

## Metal Burdens in Two Species of Fiddleheads Growing near the Ore Smelters at Sudbury, Ontario, Canada

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The usefulness of selected plant species as potential bioindicators of environmental metal pollution has been clearly demonstrated. High levels of contamination within soils of the Sudbury, Ontario region location of one of the world's largest copper-nickel mining/smelting operations with a current rated production capacity of I77 x 106 kg Ni vr-1 - are characteristically reflected in elevated plant burdens reported for the area (Hutchinson and Whitby 1974, McIlveen and Balsillie 1978). Previous studies investigating plant uptake of metals from Sudbury-area soils have been complicated, however, by the contribution of direct atmospheric deposition onto the foliage (Hutchinson and Whitby 1974. Freedman and Hutchinson 1980). The present study examines metal burdens in two fern species, Interrupted fern and Ostrich fern, resulting solely via root uptake from the soil, thus seeking to assess the indirect influences of the Sudbury-area smelters. The above condition was ensured by collecting the ferns immediately after appearance in the spring while they were still tightly curled and protected from aerial contamination by the external wooly pubescence. The latter species is of particular interest as it is widely recognized as an edible wild vegetable when harvested during this fiddlehead or crozier stage of development (Fernald and Kinsey 1958, Cruise 1972, Peterson 1978, Szczawinski and Turner 1980, Prange and vonAderkas 1985).

## MATERIALS AND METHODS

Newly-emerged fronds (fiddleheads) of Interrupted fern (Osmunda claytoniana) and Ostrich fern (Matteuccia struthiopteris) were collected as available from three experimental and two control sites. Experimental sites were located NE (Skead), N (Val Caron) and NW (Chelmsford) at a common distance (I5-25 km) from the Copper Cliff smelter (Fig. I). Sites located 155 km N (Gogama) and 130 km SW (Manitoulin Island) served as controls.

The fronds were collected by breaking the stalk close to the leaf base.

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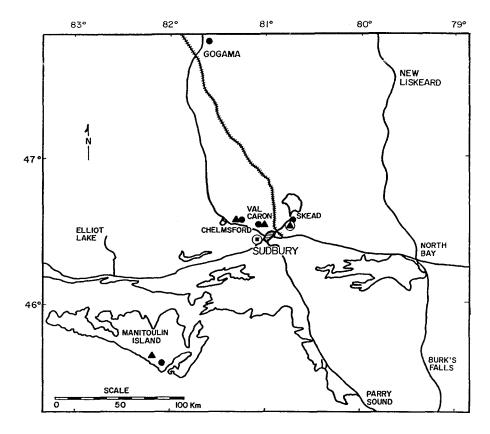


Figure 1. Map showing the location of sampling sites for Interrupted fern ( ) and Ostrich fern ( ) in relation to the ore smelters at Copper Cliff ( ) and Falconbridge ( ) near Sudbury, Ontario.

The pubescent sheath enclosing each frond was removed by hand and excluded from the sample. Each sample consisted of 12 or more fiddleheads (averaging approximately 15 cm in height) collected within an area restricted to  $< 5 \text{ m}^2$ .

Samples were oven dried for 48 hours at 45°C and subsequently homogenized using a Wiley plant mill. Approximately one gram (to the nearest mg) of the resultant powder was digested over heat using a 20:20:I mixture of HCl04, HNO3, and H2SO4. Sample residues were subsequently redissolved in 5 ml of 1% HNO3 in preparation for determination of metal content.

Concentrations of Pb, Fe, Zn, Cd, Cu and Ni in the digested samples were determined by flame atomic absorption spectrophotometry using a Perkin-Elmer 703 spectrophotometer, in accordance with procedures outlined by Perkin-Elmer (1976). The procedure employed enabled quantification of the Cd, Zn, Fe, and Cu levels of all samples. Samples

exhibiting Pb or Ni levels below detection limits (n=13 and n=2 respectively) were assigned values of 0.0  $\mu g.g^{-1}$  for that metal.

Metal levels in each species were evaluated using a one-way analysis of variance by site. The data were appropriately transformed to meet the assumptions of both normality and homogeneity of variance, deviations from which were tested using the Kolmogorov-Smirnov Test for Goodness of Fit and Bartlett's Test for Homogeneity of Variance respectively (Sokal and Rohlf 1981). Significantly different subgroups were identified using Duncan's Multiple Range Test. Between-species comparisons were performed using t-tests. All differences were deemed significant at p < 0.05.

In accordance with Sokal and Rohlf (1981), mean metal concentrations reported below are the back-transformed values followed by the 95% confidence interval. All metal concentrations are expressed in micrograms per gram ( $\mu g.g^{-1}$ ) of oven dry sample.

## RESULTS AND DISCUSSION

Mean concentrations of Ni, Cu, Cd, Zn, Fe and Pb in Interrupted fern and Ostrich fern fiddleheads are presented in Table 1.

Interrupted fern samples collected from sites in the vicinity of the Sudbury smelters showed elevated levels of Ni, Cu, Cd and Zn compared to respective levels at control sites. A similar, although less consistent, pattern of metal enrichment was likewise noted in Ostrich fern samples collected near the smelters. For two of the six elements examined, namely Fe and Pb, significant site differences were noted but no clear pattern indicative of smelter influence was apparent for either species.

