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MICROBIAL ACTIVITIES IN FOREST SOILS EXPOSED TO CHRONIC DEPOSITIONS FROM A LIGNITE POWER PLANT

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Abstract

Atmospheric emissions of fly ash and SO_2 from lignite-fired power plants strongly affect large forest areas in Germany. The impact of different deposition loads on the microbial biomass and enzyme activities was studied at three forest sites (*Picea abies* (L.) Karst.) along an emission gradient of 3, 6, and 15 km downwind of a coal-fired power plant (sites Ia, II, and III, respectively), representing high, moderate, and low emission rates. An additional site (site Ib) at a distance of 3 km from the power plant was chosen to study the influence of forest type on microbial parameters in coniferous forest soils under fly ash and SO_2 emissions. Soil microbial biomass C and N, CO_2 evolved and activities of L-asparaginase, L-glutaminase, β-glucosidase, acid phosphatase and arylsulfatase (expressed on dry soil and organic C basis) were determined in the forest floor (L, Of and Oh horizon) and mineral top soil (0-10 cm). The emission-induced increases in ferromagnetic susceptibility, soil pH, concentrations of mobile (NH_4NO_3 extractable) Cd, Cr and Ni, effective cation exchange capacity, and base saturation in the humus layer along the 15 km long transect significantly ($P<0.05$) reflected the effect of past depositions of alkaline fly ash. Soil microbial and biochemical parameters were significantly ($P<0.05$) affected by chronic fly ash depositions. The effect of forest type (i.e., comparison of sites Ia and Ib) on the studied parameters was generally dominated by the deposition effect. Alkaline depositions significantly ($\underline{P}<0.05$) decreased the microbial biomass C and N, microbial biomass C-to-N ratios, and microbial biomass C-to-organic C ratios. Microbial respiration, metabolic quotient (qCO_2) and the activities of L-asparaginase, L-glutaminase, β−glucosidase, acid phosphatase, and arylsulfatase were increased by long-term depositions from the power plants. Acid phosphatase had the highest specific (enzyme activities expressed per unit organic C) activity values among the enzymes studied and arylsulfatase the lowest. The responses of the microbial biomass and soil respiration data to different atmospheric deposition loads were mainly controlled

by the content of organic C and cation exchange capacity, while those of enzyme activities were governed by the soil pH and concentrations of mobile heavy metals. We concluded that chronic fly ash depositions decrease litter decomposition by influencing specific microbial and enzymatic processes in forest soils.

1. Introduction

Changes in the soil physico-chemical environment and in the structure of the vegetation of forest ecosystems resulting from acid (i.e., SO_2, NO_x) and alkaline (i.e., dust, soot, fly ash) air pollution have been described in many studies (Ulrich,1983; Huettl and Bellmann, 1993; Klose and Makeschin, 2003a; b; Koch et al., 2002). While the effects of acidic air pollution have been comprehensively discussed (Ulrich, 1983; Berg and Matzner; 1997), information on the ecological impacts of alkaline emissions in Central Europe is rare.

Fly ash depositions into forest soils can be detected by scanning electron microscopy, energy dispersive X-ray microanalysis and magnetic susceptibility measurements (Klose et al., 2001; 2003a). Magnetic properties of a soil depend on its mineral composition, soil-forming processes and emissions from steel industries, and coal-fired power and cement plants (Strzyszcz, 1993). Most soils and particularly the forest floor contain only small amounts of magnetic iron compounds. Therefore, ferromagnetic properties of humic horizons are of interest in studies on air pollution because high susceptibility values are a reliable indicator for inputs of fly ash and industrial dust (Strzyszcz, 1993; Klose et al., 2001; 2003a).

Atmospheric fly ash emitted in the Lusatian region substantially increased the mineral contents of organic horizons, and the concentrations of carbon, aluminum, iron, calcium, potassium, sulfur, titanium and sodium in soils (Klose et al., 2003a). Depending on the chemical composition of the fly ash, their deposition in forest ecosystems may alter soil pH levels, base saturation, contents of carbon, soluble salts, major and trace elements and heavy metals (Bellmann and Grote, 1998; Weisdorfer et al., 1998; Koch et al., 2002;

Klose and Makeschin, 2003a). As a consequence, changes the species composition of plant communities were observed in forest stands in emission areas (Amarell, 2000).

