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Effects of different wood ashes on the solubility of cadmium in two boreal forest soils

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In this study the fate of wood ash-derived cadmium (Cd) in forest soils was monitored in a field experiment and in a subsequent incubation experiment in the laboratory. The aim was to assess the distribution of cadmium between various pools differing in their bioavailability. In the field experiment the manual application caused a large variation between the subsamples and resulted in hot spots. A three-week incubation experiment carried out with mineral and peat soils using five different kinds of ashes demonstrated that ashes of dissimilar origin differ markedly in their effect on pH and cadmium dissolution. Furthermore, peat and mineral soils differed in the distribution of cadmium. Water-soluble and exchangeable cadmium, considered to represent bioavailable pools, remained low in all treatments. The results indicate that the stabilization of ash and the liming effect of the material are factors limiting the mobility of cadmium in soil even if the increase in the total amount can be high.

Introduction

More than 100 000 tonnes of wood ash is generated annually by the Finnish forest industry in the process of burning bark and other wood residues (Tilastokeskus 1995). Ash causes a disposal problem for the industry, with the main portion of the ash being currently transported to landfills. The use of ash as a fertilizer in forests could return a considerable amount of nutrients removed in wood harvest back to the natural cycle. Furthermore, oxides of alkaline and earth alkaline cations formed in the burning process exert a liming effect and counteract soil acidification. However, heavy metals accumulated in the wood ash, especially cadmium (Cd), have caused concern for environmental risks. 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 (Evald 1998, Obernberger and Biedermann 1998). The environmental risks caused by the wood ash do not only depend on the total concentration of cadmium but also on its dissolution rate. When dissolved to soil solution cadmium is easily taken up by plants and enriched especially in protein compounds where it replaces zinc. At high concentrations it also may disturb microbiological processes and, thus, affect the nutrient cycling. Many of the cadmium compounds are relatively mobile in the soil and readily taken up by plants (Kabata-Pendias and Pendias 1984, Lundborg 1998, Stevenson and Cole 1999). The most important soil factors governing the uptake are pH and the amount of organic matter (Christensen 1989, Lodenius and Autio 1989). Also microbial processes should be considered if cadmium-containing wood ash is used as a forest fertilizer (Fritze *et al*. 2000).

Metal concentrations in ash are known to vary markedly depending on the burning and granulation processes as well as on the particle size fraction (Obernberger *et al*. 1997, Dahl and Obernberger 1998, Eriksson 1998, Lundborg 1998). The solubility of cadmium in the ash is dependent on its chemical form, but the dominating forms in the different kinds of ashes have not been completely identified (Nordin and Backman 1998). Therefore, the risk assessment cannot be based merely on the total cadmium concentration, but more detailed information on reaction patterns of cadmium derived from various ash types in various soil types is needed. The purpose of this study was to investigate (1) in a field experiment, the long-term effects of wood ash on soil pH and the mobility and extractability of cadmium in mineral and peat soils, and (2) in a short-term laboratory experiment, how wood ash-derived cadmium will be distributed between various pools of dissimilar bioavailability.

Materials and methods

Field study

The study sites were situated in a forest area in Evo, southern Finland (61°14´N and 25°12´E), within the catchment areas of two small lakes, Nimetön and Tavilampi. The site by Lake Nimetön consists of mineral soil, and is classified as *Myrtillus*-type forest. *Vaccinium myrtillus* L. and both deciduous (birch *Betula bendula* Roth, aspen *Populus tremula* L., willow *Salix* sp.) and coniferous trees (pine *Pinus sylvestris* L., spruce *Picea abies* (L.) Karst.) occur in the flora. The catchment area was fertilized in 1972 and clear-cut in winter 1981–1982. The cut area was burnt over in 1983 without complete success. The catchment area of Lake Tavilampi consists of peat soil, and is classified as spruce swamp. The main tree species was spruce, and there were also rowan trees (*Sorbus aucuparia* L.), *Vaccinium myrtillus*, *Sphagnum sp*. and *Pleurozium schreberi* (Brid.) Mitt. in the flora. The study sites were founded in 1997, when Metsäteho Oy started a large study and development project. The aim was to investigate utilization of wood ash as a forest fertilizer. This included e.g. studies of ash-spreading techniques, environmental effects of wood ash to lakes, small mammals, mushrooms and vegetation.