Endogenous uptake from elevated soil burdens is believed to account for the enhanced metal levels observed in the Sudbury-area fiddleheads. That substantially elevated levels of Cu and Ni, and to a lesser extent Cd, Pb and Fe, characterize soils of the Sudbury region and those falling within a 60-km radius of the Copper Cliff smelter in particular has been well documented (Hutchinson and Whitby 1974; Whitby et al. 1976, Hazelett 1984). Uptake and accumulation of these metals by plants growing in the enriched Sudbury soils has been demonstrated in a wide variety of species including the Bracken fern studied by McIlveen and Balsillie (1978). Although direct external contamination by airborne smelter emissions, soil dusts, or contaminated biota cannot be unequivocally ruled out, uptake via such routes would appear highly improbable given that the newly-emerged frond had been shielded by the external pubescent sheath which was removed at the time of collection and excluded from the sample.

Table 1. Metal concentrations ( $\mu g.g^{-1}$  dry wt) in two fern species collected near the ore smelters at Sudbury, Ontario.

METAL	INTERRUPTED FERN		OSTRICH FERN		
Site	mean	(95% C.I.)		mean	(95% C.I.)
Nickel		•			
Skead	10.8 <sub>b</sub>	(8.6-13.4)			
Val Caron	8.4 <sub>b</sub>	(6.2-11.3)	< '	110.9 <sub>t</sub>	(83.9-146.5)
Chelmsford	1.9 <sub>a</sub>	(1.2-2.8)	<	11.4 <sub>8</sub>	(8.9-14.4)
Gogama*	1.0 <sub>a</sub>	(0.3-2.1)			(0.0.0.)
Manitoulin Is*	1.9 <sub>a</sub>	(1.3-2.7)	=	1.5 <sub>r</sub>	(0.6-2.9)
Copper Skead	61.4 <sub>d</sub>	(51.6-73.0			
Val Caron	50.9 <sub>c</sub>	•		46.6	(43.0-50.6)
	•	(44.7-58.0)	=	46.6 <sub>t</sub>	,
Chelmsford	29.2 <sub>b</sub>	(27.2-31.4)	>	18.9 <sub>r</sub>	(17.6-20.3)
Gogama* Manitoulin Is*	9.7 <sub>a</sub> 8.4 <sub>a</sub>	(8.1-11.5) (7.4-9.5)	<	26.4 <sub>s</sub>	(23.8-29.2)
Cadmium	0.4a	(7.4-3.5)	`	20.45	(20.0-20.2)
Skead	3.5 <sub>b</sub>	(2.8-4.2)			
Val Caron	4.2 <sub>b</sub>	(3.6-4.9)	=	4.3 <sub>t</sub>	(3.7-4.9)
Chelmsford	$3.9^{\circ}_{b}$	(3.4-4.5)	>	1.3s	(1.1-1.5)
Gogama*	1.5 <sub>a</sub>	(0.9-2.3)			
Manitoulin Is*	1.3 <sub>a</sub>	(1.1-1.6)	>	0.9 <sub>r</sub>	(0.8-1.0)
Zinc	75.0	(74.0.00.4)			
Skead	75.6 <sub>b</sub>	(71.2-80.1)		72.6	 (70 7 76 E)
Val Caron Chelmsford	78.5 <sub>b</sub>	(74.4-82.8)	>	73.6 <sub>s</sub>	(70.7-76.5) (53.1-57.3)
	89.0 <sub>c</sub>	(85.6-92.6)	>	55.2 <sub>r</sub>	(55.1-57.5)
Gogama*	27.2 <sub>a</sub>	(19.7-36.7)	_	60.4	 (64.2.74.0)
Manitoulin Is* Iron	26.5 <sub>a</sub>	(24.3-28.9)	<	69.4 <sub>s</sub>	(64.3-74.9)
Skead	40.5 <sub>a</sub>	(36.1-45.5)			
Val Caron	67.3 <sub>b</sub>	(61.2-73.9)	=	$70.0_{r}$	(63.8-76.8)
Chelmsford	68.1 <sub>b</sub>	(60.8-76.2)	<	110.2 <sub>s</sub>	(103.4-117.5)
Gogama*	49.3a	(35.0-69.4)			·
Manitoulin Is*	64.4 <sub>b</sub>	(54.5-76.1)	<	$118.3_{s}$	(91.6-152.6)
Lead		(0.7.4.7)			
Skead	1.1 <sub>b</sub>	(0.7-1.7)	_	0 E	(0.0.1.0)
Val Caron	1.2 <sub>b</sub>	(0.9-1.6)	>	0.5 <sub>r</sub>	(0.2-1.0)
Chelmsford Gogama*	0.6 <sub>a</sub>	(0.4-0.8) (0.2-3.7)	=	0.5 <sub>r</sub>	(0.1-1.0)
Manitoulin Is*	1.1 <sub>abc</sub> 2.1 <sub>c</sub>	(1.4-3.2)	=	0.9 <sub>r</sub>	(0.3-2.2)
Maintouin 13	· · · C	(1.4 0.2)	_	0.01	(0.0 1.1)

<sup>\*</sup>indicates control sites; within each metal x species group, site means bearing the same subscript are not significantly different (p > 0.05) as determined from ANOVA followed by Duncan's Multiple Range Test; inter-specific equalities and differences are based on t-test comparisons at each individual site; n=10-12 except at Gogama site where n=5-6.

