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Cadmium Concentrations in a Boreal Forest Ecosystem After Application of Wood Ash

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More than 100, 000 tons of wood ash are generated annually in the Finnish industry. Currently most of the ash is transported to landfills although it contains useful minerals and has a positive effect on soil pH. Application of wood ash in forestry would be a way of recycling nutrients but the contents of cadmium and other harmful substances may limit the use of wood ash as fertilizer.

The concentrations of cadmium vary widely between tree and shrub species and between different parts of trees. High concentrations are found e.g. from willow (*Salix*) species. Cadmium concentrations in wood ash typically vary between 1 and 20 μg g^{-1} ash (Korpilahti et al. 1998) and often exceed the level allowed for fertilizers used in agriculture.

MATERIALS AND METHODS

Concentrations of cadmium were studied in a forest ecosystem in Evo, south Finland (61° 14' N, 25° 12' E). Study plots were established on catchments of two small forest lakes. The study areas included plots treated with wood ash as well as untreated control plots. 4.8 t ha^{-1} of wood ash were applied in February 1998. As it contained 9.2 μg Cd g^{-1} it resulted in an input of 44 g Cd ha^{-1}, which amount is more than tenfold compared to the annual atmospheric deposition. Ash application also increased the soil pH.

Samples were collected from mineral and peat soil, fruiting bodies of mycorrhizal fungi, earthworms (*Dendrobaena octaëdra*), small mammals (bank vole - *Clethrionomys glareolus* and common shrew - *Sorex araneus*) and bird eggs (great tit - *Parus major* and pied flycatcher - *Ficedula hypoleuca*) were collected in 1999 and 2000.

Soil samples were analyzed for total cadmium and by sequential fractionation resulting in the following fractions of differently bound cadmium:
– "Total Cd": 0.5 g mineral soil or 0.25 g peat soil extracted with 10 ml HNO_3 in microwave oven according to EPA method 3051,
– "Water soluble Cd": 50 ml deionized H_2O, shaking for 1h,

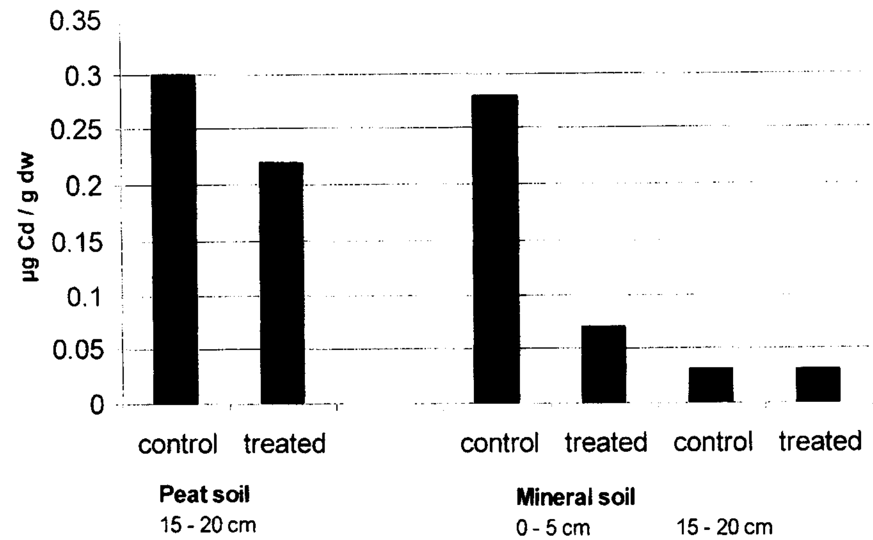


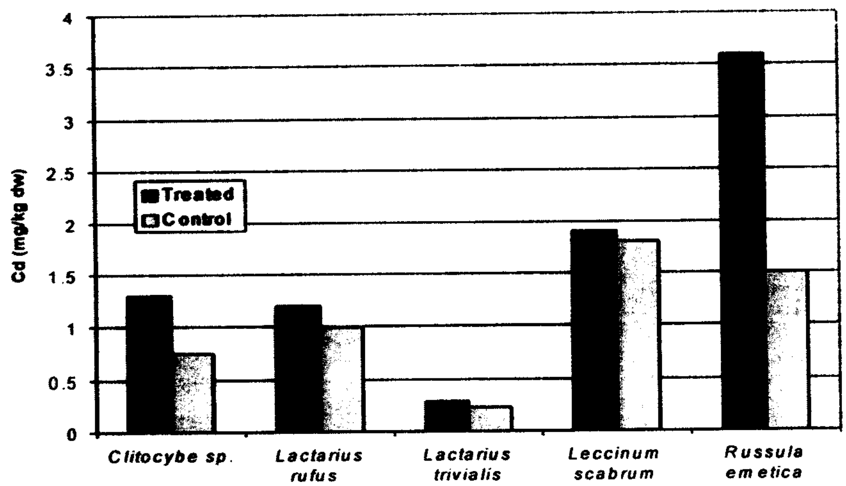
Figure 1. Exchangeable cadmium (KNO_3 extraction) in soil from treated and untreated plots (three pooled samples consisting of six subsamples from each plot; topsoil from peat soil plots excluded as they consisted of living *Sphagnum* moss)

- "Exchangeable Cd": 25 ml KNO_3, shaking for 1 h (repeated four times, supernatants combined),
- "Organically bound Cd": 50 ml 0.5 M NaOH, shaking for 16 h,
- "Oxide bound Cd": 50 ml 0.1M NH_2OH HCl, pH 2, shaking for 30 min,
- "Residual Cd" = calculated as Total – above mentioned fractions.

