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Cadmium Contamination of Wood Ash and Fire-Treated Coniferous Humus: Effect on Soil Respiration

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Atmospheric acidic deposition is known to affect soil fertility and in many countries, liming has been used to counteract anthropogenic soil acidification in coniferous forest soils. Other measures used to improve the acid neutralization capacity of forest soils are wood ash application and prescribed burning. In both cases, ash is deposited on the forest floor, resulting in a pH increase in the humus layer. Currently, application of forests with wood ash is under discussion in Finland, since the naturally occurring cadmium of forest trees is concentrated into the wood ash which then contains between 4 and 20 $\mu g\ g^{-1}$ of dry matter (Paloniemi et al. 1993). Microbes are essential for maintaining soil fertility and plant growth because they play a fundamental role in nutrient availability. Soil respiration rate, which is an indicator of the microbially-mediated nutrient turnover rate, is decreased by addition of cadmium to the soil environment (Bååth 1989).

In this paper we report on the effect of cadmium addition on the soil respiration rate of forest humus having received wood ash or fire treatments. The underlying objectives of this study were: i) to determine the cadmium level which decreases the soil respiration of a *Vaccinium* site type forest humus to half of its original value (EC_{50}), ii) to estimate how the forest treatments influence the EC_{50}, and iii) to discuss the effect of Cd addition provided by wood ash on the nutrient mineralization rate.

MATERIALS AND METHODS

The experimental soils were retrieved from a field experiment which was established in 1990 in a 100-year old Scots pine (*Pinus sylvestris* L., on dry *Vaccinium* site type) stand in Central Finland (N 62° 02' E 24° 50' alt. 130 m a.s.l.). The general tree stand characteristics are as follows: stem number, mean height, and stem volume were 330 stems ha^{-1}, 21 m, and 180 $m^3\ ha^{-1}$, respectively. The experimental stand is growing on podzolized sandy soil with a 3 cm thick humus layer.

Randomized blocks containing five treatments in four blocks were used as an ex-

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perimental design. The treatments within each block were performed on 30 x 30 m plots representing control (C), three levels of wood ash application: 1000 (A1), 2500 (A2) and 5000 (A3) kg ha^{-1} and a fire treatment (F). Ash, containing Ca 33.7 %, Mg 2.1 %, K 3.5 %, and P 1.4 % was applied to the appropriate plots on 21 and 22 May 1990. A separate analysis performed on wood-ash from the same manufacturer revealed a Cd content of 3.67 mg kg^{-1} dw. The fire treatment mimicked prescribed burning and was carried out as follows: from an adjacent clear-cut area, the logging residues of Scots pine and Norway spruce (*Picea abies*) were transported to the plots (3000 kg dry matter per plot; equalling 19 t ha^{-1}) and burnt on 14 May 1990. All the trees on the experimental area were left standing. At each plot from three blocks, one bulk sample, consisting of twelve separate samples (soil core diameter 7.2 cm), were taken from the entire humus horizon (F/H-layer) on the 25 May 1993 and analysed separately.

The 15 bulk soil samples were immediately sieved to pass through a 4 mm mesh and stored at 4 °C. Subsamples of the field moist humus were heated at 105 °C for 12 h to determine the dry weight (dw) and moisture. pH was determined in soil-water suspensions. Total organic carbon (C_{org}) and nitrogen (N_{tot}) were determined by dry combustion (Leco CHN-600) after the destruction of possible carbonate-C by adding HCl (10 %). For determination of cation exchange capacity (CEC), extractions were made with unbuffered 0.1 M $BaCl_2$ using a soil:solution volume ratio of 1:10. The suspensions were left to stand overnight before being shaken for 1 h and then filtered. Elemental concentrations of Ca, Mg, K, and Na were determined from the soil extracts using an inductively coupled plasma emission spectrophotometer (ICP-AES, ARL 3580). Exchangeable acidity (EA) was determined from the $BaCl_2$ extracts by titration with 0.05 M NaOH to pH 7 endpoint. The CEC was calculated as the sum of extractable base cations plus EA and is expressed in milliequivalent (me) of 100 g soil dw. Base saturation degree (BS) was expressed as the percentage base cations of the CEC.

After two weeks of storage, the samples were treated with an aqueous (1.6 g Cd L^{-1}) $CdCl_2$ solution (J. T. Baker Chemical Co.) to give final Cd levels of 200, 400, 1000, 2000, and 4000 µg g^{-1} dw of soil. Untreated samples served as the respective controls. Finally, the soil samples were wet to 60 % of the water holding capacity (WHC) and incubated for one month at 20 °C before respiration analysis. Distilled water was added every week to maintain the moisture at the 60 % of WHC level. Soil respiration (CO_2-evolution) was measured with an automated respirometer (Nordgren 1990) at 20 °C for seven days, taking readings every hour. The respective seven day means were used to present the results.