In February 1998, the study areas were treated with self-hardened wood ash from Äänekoski (Metsä-Botnia Ltd.). The ash was applied manually in a quantity of 4800 kg ha^{-1} (dry weight), which yielded a mean cadmium burden of 44 g ha^{-1}. Untreated control plots with similar vegetation were chosen from nearby forest areas.

Soil samples from the ash-treated and control areas were taken from two depths: 0–5 cm and 15–20 cm. On the mineral soil site (Nimetön catchment), the samples represented the humus and mineral soil layers, respectively. On the peat soil site (Tavilampi catchment), the samples represented moss (*Sphagnum* sp.) and peat soil respectively. On each plot, three pooled random samples (comprising of six subsamples) were collected per layer.

The characteristics of the soil samples are described in Table 1. The particle size distribution of mineral soil samples, determined by the pipette method (Elonen 1971), was about the same on the control and fertilized areas: < 0.002 mm 7%; 0.002–0.006 mm 4%; 0.006–0.02 mm 10%–12%; 0.02–0.06 mm 19%–20%; 0.063–0.200 mm 23%–30%, and coarser fractions 27%–30%. The bulk density was 0.2–0.3 g cm^{-3} in the humus layer and 0.8 g cm^{-3} in the mineral soil layer. The peat soil consisted of *Sphagnum* remains, and its stage of decomposition on the von Post scale was 4–5. The bulk density was 0.1–0.2 g cm^{-3}.

The organic matter content of the samples was determined as a loss on ignition (550 °C for 1 h). Soil pH($CaCl_2$) (1/2.5 v/v) was measured with Mettler DL 25 Titrator (GWB, Finland). The effective cation exchange capacity (CEC_{ef}) was determined according to the summing method: 5-g samples of mineral soil/2-g samples of peat were extracted with 1 M NH_4Cl (4 × 25 ml NH_4Cl, shaking for 1 h). The concentrations of K, Na, Mg, and Ca were determined by the AAS Varian SpectrAA-400 equipment. The exchangeable acidity was measured from 1 M KCl extraction (titrated with 0.01 M NaOH). Ammonium oxalate solution (0.029 M $(NH_4)_2C_2O_4$, 0.021 M $H_2C_2O_4$, pH 3.3) was used for extraction of hydrated Al, Fe, and Mn oxides (Niskanen 1989). Concentrations were measured by graphite furnace AAS (Al_{ox}) and flame AAS (Fe_{ox} and Mn_{ox}).

Incubation experiment

The ashes used in the incubation experiment were obtained from the Äänekoski pulp factory (Metsä-Botnia Ltd.) and the Uimaharju pulp factory (Enocell Ltd.). The ash from Äänekoski originated mainly from wood bark (pine, spruce, birch, and aspen) and from small amounts of peat and biosludge. The incineration temperature was 830–860 °C in the lower parts of the incinerator and 940–990 °C in the cyclones. The ash from Uimaharju was produced by burning wood bark (75% birch, 25% pine) at 860–870 °C on a grid arc, and the fly ash was collected at 170 °C in an electric filter. The various ash types and their total cadmium concentration (HNO_3 extraction, EPA Method 3051, flame AAS Varian SpectrAA-400) were:

A: fly ash, Äänekoski	5.5 mg kg^{-1}
B: bottom ash, Äänekoski	0.2 mg kg^{-1}
C: self-hardened ash, Äänekoski	3.1 mg kg^{-1}
D: granulated ash, Uimaharju	12.5 mg kg^{-1}
E: fly ash, Uimaharju	12.8 mg kg^{-1}

The incubation experiment was carried out with a mineral and a peat soil. The mineral soil was taken from a slope not treated with ash near the Nimetön control site, from C horizon, and the peat soil from the Tavilampi control area. The mineral soil was passed through a 2-mm sieve and the peat soil samples through a 4-mm sieve. The properties of the experimental soils, determined as described above, are given in Table 1. The particle size distribution of mineral soil was: < 0.002 mm 5%; 0.002–0.006 mm 5%; 0.006–0.02 mm 12%; 0.02–0.06 mm 17%; 0.063–0.200 mm 23%, and coarser fractions 38%. The bulk density was 1.2 g cm^{-3}. The

Table 1. Properties (mean ± S.D.) of peat and mineral soil samples from Evo ($N = 3$) and the soils used in the incubation experiments ($N = 4$).