Cadmium concentrations were analyzed by using graphite furnace AAS and the accuracy was tested using a standard reference material (Bovine liver NIST SRM 1577a) with a certified concentration of 0.44 $\pm$ 0.06 µg g^{-1} for which we obtained 0.45 $\pm$ 0.01 µg g^{-1} (N = 6, determination limit = 0.01 µg g^{-1}; Lodenius *et al.* 2002b).

RESULTS AND DISCUSSION

No clear differences in cadmium concentrations were found between control and treated plots from soil samples. Almost no cadmium could be extracted by water (water soluble Cd) or hydroxyl ammonium chloride (oxide bound Cd). The total amounts of exchangeable cadmium (KNO_3 extraction) in peat and mineral soils were higher at control plots compared to treated plots (Figure 1). At the treated plots the pH of the top soil (0-5 cm) had increased to a level near that of the bottom soil (15-20 cm) and the exchangeable fraction of cadmium in the humic layer was significantly lower (p=0.036) than at the untreated plots. A larger proportion of the top soil cadmium was in the organic fraction (NaOH extraction) at the treated plots compared to the control plots. There was a wide variation in



N	10+10	6+6	5+5	8+8	5+5
p (AOV)	0.269	0.710	0.566	0.630	0.042

Figure 2. Mean cadmium concentrations in fungi collected from treated and untreated areas.

the results from the treated areas, which is obviously due to the uneven spreading of the ash (A. Kepanen, M. Lodenius, E. Tulisalo & H. Hartikainen: Solubility of wood ash -derived Cd in forest soils. Submitted manuscript).

The mean cadmium concentration of earthworms was insignificantly higher at treated plots (5.4 ± 2.0; N=14) compared to 4.2 ± 1.5 (N=25) µg g^{-1} at untreated plots. Earthworms and insects play an important role as food items of shrews (Pernetta 1976, Saarikko 1989) and may thus affect the cadmium concentrations of these animals.

In most cases the cadmium concentrations of fungi were higher at treated plots compared to control plots (Lodenius *et al.* 2002a; Figure 2) but the differences were small and usually statistically insignificant. The cadmium levels found in Evo are similar to results from comparable areas (Kuusi et al. 1981, Rühling 1996). Results from other ash application experiments (Rühling 1996, Moilanen and Issakainen 2000) indicate that no significant changes will occur even after longer periods of time. This may partly be a result of decreasing mobility in connection with increasing pH after ash application.

The cadmium concentrations in small mammals from our study area are much lower than the levels in contaminated areas (Hunter *et al.* 1989, Read and Martin 1993) and do not significantly differ from those found from unpolluted Finnish areas (Pankakoski *et al.* 1994, Ukonmaanaho *et al.* 1998). In bank voles (subadult specimens) the cadmium concentrations were significantly lower (p=0002, 0.001 and 0.019 for muscle, liver and kidney respectively) at the treated plots compared

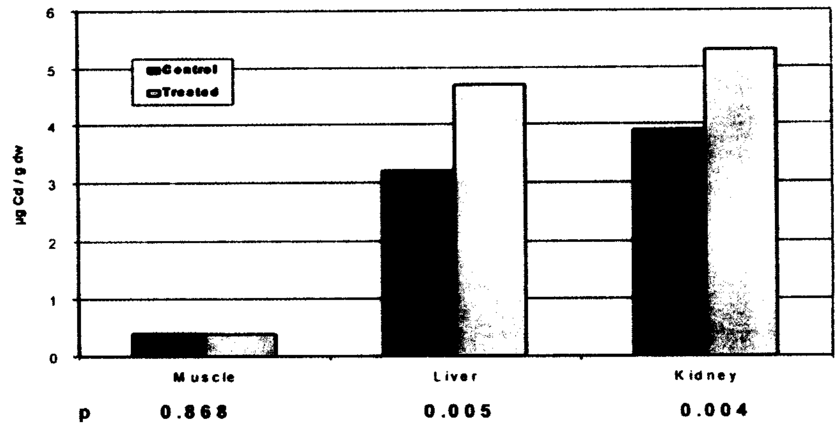


Figure 3. Cadmium concentrations in muscle, liver and kidney of juvenile common shrews from treated and untreated areas (N=38+38).

to control plots. In common shrews the cadmium concentrations were significantly higher (p=0.005 and 0.04 for liver and kidney in juvenile shrews respectively) at the treated plots compared to control plots (Lodenius *et al.* 2002b; Figure 3). The reasons for a simultaneous decrease in voles and increase in shrews remain unclear. An increase in soil pH may decrease the solubility of cadmium even when the total amount of Cd in soil increases. On the other hand, the increase of cadmium in shrews could be related to the predation on earthworms, which possibly transform ash-derived cadmium into a more bioavailable form.

