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# Trace metals in wild rice sold in the United States

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## Abstract

North American wild rice (*Zizania aquatica* L. and *Z. palustris* L.) grows in moderately soft and acidic freshwater wetlands. With the increasing pollution of such a habitat, there is some concern that the trace metal contents of the rice crop have become unduly elevated. This study finds moderately elevated levels of lead (0.5–11.5 μg/100 g dry wt.), cadmium (1.0–10.2 μg/100 g dry wt.) and arsenic (0.6–14.2 μg/100 g dry wt.) in 26 brands of wild rice sold in the United States. The high concentrations of iron (2.0–9.7 mg/100 g dry wt.), copper (0.2–1.3 mg/100 g dry wt.) and zinc (0.1–0.4 mg/100 g dry wt.) suggest that wild rice may be a good dietary source of these essential elements.

*Keywords:* Wild rice; Softwater; Lead; Copper; Cadmium; Arsenic; Iron; Zinc

## 1. Introduction

Wild rice (*Zizania aquatica* L. and *Z. palustris* L.) is an annual aquatic macrophyte and a very distant relative of the common white rice (*Oryza sativa*). It is the only cereal native to North America and historically 'was the most nutritive single food which the Indians of North America consumed. The Indian diet of this grain, combined with maple sugar and with bison, deer and other meats, was probably richer than that of the average American family' (Jenks, 1901). At one time, wild rice grew naturally over a large portion of North America, from the Hudson Bay to the Gulf of Mexico and from the Rocky Mountains to the Atlantic Ocean (Jenks, 1901). The traditional center of wild rice production, the so-called 'wild rice bowl', however, is located between Lake Superior and southern Manitoba in Canada and the adjacent states of Wisconsin and Manitoba in the United States (Aiken et al., 1988). In Canada, most of the wild rice production is still from natural stands but in the United States, as much as 90% of the processed wild rice sold is grown by paddy culture (Vennum, 1988). Between 1970 and 1984, the production of wild rice in the United States and Canada grew at a rate of 42%/year and reached 6.4 million kg in 1985 (Aiken et al., 1988). Since then, wild rice has become even

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more popular as a culinary delight. An international export market has been developed and grains with better cooking properties have been engineered (Vennum, 1988). It is estimated that wild rice production in North America now exceeds 20 million kg/year.

Wild rice is rich in protein (10–15% dry wt.), carbohydrates(70–80% dry wt.), crude fiber (0.5–3% dry wt.), vitamin B complex (especially niacin and riboflavin), iron, potassium and phosphorus (Anderson, 1976; Vennum, 1988). It is low in fat (< 5%) and starch and calories. Its nutritional value is believed to be higher than those of the 'tame' grasses (wheat, oats, barley, rye and corn) (Vennum, 1988). Its anti-oxidant properties have recently been reported (Katsanidis et al., 1994; Wu et al., 1994).

Wild rice has a distinctive nut-like flavor which endears it to gourmet cooking. It is considered a natural food and has become popular with health food enthusiasts who believe that the natural stands are unspoiled by agrochemical residues. Most of the commercial production of wild rice is retailed as a mixture with white or brown rice — the mixture has a different color, texture and aroma.

Wild rice grows best in shallow waters along the shores of rivers and streams and in low marshy areas surrounding the inlet and outlet of lakes (Jenks, 1901). In general, it will not grow well in landlocked stagnant ponds and cannot tolerate fast moving waters (Vennum, 1988). The quality of the water is also a critical factor in its growth. It prefers lakes and rivers with low to medium alkalinity, low sulfate and low chloride concentrations. The ideal substrate tends to be acidic (pH of 5–7) and rich in organic matter (Lee and Stewart, 1984).

In the relatively soft and acidic waters preferred by wild rice, one would expect the trace metals to be mobile and in a more available form to the plants. Many streams and lakes where the wild rice grows have become heavily contaminated with industrial and municipal discharges (Vennum, 1988). Substantial aerial inputs of toxic metals have become common in most of the growing areas (Nriagu and Davidson, 1986). The pollutant metals released from the watershed are concentrated in the alluvium of the wild rice fields (Chen, 1992). Birds of all kinds, especially waterfowl, feed on wild rice. It has been recognized as a principal autumn food for ducks and geese and has been planted as a lure for these game birds (Jenks, 1901; Chambliss, 1940). Wild rice fields thus represent prime hunting grounds where large quantities of lead shot have been discharged (Pip, 1993).