	Organic matter (%)	CECef (cmol(+) kg^{-1})	Al_{ox} (mg kg^{-1})	Fe_{ox} (mg kg^{-1})	Mn_{ox} (mg kg^{-1})	K (mg kg^{-1})	Na (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})
Mineral soil									
control 0–5 cm	77 ± 11	37 ± 3.3	660 ± 150	1200 ± 460	110 ± 69	600 ± 58	28 ± 2.9	4800 ± 1 100	460 ± 120
treated 0–5 cm	37 ± 15	27 ± 19	1300 ± 780	2400 ± 1300	550 ± 390	530 ± 210	31 ± 1.7	3800 ± 2 700	420 ± 210
control 15–20 cm	14 ± 7.1	9.3 ± 2.2	6800 ± 5 800	5400 ± 1700	3.6 ± 2.6	56 ± 17	6.7 ± 3.1	340 ± 250	31 ± 7.4
treated 15–20 cm	11 ± 4.8	8.1 ± 2.9	4000 ± 2 100	5100 ± 3100	19 ± 17	140 ± 68	11 ± 11	560 ± 310	57 ± 38
Peat soil									
control 15–20 cm	96 ± 0.3	33 ± 3.8	760 ± 280	1400 ± 780	3.2 ± 1.9	230 ± 53	41 ± 5.6	2700 ± 780	490 ± 140
treated 15–20 cm	95 ± 1.5	44 ± 4.2	470 ± 93	1900 ± 780	9.1 ± 4.2	370 ± 120	110 ± 5.5	5800 ± 1700	770 ± 110
Incubation									
mineral	4.7 ± 0.1	1.4 ± 0.0	11000 ± 1300	1000 ± 13	15.2 ± 0.2	60 ± 0.5	11 ± 0.6	63 ± 0.8	6.4 ± 0.1
peat	96 ± 0.1	33 ± 0.7	870 ± 33	900 ± 16	3.1 ± 0.1	230 ± 3.9	53 ± 4.0	410 ± 6.0	410 ± 6.0

peat soil consisted of *Sphagnum* remains, and its stage of decomposition on the von Post scale was 4–5. The bulk density was 0.2 g cm^{-3}.

A set of plastic pots (8 cm × 8 cm) were filled with either 50 g of moist peat soil or 200 g of air-dried mineral soil. The peat soil was not dried before the experiment because drying significantly affects the water retention capacity of peat. The amount of ash added to each pot was 6.4 g, which approximately equals 10 tonnes of ash per hectare. The reasoning behind this was twofold: firstly, it simulated the situation in the forest where the ash is distributed only on the top soil and is not uniformly mixed with the soil; secondly, elevated addition also enabled us to assess the distribution of ash-derived cadmium between various fractions in a relatively short-term incubation experiment.

After application, the ash was thoroughly mixed with the soil. The control samples were incubated without ash. The experiments were carried out in quadruplicate. During the three-week incubation at a constant temperature (25 °C) the moisture was kept at 60% of the field capacity, measured in Büchner funnels by wetting the soil and letting it reach equilibrium overnight. After incubation, the samples were air-dried at room temperature before the cadmium extractions. The volume of the moist soil samples in the pots was approximately 170 cm^3. However, the peat soil sank into a smaller volume after drying, as its water retention capacity was greater than that of mineral soils.

Cadmium analyses

Total cadmium concentrations were measured from samples of 0.5 g of the mineral soil and 0.25 g of the peat soil and humus layer of the mineral soil field experiment (0–5 cm). Samples (field: duplicate; incubation: one from each experimental unit) were extracted with 10 ml of HNO_3 in a microwave oven according to the EPA method 3051 (1996). For determination of the total cadmium of moss samples from the Tavilampi plots, 0.3 g of the dried moss was extracted in a microwave oven in closed Teflon vessels with 5 ml of HNO_3 and 1 ml of 30% H_2O_2. The accuracy of this method was tested using a standard reference material (NIST SRM 1573a Tomato Leaves), for which we obtained a value of 1.49 ± 0.06 mg kg^{-1} ($N = 8$) (certified 1.52 ± 0.04 mg kg^{-1}).

