copper–Nickel Smelters at Sudbury, Ontario, Canada

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The Sudbury basin, an elliptical 1,673 km^2 depression containing a number of freshwater reservoirs, has been subjected to extreme ecological disturbances from logging, mining and smelting activities (Winterhalder 1984). The impact of acid precipitation and heavy metal contamination on the water, soil, atmosphere and vegetation of the region has been discussed by Freedman and Hutchinson (1980) and Chan et al. (1980).

In earlier work, Bagatto and Alikhan (1987) report elevated concentrations of copper, cadmium and nickel in crayfish populations close to the Sudbury smelting works. The present study compares concentrations of zinc (Zn), iron (Fe), manganese (Mn) and magnesium (Mg) in freshwater crayfish at selected distances of the habitat from the emission source. These metals were selected since they are known to be emitted in moderately high quantities into the Sudbury environment as byproduct of the smelting process (Chan et al. 1980). Various tissue concentrations in crayfish were also examined to determine specific tissue sites for these accumulations.

MATERIALS AND METHODS

Intermoult adult *Orconectes virilis* were collected from Ramsey Lake (46° 28'N 80° 57'E) in Sudbury (Ontario), and *Cambarus bartoni* were obtained from Joe Lake (46° 44'N 81° 01'E) in Chelmsford (Ontario), and Wizard Lake (47° 44'N 81° 46'E) in Gogama (Ontario). Wizard Lake, situated at a distance of 150 km from the smelter, is an uncontaminated site whereas Ramsey Lake and Joe Lake are 12 km and 30 km downwind, respectively, and are heavily contaminated with copper, cadmium and nickel (for details, see Freedman and Hutchinson 1980).

Ten animals (5 females and 5 males, average wet weight = 5.4 g; average carapace length = 45 mm) collected from each site were separated by sex, quick frozen, and stored at -15°C. The hepatopancreas, exoskeleton, abdominal muscle, digestive gut

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(alimentary canal) and remaining viscera (including gills, green glands, reproductive organs, etc.), were oven dried for 48 h at 80°C, and dry weights were determined. Samples for analysis by Perkin-Elmer atomic absorption spectrophotometer were digested in boiling concentrated aqua regia (3 mL concentrated nitric acid: 1 mL concentrated hydrochloric acid, British Drug House standards), diluted to 20 mL with 1 M nitric acid and analysed for zinc, iron, manganese and magnesium by the flame method (Perkin-Elmer manual, 1971). Analytical grade acid, double distilled deionized water and acid washed glassware were used to minimize sample contamination.

Statistical analysis of the data was computed with the aid of a DEC-VAX/VMS computer, using SPSS^x software (SPSS, Chicago, Ill., U.S.A.). An initial three-way ANOVA evaluated the effects on metal levels by site, sex and tissue of the crayfish. Within site and tissue comparisons were made using one-way ANOVA with Duncan's Multiple Range test. All data were checked for normality (Kolgomorov-Smirnoff test) and homogeneity of variance (Bartlett-Box F test), and they were log transformed where necessary.

RESULTS AND DISCUSSION

Tables 1 to 4 summarize data on concentrations of trace metals in various tissues in freshwater crayfish from the three sampling sites. Since differences in metal concentrations between males and females at each site were not significant ($p > 0.05$), the data for the two sexes in each species were pooled for comparison purposes. The general relationship between the crayfish tissue metal concentrations at the three sites was Mn < Zn < Fe < Mg. This observed relationship, with the exception of Mn, agrees with the concentration relationship reported for these metals (Zn < Fe < Mn < Mg) in the Sudbury Environment (Yan and Miller 1982).

In general, highest tissue Zn and Fe concentrations were observed in crayfish obtained from Ramsey Lake and lowest from those collected from Wizard Lake. Tissue concentrations of Mg were highest in animals from Joe and Wizard Lakes and lowest in crayfish from Ramsey Lake. Mn levels were highest in crayfish obtained from Joe Lake and lowest in those captured from Wizard Lake. According to Yan and Miller (1982), metal levels in lake water and sediment decrease with increasing distance from the emission source. The tissue concentrations of metals observed in the present study showed a similar trend. Thus, concentrations of Zn and Fe in crayfish collected from Ramsey and Joe Lakes, which are nearest to the emission source, were highest; while they were lowest from decapods captured from Wizard Lake, which is at some distance from the smelter. The somewhat anomalous tissue accumulation of Mg and Mn may reflect other environmental or physiological parameters. Beamish and Van Loon (1977) suggest that acidic lakes in Ontario, irrespective of their locations, contain elevated Mn concentrations. The Ontario Ministry of the

Table 1. Mean concentrations of zinc (μg/g dry wt) in various tissues of crayfish collected from Ramsey, Joe and Wizard Lakes.

Tissues	Ramsey	Joe	Wizard
Hepatopancreas	190a,1 (142, 255)*	166a,1,2 (105, 263)	92a,c,2 (48, 177)
Exoskeleton	23b,1 (19, 26)	32b,2 (28, 37)	27b,2 (17, 44)
Abdominal muscles	93c,1 (72, 120)	97c,1 (88, 106)	80a,c,1 (70, 92)
Digestive gut	154a,1 (132, 180)	100c,2 (77, 130)	111c,2 (82, 151)
Viscera	72c,1 (49, 104)	76c,1 (38, 151)	60a,1 (35, 101)

* 95 per cent confidence limits.