Nutrient mineralization from fresh plant litter and soil organic matter is carried out by the enzymatic activities of microbial populations that become established on the litter-organic matter-surfaces. The rate of enzyme production, and the activity and the stability of free and adsorbed enzymes are controlled by environmental conditions and ecological interactions (Kandeler et al., 1996; Acosta-Martínez and Tabatabai, 2000; Klose et al., 1999). The levels of enzyme activities vary among the litters from different plant species (Carreiro et al., 2000; Kourtev et al., 2002). These variations have been attributed to the chemical composition and physiological status of the plant material and to edaphic conditions (Kourtev et al., 2002). Enzyme activities are determined by the factors that affect size and metabolic activity of microorganisms in soil; moisture, temperature, pH, available nutrients and toxic elements, and litter quality. Due to the significant changes in the soil physical and chemical properties of forest stands in emission areas, changes in the size of the microbiota and in enzyme activities in the forest floor and mineral soils could be expected.

Fly ash deposition decreased the litter decomposition rate in organic horizons of forest soils (Klose et al., 2003b and submitted for publication). This may have been due to suppression of cellulose and lignin degrading micro-fungi, as previously documented (Bååth et al., 1995; Wolters et al., 1995). Several short-term studies indicated that the addition of alkaline power plant fly ash to soils increased microbial respiration (Wong and Wong, 1986), N mineralization and nitrification (Cervelli et al., 1986), but inhibited the activities of some soil enzymes (Pichtel and Hayes, 1990). Bååth et al. (1995) found a significant decrease in microbial biomass contents in wood-ash fertilized forest soils. Wood ash fertilization raised the microbial activity in a boreal forest humus layer (Periömäki and Fritze, 2002).

The objectives of this study were (i) to investigate the effects of fly ash and SO_2 pollution on soil microorganisms and enzyme activities along a gradient of three a-priori coniferous forest stands subjected to chronic depositions from lignite power plants, and (ii) to evaluate the effect of vegetation type (i.e., dominantly coniferous vs. dominantly deciduous forest stands) on microbial processes in emission areas. Changes in microbial

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biomass, microbial respiration and activities of soil enzymes involved in C (β-glycosidase), N (L-asparaginase and L-glutaminase), P (acid phosphatase) and S (arylsulfatase) cycling in forest soils were studied in response to high, moderate, and low input rates of alkaline fly ash and SO_2. These results can provide useful information on changes in organic matter decomposition and in C, N, P, and S nutrient transformation in such forest ecosystems resulting from the past emissions and the recent changes in air pollution in eastern Germany.

2. Materials and methods

2.1 Field study

The studied forest area is located on the German-Polish border in the eastern part of Saxony, Germany. The area is located at an altitude of 200 to 350 m and was a-priori dominated by old spruce stands (*Picea abies* (L.) Karst.) (Klose and Makeschin, 2003b). The annual average temperature is 8 °C and the average precipitation is 650 mm. Dominant soils are luvic Cambisols (FAO classification), with stagnic features in the subsoil, developed on pleistocenic loess loams and morainic loams over granodiorite. Soil texture ranged from silt to silt loam, and humus type from fine-humus-rich raw humus/moder, fine-humus-rich moder to fine-humus-poor moder. Soil texture along the deposition gradient varied between 3 to 9 % clay, 61 to 86 % silt, and 5 to 36 % sand. Two German power plants (Hagenwerder and Hirschfelde) and the Polish power plant in Turów emitted SO_2 and fly ash for more than 95 years. The power plants in Hagenwerder and Hirschfelde were closed in the 1990s but the power plant in Turów continues to operate. From 1989/90 to 2001, the atmospheric SO_2 and fly ash emissions from the German power stations declined by approximately 98 %, and those from the Polish power plant decreased by 83 to 88 %, respectively (Deutsch-Polnische Kommission für Umweltschutz, 1995).

Three forest sites (e.g., sites Ia, II and III) were selected along a 15 km long transect at distances of 3, 6 and 15 km downwind of the active power plant in Turów. These sites represent a fly ash deposition gradient of high, medium and low input rates. The three sites are similar in forest site index, a-priori forest stand type (*Picea abies*) and stand age (older than 80 years), but vary in the species composition of the vegetation due to

deposition-related changes in chemical soil properties. Total plant species numbers decreased from 45 to 23 along the 15 km long transect. Additionally, site Ib was chosen at a distance of 3 km from Turów. This site is located about 20 m southeast of Ia, showing similar site characteristics to Ia, with the exception of the vegetation type. Site Ia is dominated by beech (*Fagus sylvatica*) and other deciduous tree species with a total coverage of 70 %, whereas more than 50 % of site Ib is covered by *P. abies*, with year-round foliation even though it is most severely damaged. Geographical location and vegetation structure are summarized in Table 1.

