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Cadmium, Copper and Lead in Wild Rice from Central Canada

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Abstract. Samples of wild rice grains available for sale in Manitoba, Canada contained <0.01–6.2 μg/g cadmium, <0.01–6.7 μg/g lead, and 1.6–14.4 μg/g copper. Rice originating from Saskatchewan and northern Manitoba contained significantly higher copper concentrations than samples from Ontario and southeastern Manitoba. Larger and heavier grains contained higher lead concentrations per unit weight. Mean content of all three metals per individual grain was exponentially correlated with grain size and weight. Total soluble carbohydrate and soluble protein concentrations were negatively correlated with copper concentrations.

Wild rice (*Zizania aquatica* L. and *Z. palustris* L.) plants are annual emergent aquatic macrophytes which are economically important as a cereal crop in Canada. These plants grow wild in rivers and lakes of low to medium alkalinity and low chloride and sulphate, where organic matter is present (Dore 1969; Pip 1988). A few commercial growers cultivate the crop in enclosures where water levels and nutrients can be regulated, but most of the rice sold in Manitoba is harvested in natural environments. Besides substantial domestic consumption, hundreds of thousands of kilograms of wild rice are exported from Manitoba to international markets (Agro-Man 1984; Aiken *et al.* 1988). Wild rice also serves as food for waterfowl and other vertebrates, and contaminants in the grain may thus enter higher trophic levels.

Metal contamination of aquatic environments is increasing as effluent discharges and atmospheric deposition continue. Macrophytes may absorb metals through both roots and shoots (Mayes *et al.* 1977), and aerial deposition may be an additional source in emergent species. Wild rice often grows in acidic habitats where metals are relatively more available. Many natural stands constitute prime hunting areas because of the waterfowl they attract, and high concentrations of lead shot may be present in the sediments. Thus it is of interest to examine metal levels in this grain.

Few data exist regarding metals in wild rice. Behan *et al.* (1979) grew the plants in tanks treated with powdered lead and found that while shoot tissue achieved high lead concentrations, the fruits did not. They concluded that lead was not readily translocated in this macrophyte. The objective of the present study was to examine concentrations of cadmium, lead and copper in samples of wild rice available for public consumption in Manitoba.

Materials and Methods

Seventeen samples of husked, parched wild rice were purchased in stores in the form they would be used by the consumer, or donated by suppliers. Of these, 6 samples originated from lakes in southeastern Manitoba, 3 from northwestern Ontario, 4 from northwestern Manitoba, and 1 from northeastern Saskatchewan, Canada. One sample was a composite from several areas, and no information could be obtained about the remaining two.

Half-gram quantities of rice grains were washed in 1% nitric acid to remove surface contamination and digested for one hour in 1:1 v/v concentrated nitric acid and 30% hydrogen peroxide in closed test tubes set in a water bath at 60°C. Metals in the digestion liquor were measured with a PDV2000 digital anodic stripping voltameter (Chemtronics Ltd., Bentley, Australia). Three 100 μl aliquots were examined for each digestion, and up to 3 separate digestions were carried out for each rice sample. The standard additions method (*e.g.*, Mann *et al.* 1974) was applied to compensate for matrix absorption effects, and consisted of three incremental additions of metal (as certified atomic absorption standards (Fisher Scientific Co., Fair Lawn, New Jersey) to each aliquot of unknown or blank. A blank, consisting of all reagents and procedures less sample material, was run with every three rice unknowns.

Rice was ground to a powder in a small mill for total soluble carbohydrate (TSC) and soluble protein (SP) determinations. For TSC, 0.1 g of powder was extracted in 5 ml 80% ethanol for 24 h at 20°C. Carbohydrate content of the extract was determined for three 0.5 ml aliquots using Roe's (1955) anthrone method, expressed as units of equivalent glucose. For SP, 0.1 g of powder was incubated as above in 0.1 N NaOH. Soluble protein was determined in three 0.1 ml aliquots of each extract using the Coomassie Blue method (Bradford 1976).

The critical significance level for all statistical tests was $p = 0.05$.

Results

The ranges of parameters obtained for the 17 samples are summarized in Table 1. Values for both cadmium and copper showed a continuous range, and Kruskal-Wallis analysis of variance indicated significant differences among samples for cadmium (Chi-square = 44.6, $p = 0.0002$) and copper (Chi-square = 34.9, $p = 0.004$). Only seven samples showed mean cadmium concentrations of < 1 μg/g, the guideline for unpol-

Table 1. Summary of the ranges of mean values found for the 17 samples of wild rice examined

Parameter	Range
Cadmium, µg/g	<0.01–6.2
Lead, µg/g	<0.01–6.7
Copper, µg/g	1.6–14.4
Total soluble carbohydrate, mg eq glucose/g	6.3–15.4
Soluble protein, mg/g	20.2–41.4
Mean grain length, mm	8.3–18.8
Mean grain weight, mg	11.4–61.0

Table 2. Correlations between mean metal content per grain and grain size and weight. All variables log transformed. N = 17

Metal	Size	Weight
Cadmium	r = 0.44 p = 0.038	r = 0.48 p = 0.026
Lead	r = 0.70 p < 0.001	r = 0.58 p = 0.007
Copper	r = 0.65 p = 0.002	r = 0.68 p < 0.001

ished brown rice in Japan (Muramoto 1990). However, all but one of the samples yielded lead concentrations of <2 µg/g, and Duncan's multiple range test showed that the single sample that yielded a mean concentration of 6.7 µg/g (from a lake near Lac du Bonnet in southeastern Manitoba) was significantly different from all other samples.