Means within each column followed by the same letter, and within each row followed by the same number are not significantly different at 5% level.

Table 2. Mean concentrations of iron (μg/g dry wt) in various tissues of crayfish collected from Ramsey, Joe and Wizard Lakes.

Tissues	Ramsey	Joe	Wizard
Hepatopancreas	368a,1 (244, 555)*	356a,1 (220,577)	183a,1 (84, 398)
Exoskeleton	204a,1 (124, 338)	253b,1 (131, 488)	89a,b,1 (60, 134)
Abdominal muscles	14b,1 (3, 70)	126b,1 (57, 277)	43b,1 (25, 76)
Digestive gut	510a,1 (254, 1026)	588a,1 (305, 1135)	881c,1 (428, 1813)
Viscera	296a,1 (193, 454)	146b,1 (80, 266)	125a,1 (101, 153)

* 95 per cent confidence limits.

Means within each column followed by the same letter, and within each row followed by the same number are not significantly different at 5% level.

Table 3. Mean concentrations of magnesium (μg/g dry wt) in various tissues of crayfish collected from Ramsey, Joe and Wizard Lakes.

Tissues	Ramsey	Joe	Wizard
Hepatopancreas	562[a,1] (301, 1050)*	775[a,1] (580, 1036)	846[a,1] (493, 1450)
Exoskeleton	949[a,1] (441, 2045)	2306[b,2] (1629, 3265)	1914[b,2] (1627, 2251)
Abdominal muscles	603[a,1] (288, 1264)	1449[c,2] (1348, 1558)	1685[b,2] (1581, 1796)
Digestive gut	1031[a,1] (517, 2053)	2302[c,2] (1976, 2682)	2260[b,2] (1984, 2574)
Viscera	838[a,1] (406, 1731)	2924[b,2] (2358, 3625)	1522[b,1] (850, 2727)

* 95 per cent confidence limits.
Means within each column followed by the same letter, and within each row followed by the same number are not significantly different at 5% level.

Table 4. Mean concentrations of manganese (μg/g dry wt) in various tissues of crayfish collected from Ramsey, Joe and Wizard Lakes.

Tissues	Ramsey	Joe	Wizard
Hepatopancreas	59[a,1] (35, 97)*	337[a,2] (183, 622)	11[a,3] (2, 75)
Exoskeleton	102[a,1] (61, 170)	293[a,2] (174, 493)	32[a,3] (24, 43)
Abdominal muscles	11[b,1] (8, 15)	45[b,2] (30, 68)	4[b,3] (2, 5)
Digestive gut	424[c,1] (259, 695)	1148[c,2] (847, 1555)	130[c,3] (69, 247)
Viscera	101[a,1] (63, 163)	230[a,2] (146, 362)	32[a,3] (22, 45)

* 95 per cent confidence limits.
Means within each column followed by the same letter, and within each row followed by the same number are not significantly different at 5% level.

Environment (1983) reports that Joe Lake, due to its low alkalinity, is extremely sensitive to acid loading from acidic precipitation. These may be the reasons for the relatively higher Mn tissue concentrations in crayfish from Joe Lake.

The distribution of each metal in crayfish tissues was not identical. Zn concentrations were highest in the hepatopancreas and digestive gut and lowest in the exoskeleton. This would confirm that Zn is of considerable metabolic importance to decapod crustacea (Bryan 1968). Excessive Zn tissue accumulation in freshwater decapods is associated with metal-binding proteins (Lyon et al. 1982), and metal containing granules (Brown 1982).

Fe was somewhat evenly distributed among various tissues and its lowest concentrations were observed in abdominal muscles. Fe is an important trace metal constituting the nucleus of enzymes and pigments of the protoporphyrin group (Martin 1973). This may explain the presence of high concentrations of this metal in digestive tissues and the exoskeleton. Fe has also been found in the granules contained within the hepatopancreas (Loizzi 1971). It is contended that the higher environmental levels of Fe, and heavy metals in general, are correlated with an increase in the quantity and the size of these granules. According to Hopkin et al. (1985) storage of metals as granules is preferred over excretion by crustacean species in order to conserve energy.

Mg levels in various tissues were not significantly different in crayfish obtained from Ramsey Lake. However, hepatopancreatic concentration of this metal in crayfish from Joe and Wizard Lakes was significantly lower than that observed in other tissues. Zanders (1978) suggests that many crustaceans maintain Mg blood levels hypoionic relative to the medium by excreting it in the urine. Hyperregulation of blood Mg occurs in some decapods exposed to low or Mg free media (Holliday 1980).

Mg concentrations observed in the present study, in general, were higher in the exoskeleton than in any other tissue. The reason for this may be the physiological functional similarity between Mg and Ca. Similar observations for tissue accumulation of copper and cadmium in isopods have been made by Hopkin et al. (1985).

Highest concentrations of Mn were found in the digestive gut and the lowest in the abdominal muscles. This is not surprising since Mn is especially active in digestive and catabolic enzymes (Vallee 1970). High Mn concentrations in the exoskeleton may be related to its ability to compliment or to substitute for Mg.

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