The solubility of ash-derived cadmium was investigated by a sequential fractionation analysis to monitor its distribution between various pools of decreasing bioavailability as follows:

- "Water soluble": 50 ml of deionized H_2O, shaking for 1 h.
- "Exchangeable": 25 ml of KNO_3, shaking for 1 h (extraction was repeated four times and the supernatants obtained were combined).
- "Organically bound": 50 ml of 0.5 M NaOH, shaking for 16 h.
- "Oxide bound": 50 ml of 0.1 M $NH_2OH \times HCl$, pH 2, shaking for 30 min.
- "Residual": Total minus above-mentioned fractions.

The procedure was adopted from different extraction methods described by Sposito *et al.* (1982), Miller and McFee (1983), Xian and Shokohifard (1989), Amacher (1996), Ma and Rao (1997), and Narwal *et al.* (1999). The air-dry sieved samples were weighed (5 g of mineral soil and 2 g of peat) into a centrifuge tube. After shaking (180 rpm), the suspension was centrifuged (10 min, 2500 rpm, 1500 × *g*) and the supernatant solution was decanted and filtered (S&S 589[1] black ribbon filter paper). After KNO_3 and NaOH extractions, the sample was washed with 25 ml of ethanol three times before the next extraction. The extraction of the field experiment samples were carried out in duplicate. In the incubation experiment, a subsample taken from each replicated experimental unit was analyzed separately.

The cadmium concentrations of all the samples were determined with a graphite furnace AAS (Varian SpectrAA-400 equipped with GTA-96). The detection limit was 0.01 mg kg^{-1}.

Statistical procedures

Statistical comparisons were made for soil pH, cadmium concentrations and proportional distribution of cadmium between different fractions. Comparisons between treated and untreated forest areas, between surface and deeper soil layers, and between mineral and peat soils were made with a two-sample *t*-test. To compare results between different ash treatments in the incubation experiment, analysis of variance- (ANOVA) and Tukey's test ($p < 0.05$) were applied. In ANOVA, Cochran's *Q* values were used to test variances. The Statistix for Windows 4.0 software was used for the statistical analyses.

Results

Field study

Two years after the ash-spreading, there were no statistically significant effects on soil pH between the fertilized and the control areas (Table 2). However, in the control area of the mineral soil, the deeper soil layer had a significantly higher pH than the surface layer (p = 0.015), whereas on the ash-treated plot, no such difference existed.

The mineral soil samples contained practically no water-soluble or hydroxyl ammonium chloride-extractable (oxide-bound) cadmium (Table 2). There were no statistically significant differences between the fertilized and the control area in the cadmium concentrations in any pool. However, differences were found in the proportional distribution of cadmium: the proportion of organic fraction was greater in the humus layer on the fertilized area (17%) than on the control (11%) (p = 0.018) and that of exchangeable fraction in the humus layer was significantly (p = 0.036) larger on the control area (55%) than on the fertilized one (21%). In the deeper layer, none of the cadmium fractions studied were affected by the ash.

In the peat soil samples taken from a depth of 15–20 cm, some tendencies of higher total cadmium concentrations and residual-proportions in fertilized area were observed, but none of the differences were statistically significant. The cadmium concentration in the *Sphagnum* moss (top layer of the peat soil) seemed to be higher in the fertilized site as compared with that in the control, but the difference was not statistically significant because of the large variation between the subsamples from the fertilized area (Table 2). In the control area, the cadmium concentrations of the moss layer clearly varied less than in the fertilized area, where the range was 0.20–1.9 mg kg^{-1}.

Incubation experiment

In the incubation experiment, all ash treatments significantly increased soil pH, although they

Table 2. Soil pH and cadmium concentrations (mean ± S.D., mg kg^{-1} dry weight) in the soil samples extracted sequentially with various solutions, and the residual fraction and total amount of cadmium in the field study, $N = 3$.