Two way analysis of variance (ANOVA) followed by Tukey's test was performed on the measured variables to distinguish the effect of the treatments and the blocks using the Statistix 4.0 (NH Analytical software) statistical program. EC_{50} values were determined by linear regression on log transformed Cd values.

Table 1. Characteristics of the soil samples

TRT[a]	Variable[b,c]				
	pH	C	N	CEC	BS
C	3.79[1] ±0.03	50.3[1] ±0.44	0.99[1] ±0.03	34.9[1] ±0.35	55.9[1] ±0.98
A1	4.44[2] ±0.06	46.1[1] ±1.07	0.88[1] ±0.01	42.1[1] ±1.87	84.7[2] ±1.57
A2	5.12[3] ±0.25	48.8[1] ±1.32	0.97[1] ±0.04	62.8[2] ±7.17	94.2[3] ±3.10
A3	6.18[4] ±0.16	45.8[1] ±0.29	0.89[1] ±0.02	89.4[3] ±5.18	99.0[3] ±0.46
F	4.51[2] ±0.03	49.4[1] ±1.89	1.05[1] ±0.07	42.9[1] ±3.01	85.2[2] ±1.42

[a] Treatments (TRT) were: control (C); wood ash applications of 1000, 2500, and 5000 kg ha^{-1} (A1, A2, and A3, respectively); and a fire treatment (F). Standard errors of the means (n = 3) are presented.

[b] pH was measured from water suspensions, carbon (C) and nitrogen (N) are given as percentage of soil dry weight, cation exchange capacity (CEC) is given in milliequivalent per 100 g soil dw and base saturation (BS) as the percentage of CEC.

[c] Means indexed with the same number were not significantly different between treatments (ANOVA followed by a Tukey's means test)

RESULTS AND DISCUSSION

Heavy metals are toxic to all organisms if present in high concentrations and microorganisms are no different in this respect. Respiration, which is considered to represent overall soil microbial activity, is a commonly analyzed variable in environmental pollution studies. In laboratory experiments, the addition of heavy metals such as Cr, Cd, Cu, Zn, and Mn (Chang and Broadbent 1981), or Cd, Ni, and Zn (Wilke 1991) to soil samples decreased respiration. This is confirmed in this study, where the control soil samples (characterized by a pH of 3.8, carbon and nitrogen percentages of 50 and 1 of the soil dw, respectively, and a base saturation of 56 % of the cation exchange capacity; Table 1) needed an addition of over 1000 μg g^{-1} of Cd to decrease respiration to 50 % of their initial values (Table 2).

Bååth (1989) listed, in a review, studies done with heavy metals and their effect on soil microbial variables. This review reports studies where the addition of Cd was between 10 and 1000 μg g^{-1} dry soil to reach the same percentage inhibition of respiration. The large variation in the effective cadmium concentration is due to different soil types, which makes the studies hard to compare one to annother.

Table 2. a) Treatment-related soil respiration rate (CO_2; µg h^{-1} g^{-1}) at different levels of added cadmium and b) the resulting EC_{50} values.

	a) Cadmium added to soil (µg g^{-1})						b)
TRT[a]	0	200	400	1000	2000	4000	EC_{50}[b]
C	50.77 ±4.39	42.81 ±2.63	38.36 ±2.47	27.78 ±1.78	23.96 ±1.42	21.36 ±1.15	1570[1] ±237
A1	67.06 ±10.48	53.56 ±7.78	48.62 ±6.70	39.59 ±6.24	31.33 ±3.77	25.37 ±3.05	1690[1] ±235
A2	66.21 ±3.86	59.84 ±3.35	51.68 ±5.03	47.38 ±3.87	37.67 ±3.81	24.47 ±2.18	2550[1] ±100
A3	62.14 ±2.89	58.34 ±5.01	52.42 ±3.31	44.31 ±3.04	41.12 ±1.72	32.36 ±2.52	5690[2] ±250
F	60.87 ±10.56	48.92 ±8.81	39.17 ±6.25	25.62 ±3.92	19.73 ±3.30	13.84 ±1.44	865[3] ±101

[a] See footnote of Table 1.
[b] EC_{50} for Cd is given in µg g^{-1} dry soil and the calculation is based on linear regression of respiration data when calculated as % of the treatment respective value at zero Cd addition from the individual plots (means shown in Fig. 1) and log transformed Cd values. Means indexed with the same number were not significantly different between treatments (ANOVA followed by a Tukey's means test) as calculated on log transformed EC_{50} values.