((Table 1))

2.2 Sampling, storage and preparation

Four composite samples from the L, Of and Oh horizons and the mineral topsoil (0-10 cm) were collected from all sites in spring and fall of the years 1999 and 2000. Composites were made from 5 to 8 random samples from an area of 400 cm^2 each from the northern, eastern, southern and western directions from the centre of the plot (total size: 400 m^2) to obtain multiple observations from each plot. The samples were passed through 5 and 2 mm sieves for humus and mineral soils, respectively, and stored at 4°C before microbial analysis. Microbial analysis and enzyme assays were conducted within four weeks of obtaining the soil samples. Subsamples of the composite soils were air-dried and ground to pass through a 180 μm sieve for physical and chemical analyses.

2.3 Physical and chemical analysis

Because persistent residues of lignite-derived fly ash are associated with magnetic Fe compounds and mineral particles (Klose et al., 2001; 2003a), the soils were analyzed for magnetic susceptibility (X^2) as described by Klose et al. (2003a). Because of the deposition of other soluble salts, and residual lignite carbon ("black") C, soil pH, effective cation exchange capacity, base saturation and total organic C and N were determined by the methods described previously by Klose et al. (2001) and Klose and Makeschin (2003a). Concentrations of mobile heavy metals were determined after extraction in 1M NH_4NO_3 solution (1:25 and 1:50 w/v for mineral and organic soils, respectively) by shaking at 180 rev min^{-1} for 24 h (overhead shaker), and centrifuging at

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2500 rev min^{-1} for 15 min as described by Zeien and Brümmer (1989). The element concentrations in the extracts were analyzed by an ICP-OES.

2.4 Microbial Analysis

Soil microbial biomass C and N were estimated by extracting 25-g and 5-g oven-dry equivalents of field-moist mineral and humus soil samples, respectively, in 0.5 M K_2SO_4 (1:4 and 1:20 w/v for mineral and organic soils, respectively), by the chloroform-fumigation-extraction method described by Vance et al. (1987) and Brookes et al. (1985). The concentrations of organic C and N in the extracts were determined by a CN analyzer (Jena Analytics) after acidification with one drop of 2 M HCl to remove any dissolved carbonate. Biomass C and N were calculated using a k_{EC} and k_{EN} factor of 0.30 (Sparling et al., 1990) and 0.45 (Jenkinson, 1988), respectively. The chosen k_{EC} and K_{EN} factors were suggested for soils with high organic matter contents, such as organic horizons in forest soils. Basal soil respiration was determined on 20-g, 10-g, 10-g and 5-g oven-dry equivalents of field-moist mineral soil and H, F and L horizon samples, respectively, incubated in closed jars (250 ml Schott bottles, Merck Co.) as described by Jäggi (1976). Soil samples were conditioned at 22°C for 48 h before respiration measurements. The CO_2 production after incubation at 25°C for 24 h was estimated by titration with 0.05 *M* HCl after adding 0.5 *M* $BaCl_2$ and phenolphthalein indicator.

2.5 Soil enzyme assays

The enzyme activities were assayed at their optimal pH values as described by Tababatai (1994). The volume of the buffer solution was increased from 4 to 8 mL for the assay of β-glucosidase, acid phosphatase and arylsulfatase activities to ensure a thorough mixing of the soil-buffer-substrate suspension, especially when working with organic soils. The THAM buffer (pH 12) was used instead of 0.5 M NaOH solution in order to avoid the extraction of humic acids from organic soils. The later would disturb the colorimetrical determination of the *p*-nitrophenol (PN) the product of the enzyme reaction.

L-asparaginase and L-glutaminase activities were assayed by incubating a 5-, 2.5-, 2.5 or 1.25-g oven-dry equivalent sample of mineral soil, H, F, and L horizon, respectively. All buffers and reagents were prepared as described by Tabatabai (1994).