There was a small but significant difference in the relative size of the kidneys for both voles and shrews, which may indicate an effect of pollutants. There seemed to be a seasonal variation with increasing cadmium concentrations in voles during the sampling period from July to September. A similar increasing trend could be detected in an unpolluted area in leaves of *Salix caprea* but not in leaves of *Vaccinium myrtillus* (Lodenius 2002). This seasonal variation in plants may at least partly explain the increase of cadmium in voles.

Table 1. Eggshell index and mean cadmium concentrations ($\mu g\ g^{-1}$ dw; number of samples in parenthesis) in albumin, yolk and shells of eggs of Great tit (*Parus major*) and Pied flycatcher (*Ficedula hypoleuca*) from treated and untreated areas.

		EI	Cd-Alb	Cd-Yolk	Cd-shell
Parus	Treated	0.91 (2)	0.05 (3)	0.03 (10)	0.01 (10)
	Untreated	0.99 (5)	0.05 (2)	0.01 (5)	0.03 (5)
Ficedula	Treated	0.95 (9)	0.02 (10)	0.02 (12)	0.01 (11)
	Untreated	0.91 (18)	0.03 (15)	0.02 (22)	0.02 (22)

(EI; shell weight/length*breadth)

In the eggs of the two insectivorous birds no significant differences were detected in egg size and the cadmium concentrations were very low in albumin, yolk and shell (0.01 - 0.07 μg g^{-1} dw). Nor were any differences between control and treated areas found (Table 1).

Application of wood ash increases the cadmium reserves in soil, but mostly in biologically unavailable form. However, different ashes may have significantly different effects on pH, cadmium concentration and cadmium species in the soil. Cadmium is strongly bound to wood ash and only small amounts can be extracted. The leaching of cadmium from granulated ash may, at least on short term, be small even when the total cadmium concentration is high.

In the study area higher concentrations were found at treated areas from earthworms, macrofungi and shrews but the differences were small. In a few years perspective there does not seem to be any significant changes in the cadmium status of the forest ecosystem. It is, however, difficult to assess the long term environmental risk related to the application of wood ash in forests.

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REFERENCES

Hunter BA, Johnson MS, Thompson DJ (1989) Ecotoxicology of copper and cadmium in a contaminated grassland ecosystem. IV. Tissue distribution and age accumulation in small mammals. J Appl Ecol 26:89-99

Korpilahti A, Moilanen M, Finér L (1998) Biomass ash utilization in Finland. In: Obernberger I (ed.): Ashes and particulate emissions from biomass combustion. Formation, characterisation, evaluation, treatment. Inst Chem Eng Technol Univ Graz 3:43-54

Kuusi T, Laaksovirta K, Liukkonen-Lilja H, Lodenius M, Piepponen S (1981) Lead, cadmium and mercury contents of fungi in the Helsinki area and in unpolluted control areas. Z Lebensm Unters Forsch 173:261-267

Lodenius M (2002): Seasonal variations in cadmium concentrations of plant leaves. Bull Environ Contam Toxicol 69:320-322

Lodenius M, Soltanpour-Gargari A, Tulisalo E (2002a) Cadmium in forest mushrooms after application of wood ash. Bull Environ Contam Toxicol 68:211-216

Lodenius M, Soltanpour-Gargari A, Tulisalo E, Henttonen H (2002b) Effects of ash application on cadmium concentrations in small mammals. J Environ Qual 31:188-192

Moilanen M, Issakainen J (2000) Tuhkalannoituksen metsävaikutukset [In Finnish; Effects of ash fertilization on forests]. Metsätehon raportti 93. Helsinki. 38 p

Pankakoski E, Koivisto I, Hyvärinen H, Terhivuo J (1994) Shrews as indicators of heavy metal pollution. JF Merritt, GL Kirkland & RK Rose (eds): Advances in the Biology of Shrews. Carnegie Mus Nat Hist, Spec Publ 18:137-149
Pernetta JC (1976) Diets of shrews Sorex araneus L. and Sorex minutus L. in Wytham grassland. J Anim Ecol 45:899-912
Read H, Martin M (1993) The effect of heavy metals on populations of small mammals from woodlands in Avon (England) with particular emphasis on metal concentrations in *Sorex araneus* L. and *Sorex minutus* L. Chemosphere 27:2197-2211
Rühling Å (1996) Upptag av tungmetaller i svamp och bär samt förändringar i florans sammansättning efter tillförsel av aska till skogsmark. NUTEK Rapport 1996:49, Stockholm, 46 p
Saarikko J (1989) Foraging behaviour of shrews. Ann Zool Fennici 26:411-423
Ukonmaanaho L, Starr M, Hirvi J-P, Kokko A, Lahermo P, Mannio J, Paukola T, Ruoho-Airola T, Tanskanen H (1998) Heavy metal concentrations in various aqueous and biotic media in Finnish Integrated Monitoring catchments. Boreal Environ Res 3:235–249