Different respiration responses with respect to soil type were reported following the addition of Cd, Cr, Cu, Pb, Ni, or Zn (Doelman and Haanstra 1984) and Cd to the soils (Reber 1989). The critical load for a metal is strongly dependent on the soil texture and its physicochemical properties, e.g. pH, inorganic cations and organic matter (Collins and Stotzky 1989).

Wood ash application or prescribed burning treatments change the physicochemical characteristics of a soil. There are no reports on the response of soil respiration to increased cadmium levels due to such treatments of the same soil type. This knowledge is important, since cadmium bound in the vegetation is liberated into the soil during ash application or prescribed burning.

The physicochemical characterization of the soil samples before Cd addition are reported in Table 1. An ash-induced pH increase from 4.4 to 6.2, as compared to the control pH of 3.8, was detected at every level of ash application (A1, A2, and A3, respectively; Table 1). The fire treatment (F) shifted the humus pH to the same level as in the A1 treatment. The degree of base saturation also reacted in a similar manner to the pH, being 56 % in the control plots and then subsequently rising to higher values between 85 and 99 % with the three doses of ash application. Both the A1 and F treatment had near identical BS around 85 %. The

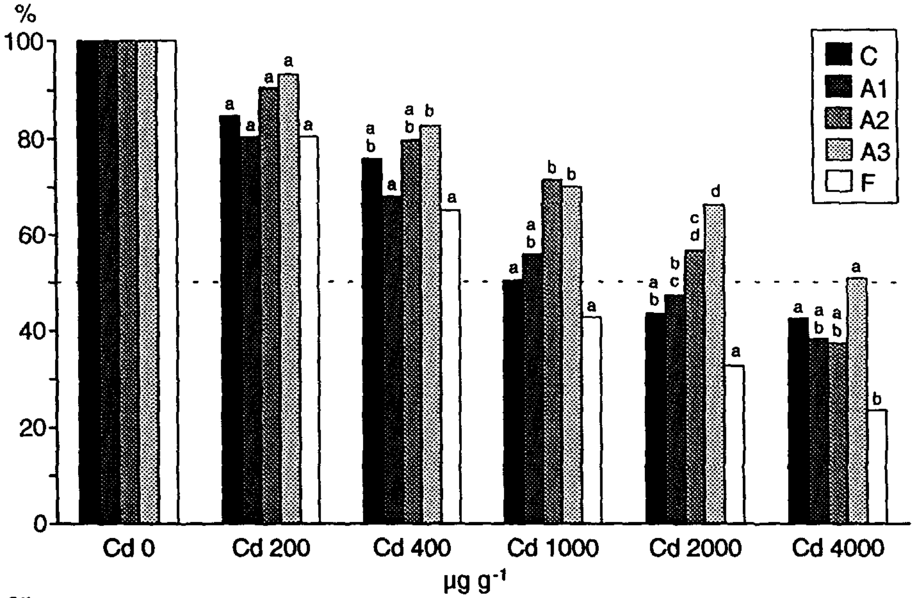

Figure 1. Percentage respiration activity of the soil treatment respective Cd 0 value. Bars indexed with the same letter were not significantly different between treatments (ANOVA followed by Tukey's means test). For identification of the treatments see footnote of Table 1.

cation exchange capacity (CEC) also varied in a similar manner to the pH and the base saturation, rising from the control level of 35 me 100 g^{-1} dw to 89 me 100 g^{-1} dw in the highest dose of the wood ash treatment. The A1 and the F treatments had the same CEC of about 42 me 100 g^{-1} dw. No treatment-related statistical differences in the soil organic carbon and total nitrogen concentration could be seen, these values being around 48 % and 0.95 % of the soil dry weight, respectively in all treatments.

Wood ash application at all three levels and the fire treatment increased the soil respiration rate (Table 2a; no Cd additions). The production of CO_2 usually increases after liming, although this has often been a short-term effect (Zelles et al. 1987; Haynes and Swift 1988; Shah et al. 1990; Illmer and Schinner 1991, Priha and Smolander 1994). Wood ash application also increases the soil respiration rate in coniferous forest soil (Fritze et al. 1994b). Fire treatments of coniferous forest soil have been reported to decrease respiration rates. The degree of inhibition was strongly correlated with the amount of water in the soil sample (Pietikäinen and Fritze 1993, Fritze et al. 1994b). The present experiment confirmed their results and showed that long term incubation of burnt soils at a constant water level resulted in detection of soil respiration rates above the control level (Table 2a).