There is growing concern that the widespread contamination of the wild rice habitat may have resulted in elevated levels of toxic metals in the grains. Accumulation of toxic metals in wild rice represents a potential health hazard to the wildlife and the human consumer. A recent study of wild rice grains available for sale in Canada found that about 60% of the samples had Cd concentrations above 1.0 μg/g (Pip, 1993), the guideline for unpolished brown rice in Japan (Muramoto, 1990). High concentrations of lead (< 0.01–6.7 μg/g) were also reported in Canadian wild rice (Pip, 1993). We are not aware of a comparable study on trace metals in the wild rice of the United States. This report presents the concentrations of Pb, Cd, As (a metalloid traditionally included among the toxic 'metals' of environmental concern), Cu, Fe and Zn in samples of wild rice sold for public consumption in the Midwestern region of the United States.

## 2. Samples and methods

Twenty six wild rice samples were purchased from retail stores in southeastern Michigan. Nine of the samples consisted of mixtures of wild rice with long-grain white or brown rice; the wild rice grains which make up 8–15% of the mixtures were picked out by hand. The other 17 samples consisted of either individual wild rice packages or small quantities from bulk supplies sold in health food stores. The labels on the packages showed that three of the samples were from Minnesota, four from California, three from Saskatchewan (Canada) and the exact origin of the other samples (especially the mixtures) could not be determined.

The samples were air-dried overnight at 60°C and then ground in a small mill. One-gram aliquots of each sample were digested with concentrated nitric acid in the high pressure vessel of

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a microwave digestion system. At the end of the digestion cycle, a clear brown liquid was obtained which was diluted to 25 ml. Each batch of 12 samples digested included the Reference Rice Flour (US National Institute of Standards and Technology Reference Material No. 1568a).

The concentrations of trace metals in dissolved wild rice were determined by means of a graphite furnace atomic absorption spectrometer equipped with a Zeeman background corrector (Perkin Elmer 4100ZL). The reproducibility in the digestion and analysis of the samples is estimated to be ± 10% of the reported values.

## 3. Results and discussion

The concentrations of lead in the samples are moderately elevated (Table 1), the mean value being 4.2 μg/100 g dry wt. (or 42 ng/g dry wt.) and the range is 0.5–11.5 μg/100 g dry wt. There is no obvious difference in lead contents of the pure brands and the mixed grains. The current values are much lower than the < 1.0–670 μg/100 g dry wt. reported for Canadian wild rice (Pip, 1993). The difference may be related to the fact that most of the wild rice grains sold in Canada are harvested from natural stands whereas paddy culture dominates the US production (Vennum, 1988; Aiken et al., 1988). Our average for wild rice is higher than the mean value of 0.8 μg Pb/100 g dry wt. for raw rice (*Oryza sativa*) from major US growing areas uncontaminated by human activities other than normal agricultural practices (Wolnik et al., 1983, 1985). The fivefold difference in Pb contents of the wild and white rice presumably reflects the difference in the level of contamination of the habitats for these crops in the United States. The fact that grain crops do not bioconcentrate lead in their seeds is well established and may explain the still low levels of Pb even in wild rice grown in contaminated environments. Behan et al. (1979), for instance, found low concentrations of lead in seeds of wild rice plants grown in tanks treated with powdered lead.

The concentrations of Cd in the samples are also elevated; the range is 1.0–10.2 μg/100 g dry wt. with the mean being 5.3 μg/100 g dry wt. (Table 1). These values are lower than the < 1.0–620 μg/100 g dry wt. in the Canadian wild rice (Pip, 1993). Cultivation in pond enclosures with better control of water quality may also be a factor in the low Cd concentrations found in the US wild rice. Wolnik et al. (1985) found that the concentrations of Cd in 'tame' rice grown in the US averaged only 1.3 μg/100 g dry wt. Numerous studies in Asia and elsewhere have shown that Cd contamination in the environment is readily transferred to the rice (*Oryza sativa*) grains (Kloke et al., 1984; Adriano, 1986). The present data suggest that wild rice plant shares this ability to translocate Cd along its tissues. As is the case for Pb, the higher concentrations of Cd in the wild rice compared to white rice may be related to the fact that the wild variety is mainly grown in areas with a long history of trace metal pollution. It should be noted that the allowable levels of Cd in white rice grain is 40 μg/100 g in mainland China, 50 μg/100 g in Taiwan and 100 μg/100 g in Japan (Chen, 1992). The concentrations of Cd in wild rice grown in the United States are still below these guideline values.