Samples were grouped into those originating from southeastern Manitoba and northwestern Ontario (Region 1) and from northwestern Manitoba and northeastern Saskatchewan (Region 2). T-tests showed no significant differences between regions for cadmium or lead. However copper concentrations were significantly ($p = 0.003$) higher in Region 2 ($\bar{x} = 11.2 \pm 1.1$ S.E.) than Region 1 ($\bar{x} = 6.8 \pm 0.9$ S.E.).

Cadmium and lead concentrations were highly significantly linearly and positively correlated with each other ($p < 0.0001$), while cadmium and copper were inversely correlated ($p = 0.001$). Lead was not significantly correlated with copper ($p = 0.42$).

Mean grain size and weight were significantly correlated with each other ($r = 0.91$, $p < 0.0001$, $n = 17$). SP and TSC concentrations were marginally ($r = 0.43$, $p = 0.05$, $n = 16$) positively intercorrelated, suggesting that samples which were rich in soluble carbohydrate also tended to contain more soluble protein. TSC concentrations were inversely correlated with grain weight (weight log transformed) ($r = -0.48$, $p = 0.03$, $n = 16$), but correlation with size (size log transformed) was not significant ($r = -0.39$, $p = 0.07$); heavier grains contained less TSC per unit weight. SP concentration was not correlated with either size or weight of grains. T-tests showed no significant differences between Regions 1 and 2 for any of TSC, SP, grain size, or grain weight.

Of the three metals, only lead showed significant correlations (as µg/g), in each case positive, with grain size ($r = 0.55$, $p = 0.01$, $n = 17$) (both variables log transformed) and weight ($r = 0.46$, $p = 0.03$, $n = 17$) (both untransformed); larger and heavier grains tended to accumulate more lead per unit weight.

When mean metal content was examined per grain (as opposed to concentration per unit weight), metal content was positively correlated with grain size and weight for all three metals. These relationships appeared to be exponential (Table 2).

With respect to TSC and SP, copper concentrations (as µg/g) showed significant inverse correlations with each of SP ($r = -0.53$, $p = 0.017$, $n = 16$) (untransformed), and TSC ($r = -0.50$, $p = 0.024$, $n = 16$) (both variables log transformed). Thus samples which were carbohydrate and protein rich tended to contain less copper per unit weight. Cadmium and lead were not significantly correlated with TSC or SP.

Discussion

The ranges of values found for the metals in the wild rice grains were similar to concentrations reported in other macrophyte species in one of the lakes (Shoal Lake) (Pip 1990) from which the rice originated. Watts (1980 in Agro-Man 1984) compared the nutritional characteristics of wild and cultivated rice and found that wild rice contained more protein and copper, but less zinc and manganese, than cultivated brown rice. His value of 13 µg/g for copper in wild rice was within the range of values obtained in the present study.

Copper concentrations were significantly higher for samples from Saskatchewan and northwestern Manitoba, and soil copper levels were higher in this region as well. However, Lee and Stewart (1983) reported inverse correlations between sediment and leaf copper concentrations in wild rice. The results of the latter workers were supported for other macrophytes by Pip and Stepaniuk (1992), who found that shoot:sediment concentration ratios for cadmium, lead and copper increased as sediment metal concentrations decreased, suggesting that proportionately less uptake and/or retention occurred at higher sediment metal levels. This attenuation also appears to be true for terrestrial plants (Pip 1991). A contributory factor towards the higher copper levels in the rice from Region 2 may have been aerial deposition once the wild rice plants passed the submerged leaf stage. A large zinc-copper smelter is located at Flin Flon, in northwestern Manitoba, and it has been suggested for terrestrial plants in the Flin Flon region that leaf metal content is related to surface area of leaves exposed to metal fallout (Pip 1991). Unlike lead, copper is readily translocated in plants (Peter *et al.* 1979) and thus may enter the fruits.

Wild rice is graded and priced primarily on the basis of grain size and weight. It is interesting that, from a nutritional standpoint, larger grains contained less total soluble carbohydrate and more lead per unit weight than smaller grains. Grains with less soluble carbohydrate and protein accumulated more copper. Less soluble carbohydrate in the grains may reflect reduced vigor of the plants. Pip and Stepaniuk (1992), reported that copper concentrations were higher in Cyperaceae spp. infected with rust fungi than in uninfected plants. Thus, stress such as disease may be associated, through a mechanism yet unkown, with greater copper uptake and retention by some macrophytes. Wild rice is susceptible to a variety of fungal infections, as well as predation from insects and muskrats (Dore 1969; Aiken *et al.* 1988). Flooding also creates severe stress and causes declines in soluble carbohydrate levels in wild rice (Pip and Stepaniuk 1988). Other variables which may affect condition of the plants and metal uptake include sediment redox potential (Painchaud and Archibold 1990), nutrient availability, competition, length of the growing season and genetic factors:

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