	Extractant						
	pH	H_2O	KNO_3	NaOH	$NH_2OH \times HCl$	Residual	Total (HNO_3)
Mineral soil							
Humus layer							
0–5 cm, control	3.3 ± 0.1	0.00	0.28 ± 0.10	0.05 ± 0.01	0.00	0.17 ± 0.05	0.50 ± 0.07
0–5 cm, treated	4.1 ± 0.4	0.00	0.07 ± 0.02	0.06 ± 0.04	0.00	0.25 ± 0.11	0.38 ± 0.15
Mineral layer							
15–20 cm, control	3.8 ± 0.2	0.00	0.03 ± 0.02	0.00	0.00	0.05 ± 0.02	0.08 ± 0.04
15–20 cm, treated	4.0 ± 0.3	0.00	0.03 ± 0.02	0.00 ± 0.01	0.00	0.08 ± 0.04	0.11 ± 0.06
Peat soil							
Moss							
0–5 cm, control	–	–	–	–	–	–	0.34 ± 0.03
0–5 cm, treated	–	–	–	–	–	–	0.92 ± 0.91
Peat							
15–20 cm, control	2.8 ± 0.1	0.00	0.30 ± 0.03	0.03 ± 0.01	0.00	0.19 ± 0.08	0.52 ± 0.09
15–20 cm, treated	3.3 ± 0.4	0.00	0.23 ± 0.08	0.03 ± 0.01	0.00	0.14 ± 0.05	0.40 ± 0.02

Table 3. Cadmium dose (mg kg^{-1} soil), soil pH and Cd concentrations in various fractions (mg kg^{-1} dry weight) in the mineral soil (C horizon) and peat samples, incubated with different ashes. Differences between the means are indicated: means with the same letter do not differ significantly (Tukey's test: $p \leq 0.05$), $N = 4$.

	Cd dose	pH	H_2O	KNO_3	NaOH	$NH_2OH \times HCl$	Residual	Total (HNO_3)
Mineral soil								
Control	0.00	5.0 ± 0.1e	0.00	0.00 ± 0.01	0.00	0.00	0.04 ± 0.01b	0.05 ± 0.01c
A fly ash	0.18	8.5 ± 0.2a	0.00	0.00	0.01 ± 0.00	0.05 ± 0.01b	0.24 ± 0.05a	0.29 ± 0.05b
B bottom ash	0.01	8.0 ± 0.2b	0.00	0.00	0.00	0.00 ± 0.01c	0.05 ± 0.01b	0.05 ± 0.00
C self-hardened ash	0.10	7.2 ± 0.2c	0.00	0.00	0.00	0.03 ± 0.01b	0.08 ± 0.02b	0.10 ± 0.03c
D granulated ash	0.40	6.0 ± 0.4d	0.00	0.01 ± 0.01	0.00	0.00 ± 0.01	0.03 ± 0.01b	0.04 ± 0.00c
E fly ash	0.41	8.1 ± 0.1ab	0.00	0.00	0.00 ± 0.01	0.13 ± 0.01a	0.29 ± 0.10a	0.44 ± 0.11a
Peat soil								
Control	0.00	2.9 ± 0.1d	0.00	0.19 ± 0.01a	0.02 ± 0.01e	0.00	0.09 ± 0.06d	0.30 ± 0.05d
A fly ash	0.70	8.6 ± 0.1a	0.00 ± 0.01	0.01 ± 0.01c	0.30 ± 0.01b	0.01 ± 0.01b	1.17 ± 0.06b	1.49 ± 0.07b
B bottom ash	0.03	7.6 ± 0.4b	0.00	0.00	0.07 ± 0.01d	0.00	0.24 ± 0.08cd	0.32 ± 0.08d
C self-hardened ash	0.40	7.0 ± 0.3b	0.00	0.00	0.20 ± 0.01c	0.00 ± 0.01b	0.57 ± 0.21c	0.77 ± 0.22c
D granulated ash	1.60	4.1 ± 0.7c	0.00	0.06 ± 0.02b	0.06 ± 0.01d	0.00	0.11 ± 0.02d	0.23 ± 0.01d
E fly ash	1.64	7.6 ± 0.1b	0.01 ± 0.00	0.01 ± 0.01c	0.69 ± 0.04a	0.05 ± 0.01a	3.14 ± 0.30a	3.90 ± 0.29a

differed markedly in their liming efficiency (Table 3). The increase was lowest for the granulated ash obviously due to its limited solubility. In most cases, total cadmium increased notably after the ash applications, expect for granulated ash. Water-soluble and oxide-bound ($NH_2OH \times HCl$ extraction) fractions were very small in all ash treatments. Furthermore, almost no cadmium was recovered in the organically bound (NaOH extraction) form in the mineral soils, while in the peat soil this fraction was very dissimilarly affected by various ashes: the fly ashes and self-hardened ash resulting in the highest concentrations. When comparing the soils, it should be noticed that the results are given per kg. This means that they are relatively high in the peat soil because of its low dry bulk density. Table 4 summarizes the differences between the peat and mineral soils regarding the cadmium distribution in various fractions. As expected, in the mineral soil, a larger portion of the cadmium was bound in the oxides, while the organically bound fraction was bigger in the peat soil than in the mineral soil.