The concentrations of As in the samples range from 0.6 to 14 μg/100 dry wt. (Table 1) and average 6.6 μg/100 g dry wt. We are not aware of any recent measurements of As in wild rice in the United States. The rice plant is a member of the silicicolous Gramineae family that selectively accumulate silicon. The silicon content of rice plants can reach 5–20% at harvest depending on the availability of silicon in soils (de Lumen and Chow, 1991). The concentrations of Si in six varieties of milled white rice averaged 46 mg/100 g dry wt. with the range being 13–100 mg/100 dry wt. (de Lumen and Chow, 1991). Phosphorus is also one of the most abundant elements in rice, typical concentrations in wild rice being 250–500 mg/100 g dry wt. (Vennum, 1988; Aiken et al., 1988). Arsenic and phosphorus and, to a lesser extent, Si show a strong natural affinity in their biogeochemical behavior especially in aquatic ecosystems (Azcue, 1993). One would therefore expect a high accumulation potential for As in wild rice. The low As concentrations in the samples analyzed is somewhat surprising and conceivably may be due to some physiological exclusion processes in the wild rice plant or to low levels of As in the habitat.

Table 1
Trace metals in various brands of wild rice sold in the United States

| Sample No. | Description | Cd ( μg/100 g) | Pd ( μg/100 g) | As ( μg/100 g) | Cu (mg/100 g) | Zn (mg/100 g) | Fe (mg/100 g) |
|---|---|---|---|---|---|---|---|
| 1 | National brand, 4.2-oz mixture of long grain (LG) and wild rice (WR) | 5.23 | 9.51 | 4.39 | 1.22 | 3.26 | 3.46 |
| 2 | National brand, 4.5-oz mixture of LG and WR | 5.21 | 3.63 | 9.55 | 1.05 | 2.36 | 3.36 |
| 3 | 'Extra fancy' WR, 6-oz package | 7.60 | 1.79 | 6.73 | 1.12 | 2.86 | 2.34 |
| 4 | WR, 8-oz package | 3.29 | 7.34 | 3.15 | 1.12 | 2.47 | 5.42 |
| 5 | LG and WR mixture with seasoning | 1.03 | 2.48 | 11.64 | 0.91 | 1.87 | 3.23 |
| 6 | WR and 'premium' brown rice | 4.41 | 2.80 | 10.19 | 0.89 | 2.44 | 2.03 |
| 7 | Bulk food WR sample | 4.60 | 3.40 | 10.92 | 0.58 | 2.11 | 2.01 |
| 8 | LG and WR with spices | 6.84 | 3.40 | 4.18 | 0.69 | 2.24 | 3.31 |
| 9 | LG and WR pilaf | 3.58 | 4.02 | 8.34 | 1.24 | 2.03 | 3.76 |
| 10 | WR, 5-oz package | 10.18 | 5.48 | 2.29 | 1.32 | 2.08 | 2.99 |
| 11 | WR, 12-oz package | 2.81 | 5.32 | 0.66 | 0.36 | 1.8 | 26.47 |
| 12 | Bulk food WR sample | 5.98 | 3.61 | 8.37 | 1.07 | 2.0 | 32.94 |
| 13 | National brand, LG and WR, 6-oz mixture | 7.93 | 4.63 | 10.12 | 1.14 | 1.58 | 6.02 |
| 14 | WR, 5-oz package | 4.78 | 5.27 | 7.45 | 1.31 | 2.37 | 4.88 |
| 15 | 'Paddy grown' WR, 4-oz | 8.60 | 3.81 | 9.64 | 0.27 | 0.66 | 0.65 |
| 16 | Bulk food WR sample | 5.13 | 1.88 | 8.79 | 0.45 | 1.12 | 3.04 |
| 17 | LG and WR, 5-oz mixture | 6.98 | 4.88 | 8.87 | 0.72 | 2.05 | 5.02 |
| 18 | WR, 4-oz package | 3.86 | 5.41 | 3.93 | 1.03 | 1.73 | 3.52 |
| 19 | WR, 4-oz package | 2.79 | 2.14 | 5.73 | 0.81 | 1.75 | 2.58 |
| 20 | WR, 8-oz package | 2.61 | 0.49 | 2.18 | 0.74 | 2.29 | 2.36 |
| 21 | Locally mixed LG and WR, 14-oz bag | 7.73 | 1.65 | 0.76 | 0.98 | 3.92 | 2.04 |
| 22 | Bulk food WR sample | 5.60 | 0.95 | 1.27 | 0.91 | 3.61 | 1.96 |
| 23 | Bulk food WR sample | 0.99 | 7.34 | 8.97 | 0.45 | 3.76 | 5.42 |
| 24 | WR, 16-oz package | 4.03 | 3.20 | 14.20 | 1.22 | 2.3 | 43.71 |
| 25 | LG and WR, 6-oz mixture | 9.57 | 11.46 | 9.36 | 0.83 | 3.54 | 3.05 |
| 26 | WR, 6-oz package | 7.08 | 1.88 | 0.57 | 0.26 | 2.12 | 2.44 |
|  | Average | 5.32 | 4.15 | 6.63 | 0.87 | 2.32 | 3.39 |