Addition of Cd to the soil samples decreased the soil respiration rate (Table 2a). The degree of inhibition at increasing Cd levels was influenced by the treatments carried out on the sample plots. In Fig. 1 the respiratory activities of the various

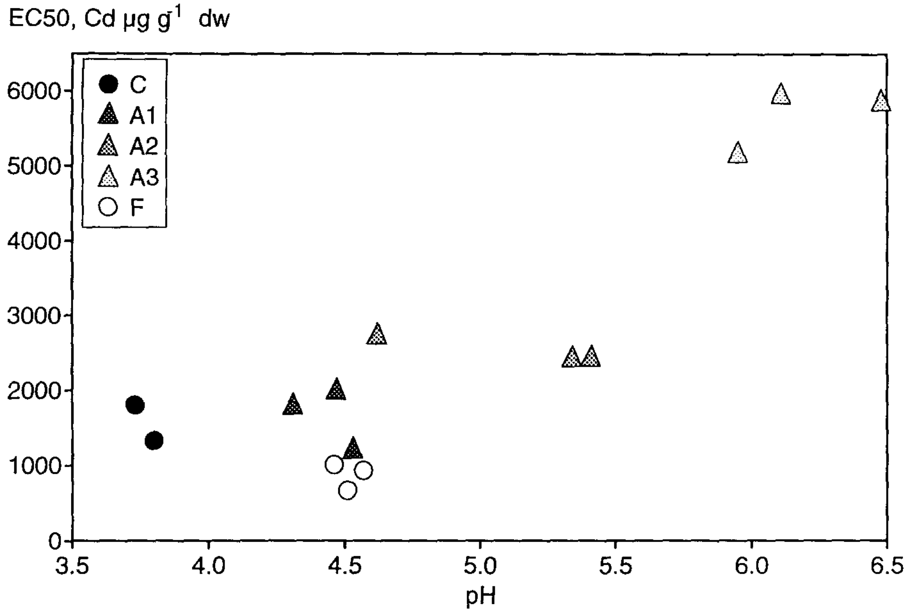

Figure 2. Relation between treatments, EC_{50}, and pH. For identification of the treatments see footnote of Table 1.

treatments calculated as % of the value at zero Cd addition are presented showing the fire-treated soil samples to exhibit the highest proportional activity loss and the highest level of wood ash treatment (A3) resulted in the lowest proportional activity loss. The control and first level wood ash fertilized humus (A1) had practically the same EC_{50} value, whereas the higher level wood ash fertilized humus samples reached their EC_{50} at much higher cadmium concentrations than did the untreated control samples (Table 2b). The EC_{50} value from the fire treatment was half of the control value (Table 2b).

Judged upon the EC_{50} values this experiment showed that coniferous forest soils treated with a single dose of wood ash withstand Cd additions to the soil ecosystem, when interpreted on a soil respiration basis, as good or better than control soils (Table 2b). With the higher level wood ash applicated soils, the decrease of Cd toxicity correlates with the treatment dose-dependent rise of pH of these soils (Fig. 2). This is in accordance with the observation of Herrero and Martín (1993) who reported the greater solubility of cadmium in acid soils. In the fire-treated soil, additional factors other than pH seem to influence the Cd toxicity since the first level wood ash fertilized (A1) and fire-treated soils (F) exhibit basically the same pH, while the F soils lose their respiratory activity faster with increasing Cd additions than the A1 soils (Fig. 2). One possible explanation is the treatment dependent change in organic matter quality which separates the F soils from all other soils in this field experiment when characterized by near infrared analysis (Fritze et al. 1994a). The total soil C content fails to show such differences.

From Table 2a, the relative influence of the forest treatments on respiratory activity can be calculated as a percentage of the 0 Cd addition in the control treatment. At the Cd addition level of 1000 µg g^{-1} soil dw, the control soil exhibits 55 % of its original activity whereas the wood ash treatments at all three levels still show between 78 to 93 % of the control Cd 0 treatment respiratory activity. When judged by this criteria values of 50 % of the respiratory activity of the control Cd 0 treatment in the wood ash fertilized soils are reached with Cd additions between 3000 and 4000 µg g^{-1} soil dw.

In conclusion, it can be stated that, when applying wood ash as a single dose between 1000 and 5000 kg ha^{-1} on coniferous forest humus, the naturally occurring amount of Cd in the wood ash, varying between 4 and 20 µg g^{-1} dw, does not negatively influence the mineralization rate of soil nutrients. This is to be seen from the EC_{50} values in Table 2b and that Cd concentrations of 400 µg g^{-1} soil dw are needed to decrease the soil respiration rate of wood ash treated plots to uncontaminated control treatment levels (Table 2a).

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