In the peat soil, the ash treatments tended to decrease the proportion of biologically available cadmium. In the control sample, the exchangeable cadmium was the dominating fraction (66%), whereas in the sample treated with the granulated ash it made up 25% of the recovered cadmium, and in the other ash treatments almost no cadmium was found in this fraction. The proportion of the residual fraction was 26% in the control sample, but it increased up to 48%–80% in the ash-treated ones. The organically bound fraction showed a similar distribution pattern: in the control sample, only 8% of the cadmium was recovered in this form, whereas in the ash-treated soils this fraction amounted to 18%–27%. In the mineral soil, the relative proportion of the residual fraction was much greater than in the peat soil, being 89% in the control and 65%–89% in the ash-treated soils. The treatments did not differ significantly in exchangeable, organically bound, or residual fractions. The proportion of oxide-bound cadmium was 8%–30% in the ash-treated soils but remained 0% in the control soil.

The distribution data show that the recovery of ash-derived cadmium in the incubation experiment varied widely between different ashes. Fly ashes were very soluble and the recovery of their cadmium ranged from 61% to 136%, whereas almost no cadmium was dissolved from the granulated ash in three weeks. Cadmium recovery from self-hardened ash was 43%–50% and from bottom ash 0%–28%. Recovery rates were greater in the mineral soil than in the peat soil for all but self-hardened ash.

Discussion

When interpreting the two-year field study results, it is worth noting that due to uneven spreading of the ash, some of the samples may have been collected from heavily fertilized locations, and others from locations receiving no ash. This could have caused the large variation between samples. This variation rendered the differences between treatments statistically insignificant, and the actual behavior of ash-derived cadmium could not be monitored accurately. The results showing a ten-fold variation in the cadmium concentration in the moss, point out that uneven spreading may result in hot spots, which can cause an environmental risk of increased levels of bioavailable cadmium. On the other hand, in the humus layer of ash-treated mineral soil the exchangeable cadmium pool considered bioavailable was decreased. This was confirmed in the short-term incubation experiment where the relative proportion of exchangeable fraction in the peat soil diminished in the ash treatments. It is likely that Cd^{2+} bound to humic compounds was retained in a complexed rather than exchangeable form. An increase in the organically bound fraction in the ash treatments agrees with the fact that high pH favors the stability of metal-humic acid complexes.

In the three-week incubation experiment, the main part (48%–89%) of ash-originating cadmium was recovered in the residual fraction difficult to dissolve (Table 3). The other fractions, excluding water soluble and exchangeable ones, can be taken to represent cadmium supplies potentially mobilizable. Almost all cadmium in these potentially mobilizable pools was recovered in the fraction assumed to be organically (peat soil) or oxide-bound form (mineral soil). These responses suggest that immediately after the ash application, the risk of markedly increased concentration of bioavailable cadmium is very low.

The effective binding of the ash-derived cadmium in the organic and oxide-bound fractions can be explained by the liming effect of ash. Both specific sorption of cadmium on hydrated oxide surfaces and nonspecific sorption on cation exchange sites will increase, when pH increases. Thus, the very effective increase in pH due to Äänekoski fly ash (up to 8.6) could favour the specific sorption of soluble cadmium as a hydroxycomplex $CdOH^+$ to oxide surfaces ($pK_a(Cd^{2+}) = 10.1$). However, at the additions levels normally used, in boreal forest soil pH does not normally reach the levels achieved in the present incubation experiment (pH 7–8), which could be seen also in our field experiment (Table 2). On the other hand, in hot spots high pH values are possible. Egnell *et al.* (1998) compiled data from diverse ash studies (fly ash, hardened ash, and granulated ash, 1–11 years after spreading) and reported an increase of 0.4–2.5 pH units in peat soils and 0–1 pH units in mineral soils.

Table 4. Comparison of the peat and mineral soil regarding the distribution of cadmium in various fractions; P = significantly greater relative portion in peat soil, M = significantly greater relative portion of Cd in the mineral soil, – = no significant difference between the soils, * = not possible to test statistically (too large differences between portions or concentrations below detection limit).