Wild rice is often advertized as an important dietary source of iron. The high concentration of Fe (range 0.65–6.4 mg/100 g dry wt.) found in this study tends to confirm this widely held view. The current data are similar to those of other studies which generally found the Fe concentrations to be in the range of 1–5 mg/100 g dry wt. (Anderson, 1976; Vennum, 1988). The concentrations of Fe in white rice grown in the US average only 0.4 mg/100 g (Wolnik et al., 1985), implying that wild rice has a more nutritive value for Fe than the 'tame' variety. It should, however, be noted that the mean Fe content of the samples studied (3.6 mg/100 g dry wt.) is lower than the average values observed in onions, spinach, field corn and tomatoes harvested in various areas of the United States (Wolnik et al., 1985).

The Cu concentrations in our samples (mean 0.9 mg/100 g and range 0.3–1.3 mg/100 g dry wt.) are similar to the values of 0.16–1.4 mg/100 g dry wt. reported for the Canadian wild rice (Pip, 1993). It is also interesting that white rice (0.21 mg/100 g average), field corn (0.18 mg/100 g dry wt.), onions (0.36 mg/100 g dry wt.), spinach (0.86 mg/100 g dry wt.), and tomatoes (1.0 mg/100 g dry wt.) grown in the United States all have similar Cu contents (Wolnik et al., 1985). Copper is phytotoxic and it would appear that a homeostatic mechanism is used to limit the Cu uptake to what the vegetable crops essentially need.

The Zn contents of the samples range from 1 to 4 mg/100 g (Table 1) and average 2.3 mg/100 g dry wt. The current results are in the range of 3–6 mg/100 g dry wt. reported by Anderson (1976) and Vennum (1988). A study done in Manitoba, Canada showed that wild rice contained less Zn than cultivated brown rice (Agro-Man, 1984). This observation is inconsistent with the lower Zn concentrations (mean 1.5 mg/100 g, range 0.97–2.2 mg/100 g dry wt.) in white and brown rice grown in various agricultural fields of the United States (Wolnik et al., 1985). Our results suggest that wild rice may also be a good nutritional source of Zn.

Pip (1993) found a significant linear relationship between Pb and Cd and an inverse relationship between Cu and Cd in the samples that were analyzed. The present study finds no significant relationships between any pair of elements (Table 2). The concentrations of trace metals in wild rice can be affected by plant factors (such as growing season and genetic factor), water chemistry, soil characteristics as well as the source and form of the metal input into the particular habitat (Adriano, 1986). The lack of significant correlations between metals suggest that there is no dominant pathway in the transfer of the metals from the different environmental media to the wild rice grains.

Table 2
Correlation coefficients between the various trace metals in wild rice samples

| Element | Correlation coefficient ($R$) | | | | | |
|---|---|---|---|---|---|---|
| | Zn | Cd | Pb | Cu | As | Fe |
| Cd | 0.001 | | 0.132 | 0.083 | 0.110 | 0.226 |
| Pb | 0.235 | 0.135 | | 0.154 | 0.106 | 0.363 |
| Cu | 0.324 | 0.083 | 0.154 | | 0.036 | 0.086 |
| As | 0.295 | 0.110 | 0.034 | 0.036 | | 0.150 |
| Fe | 0.198 | 0.226 | 0.36 | 0.086 | 0.150 | |

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