Site comparisons for those elements showing smelter-related elevations revealed that in seven out of eight cases, plant burdens at the three experimental sites ranked in the following order: Skead  $\geq$  Val Caron  $\geq$  Chelmsford. The trend toward significantly greater elevations in plants at the NE (Skead) and N (Val Caron) sites is believed to reflect the higher level of airborne fallout and contamination accrued at these sites owing to the north-easterly direction of prevailing winds within the area. A similar north-easterly bias has been shown to characterize the SO<sub>2</sub> fumigation zones and metal fallout patterns prevailing in the vicinity of the Sudbury-area smelters (Dreisinger and McGovern 1971, Semkin and Kramer 1976).

Failure to observe well-defined patterns of Fe and Pb enrichment in the Sudbury-area plants may reflect natural variability in soil metal burdens and/or selectivity in metal uptake responses. Substantial variability in both Fe and Pb levels present, as indicated by the relatively large confidence intervals, was noted even amongst the control samples collected from noncontaminated sites. In view of the ubiquitous nature of Fe in soils, such marked variability may reflect highly-localized iron-contaminating conditions both within and between the study sites investigated. A low plant uptake of iron in the presence of high Ni concentration is also known to occur in certain species (Mishra and Mar 1974). Variability in soil Pb profiles with potential to confound any apparent effect of the Sudbury smelters on fern levels may relate to site differences in environmental Pb contamination resulting from other anthropogenic sources including traffic emissions (see Smith 1976).

In a comparable study on Bracken fern, McIlveen and Balsillie (1978) reported elevated levels of both Ni and Cu in plants collected in the vicinity of the Sudbury-area smelters. Concentrations declined with increased distance along a NE transect from the stacks. As in the present study, plants collected in the vicinity of the smelters failed to indicate elevated levels of either Fe or Pb (likewise Zn).

Species comparisons generally indicated comparable to only modestly-differing metal levels in plants at the noncontaminated Manitoulin site. Amongst the most striking species differences noted, however, was the substantially higher levels of Ni accumulated by the Sudbury-area Ostrich ferns; levels in Chelmsford and Val Caron fronds exceeded background levels by factors of 7 and 72 respectively whereas elevations in Interrupted fern at the Val Caron and Skead sites reached only 5 to 6-fold increases. The approximately 10-fold higher levels noted in the Ostrich fern fiddleheads suggest that this species is an accumulator species with considerable potential as an effective and sensitive biomonitor of environmental Ni burdens.

Hohne and Richter (1981) examined the mineral content of Ostrich fern from a natural habitat in Germany and reported concentrations of 877  $\mu g.g^{-1}$  for Fe, 66  $\mu g.g^{-1}$  for Zn and 6.2  $\mu g.g^{-1}$  for Cu. In other samples

obtained from botanical gardens in the area, mean concentrations of 836 (range 375-1250)  $\mu g.g^{-1}$  Fe, 59 (range 33-125)  $\mu g.g^{-1}$  Zn and 4.9 (range 4.6-5.4)  $\mu g.g^{-1}$  Cu were observed. Stetsenko and Tabachnyi (1984) reported Fe, Zn, Cu and Ni values of 14000, 100, 60 and 36  $\mu g.g^{1}$  respectively in Ostrich fern fiddleheads collected from a botanical garden in Kiev. Whereas mean Zn, Cu and Ni values of the present study fall within the ranges reported by these earlier workers, Fe values reported here are substantially lower. Reasons for the more than 100-fold disparity in Fe values between studies are not clear; however, the possibility that such discrepancies reflect differences in the mineralogy of the areas involved cannot be ruled out.

For the most part, metal levels within the two fiddlehead species examined fell well below levels considered to be "excessive" for plant Guidelines established by the Ontario Ministry of the Environment (Feb 1986) as indicative of contamination above average normal levels but not necessarily reflecting toxic concentrations have been set at 30 μg.g-1 Cu, 800 μg.g-1 Fe, 100 μg.g-1 Pb, 30 μg.g-1 Ni, μg.g-1 Zn and 5 μg.g-1 Cd. Thus, whereas Pb, Zn, Fe and Cd levels observed in ferns of the present study were well below the MOE guidelines, the Cu and Ni guidelines were exceeded on several occasions. Interrupted fern contained excessive levels of Cu at Skead, Val Caron and Chelmsford (100%, 100% and 50% of the samples respectively). Excessive Ni and Cu concentrations were found in 100% of the Ostrich fern sampled at Val Caron. Although the effects of consuming fiddleheads containing excessive levels of Ni and/or Cu presently remain unknown, it is recommended that caution be exercised in collecting fiddleheads for human consumption from sites of known or suspected environmental contamination by metals.

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