	H_2O	KNO_3	NaOH	$NH_2OH \times HCl$	Residual
Control	*	P ($p = 0.001$)	P ($p = 0.009$)	*	M ($p = 0.001$)
A fly ash	*	– ($p = 0.360$)	P ($p = 0.000$)	M ($p = 0.005$)	– ($p = 0.481$)
B bottom ash	*	*	P ($p = 0.009$)	*	M (p = 0.040)
C self-hardened ash	*	*	P ($p = 0.002$)	M ($p = 0.002$)	– ($p = 0.941$)
D granulated ash	– ($p = 0.471$)	– ($p = 0.258$)	*	*	– ($p = 0.056$)
E fly ash	– ($p = 0.304$)	– ($p = 0.191$)	P ($p = 0.000$)	M ($p = 0.002$)	P ($p = 0.012$)

The three-week incubation experiment demonstrated that in the laboratory the effects of ash-fertilization on pH, cadmium concentration, and cadmium species in the soil can be found rather soon. It also showed that the short-term risks of increased concentrations of bioavailable cadmium due to application of different ashes are not related to their cadmium content. The release of cadmium from the granulated ash may, at least in the short term, be small despite its high total cadmium content. On the other hand, the efficiency of this material as a liming agent is also lower. Earlier studies have also shown that the stabilization of the wood ash by granulation or self-hardening retards the liming effect as well as the solubilization of metals (Eriksson 1998, Lundborg 1998). Granulation seems to be a more efficient stabilization method than self-hardening. Steenari *et al*. (1999) reported the same kind of conclusions in their study. Consequently, granulation could be a practical method for avoiding hot spots.

Thus, the wood ash-induced increase in soil pH is dependent on the type and quantity of ash used in the fertilization. Although the effect on pH can be long-lasting (Hakkila 1986), the immediate high pH effect is more likely to be of short duration. Likewise, the enhanced binding of cations after ash application is probably temporary and will gradually disappear (Zhan *et al*. 1996). Further studies in freely-drained soil systems are needed to find out the duration of pH increase and the fate of cadmium after the pH effect has leveled off. More information is also needed how the other cations, gradually released from the ash, affect in the long run cadmium retention and chemical and biological processes in the soil.

Application of wood ash increases cadmium reserves in soil, even though most of it is at least in the beginning in biologically unavailable form. The amount of ash usually applied is approximately equal to the quantity in residues left on the soil in clear cutting (Nilsson *et al*. 1998). In Sweden, Egnell *et al*. (1998) recommend a maximum application of 3000 kg of stabilized ash per hectare. Significant reduction of the concentrations of cadmium and other heavy metals in ash may also be possible by optimizing incineration conditions (Obernberger and Biedermann 1998).

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References

Amacher M.C. 1996. Nickel, cadmium, and lead. In: Sparks D.L., Page A.L., Helmke P.A., Loeppert R.H., Soltanpour P.N., Tabatabai M.A., Johnston C.T. & Sumner M.E. (eds.), *Methods of soil analysis, part 3, Chemical methods*, SSSA Book Series No. 5. Soil Science Society of America Inc., American Society of Agronomy Inc., Madison, Wisconsin, USA, pp. 739–768.

Christensen T.H. 1989. Cadmium soil sorption at low concentrations: VIII. Correlation with soil parameters. *Water Air and Soil Pollution* 44: 71–82.

Dahl J. & Obernberger I. 1998. Heavy metal recovery from contaminated biomass ashes by thermal ash treatment. *Thermal Biomass Utilization* 3: 171–190.

Egnell G., Nohrstedt H.-Ö., Weslien J., Westling O. & Örlander G. 1998. *Miljökonsekvensbeskrivning (MKB) av skogbränsleuttag, asktillförsel och övrig näringskompensation*. Skogsstyrelsen, Rapport 1, SVJ, Jönköping.

Elonen P. 1971. Particle-size analysis of soil. *Acta Agr. Fenn.* 122: 1–122.

EPA Method 3051 1996. Microwave assisted acid digestion of sediments, sludges, soils, and oils 1994. In: *SW-84.6, Test methods for evaluating solid waste, physical/chemical methods*. U.S. Environmental Protection Agency's Office of Solid Waste (also available on the web at http://www.epa.gov/epaoswer/hazwaste/test/3051.pdf).

Eriksson J. 1998. Dissolution of hardened wood ashes in forest soils: studies in a column experiment. *Scandinavian Journal of Forest Research* Suppl. 2: 24–31.

Evald A. 1998. Ashes from straw and wood combustion and from wood gasification plants — possibilities of fractionated metal separation and ash utilization in Denmark. *Thermal Biomass Utilization* 3: 77–88.

Fritze H., Perkiömäki J., Saarela U., Katainen R., Tikka P., Yrjälä K., Karp M., Haimi J. & Romantschuk M. 2000. Effect of Cd-containing wood ash on the microflora of coniferous forest humus. *FEMS Microbiology Ecology* 32: 43–51.

Hakkila P. 1986. Recycling of wood and bark ash. A state-of-the-art review for programme group C under the IEA Forest Energy Agreement. *Metsäntutkimuslaitoksen tiedonantoja* 11, Helsinki.

Kabata-Pendias A. & Pendias H. 1984. *Trace elements in soils and plants*. CRC Press Inc, Boca Raton.

Korpilahti A., Moilanen M. & Finér L. 1998. Biomass ash utilization in Finland. *Thermal Biomass Utilization* 3: 43–54.

Lodenius M. & Autio S. 1989. Effects of acidification on the mobilization of cadmium and mercury from soils. *Arch Environ. Contam. Toxicol.* 18: 261–267.

Lundborg A. 1998. Ecological and economical evaluation of biomass ash utilization — the Swedish approach. *Thermal Biomass Utilization* 3: 29–41.

Ma L.Q. & Rao G.N. 1997. Chemical fractionation of cadmium, copper, nickel, and zinc in contaminated soils. *Journal of Environmental Quality* 26: 259–264.

Miller W.P. & Mc Fee W.W. 1983. Distribution of cadmium, zinc, copper, and lead in soils of industrial northwestern Indiana. *Journal of Environmental Quality* 12: 29–33.

Narwal R.P., Singh B.R. & Salbu B. 1999. Association of cadmium, zinc, copper, and nickel with components in naturally heavy metal-rich soils studied by parallel and sequential extractions. *Commun. Soil Sci. Plant Anal.* 30: 1209–1230.

Nilsson K., Sfiris G. & Ericson S.-E. 1998. Ashes from CFB combustion and gasification plants using woody biofuels — results from test runs. *Thermal Biomass Utilization* 3: 89–103.

Niskanen R. 1989. Extractable aluminum, iron and manganese in mineral soils: II. Extractability by oxalate and pyrophosphate. *J. Agric. Sci. Finland* 61: 79–87.

Nordin A. & Backman R. 1998. Heavy metal behaviour during combustion and gasification of biomass fuels — comparison between chemical equilibrium and experimental results. *Thermal Biomass Utilization* 3: 119–134.

Obernberger I. & Biedermann F. 1998. Fractionated heavy metal separation in Austrian biomass grate-fired combustion plants approach, expenses, results. *Thermal Biomass Utilization* 3: 55–76.

Obernberger I., Biedermann F., Widmann W. & Riedl R. 1997. Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. *Biomass Bioenergy* 12: 211–224.

Sposito G., Lund L.J. & Chan A.C. 1982. Trace metal chemistry in aridzone field soils smended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases. *Soil Science Society of America Journal* 46: 260–264.

Steenari B.-M., Karlsson L.G. & Linqvist O. 1999. Evaluation of the leaching characteristics of wood ash and the influence of ash agglomeration. *Biomass Bioenergy* 16: 119–136.

Stevenson F.J. & Cole M.A. 1999. *Cycles of soil carbon, nitrogen, phosphorus, sulfur, micronutrients*, 2nd ed., John Wiley & Sons Co., New York.

Tilastokeskus 1995. Teollisen toiminnan jätteet 1992. *Ympäristö* 7.

Xian X. & Shokohifard G.Å. 1989. Effect of pH on chemical forms and plant availability of cadmium, zinc, and lead in polluted soils. *Water Air and Soil Pollution* 45: 265–273.

Zhan G., Erich M.S. & Ohno T. 1996. Release of trace elements from wood ash by nitric acid. *Water Air and Soil Pollution* 88: 297–311.

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