2.6 Statistical analyses

Specific activities of soil enzymes in the humic layer and mineral surface soils were expressed per unit organic carbon (mg PN or NH_4-N kg^{-1} organic C). Soil chemical analyses and microbial biomass C and N were determined in duplicates, and microbial respiration in triplicate. Soil enzyme assays were performed in duplicate with one control. All data were calculated on the basis of oven-dry (105°C) soil weight and are presented as arithmetic means of four observations for each site. Different statistical analyses were performed separately on the microbial and enzyme activity data sets for each horizon using the Statistical Package for the Social Sciences (SPSS version 10.0.7 for Windows). These tests included (1) multivariate analysis of variance (MANOVA) for site, horizon, year and season, (2) separation of means by the Mann-Whitney U test (where main effects were significant), (3) correlation analyses by Spearman and Pearson, and (4) principal components analysis (PCA) for reflection of any intrinsic pattern in the multidimensional data swarm. PCA was performed separately for microbial biomass and respiration data and for enzyme data. Mean factor score values for the first two PCs for samples of each forest site were compared for significant differences by the Mann-Whitney U test. Factor loadings of the first two PCs were plotted and correlated (analysis by Pearson) with soil physical and chemical properties to identify possible relationships between microbial and environmental parameters. Multiple linear regression analysis was performed on the factor scores for the first two PCs for the microbial biomass and respiration data and enzyme data and soil physical and chemical properties that showed significant influence on the studied parameters after normalizing the data (e.g. dividing the original data by the maximum value of the data set) using SigmaStat (version 2.03). The results of the multiple linear regression analysis reveal which of the environmental parameters contribute to predicting the first two PCs for both microbial biomass and respiration data, and enzyme data.

3. Results

3.1 Soil physical and chemical properties

Long-term fly ash deposition to forest soils in eastern Germany caused an accumulation of ferromagnetic fly ash constituents in the organic layer of heavily affected sites, particularly in the Of and Oh horizons (Table 2). Magnetic susceptibility values were higher at the predominantly coniferous site Ib compared to the predominantly deciduous site Ia. Fly ash accumulation resulted in significant increases in soil pH, concentrations of NH_4Cl-extractable cations, effective cation exchange capacity and base saturation. Magnetic susceptibility was correlated with concentrations of Mg and effective cation exchange capacity ($r \geq 0.43$, $P \leq 0.05$) in the Of horizon, and with pH and effective cation exchange capacity ($r \geq 0.60$, $P \leq 0.001$) in the Oh horizon. In contrast, concentrations of total organic C and N in the humus floor and mineral topsoil decreased with increasing deposition loads, while the C-to-N ratio of the soil showed only little differences. Concentrations of mobile Cd, Cr and Ni were increased in forest topsoil by high and moderate deposition loads compared to sites with low loads, while concentrations of Pb were decreased. The mobile fractions of Cd, Cr and Ni were positively correlated with soil pH and magnetic susceptibility ($r \geq 0.552$, $P \leq 0.013$), while Pb revealed the opposite trend ($r \geq -0.701$, $P = 0.001$).

((Table 2))

Concentrations of organic C and C-to-N ratios of the soil were in general higher at site Ib compared to Ia, while base saturation was lower in the former. All other chemical soil properties differed only slightly between these two sites.

3.2 Microbial Biomass

Microbial biomass C and N were significantly lower in the humus layers and mineral topsoil (0-10 cm) of forest sites most heavily affected by fly ash depositions, e.g. sites Ia and Ib ($P<0.05$) compared to less affected sites II and III (Table 3). In the Oh horizon, microbial biomass was significantly higher at site Ib (pure coniferous stand) relative to site Ia (dominantly deciduous stand).

((Table 3))

Microbial biomass C-to-microbial biomass N ratio was significant lower in the organic layers of forest sites Ia and Ib (high deposition-load sites) compared to sites II and III (moderate and low deposition-load sites, respectively). The microbial biomass in the Oh and Of horizon of the four forest sites was inversely correlated with magnetic susceptibility (X^2) values ($r \geq -0.33$, $P=0.003$) and soil pH ($r \geq -0.40$, $P=0.000$).

A change in the size of the soil microbial biomass with increasing deposition loads also became evident when microbial C and N of the four forest sites along the deposition gradient were compared using PCA (Fig. 1A). The PCA results shown are for the Oh horizons as representatives of the trends in the soil layers studied. The first PC accounted for 57% of the variation in the biomass data and significantly ($P=0.000$) separated sites Ia and III. The second PC accounted for a further 21% and significantly ($P \leq 0.014$) separated a great portion of the biomass data of site Ib and all other sites.

The loadings of the first two PCs of the microbial biomass C and N and the C-to-N ratio of the microbial biomass for the Oh horizons as representatives of the trends in the forest soils are shown in Fig. 1B. The biplot given in this figure showed that the differences in microbial biomass C and N between the four sites were due to higher concentrations of mobile (NH_4NO_3 extractable) Cd and Cr, and magnetic susceptibility, while the microbial biomass C-to N ratio was largely controlled by the effective cation exchange capacity and the C-to-N ratio of the soils.

The two PCs were correlated with soil physical and chemical parameters by multiple regression analysis revealing that PC1 can be predicted ($r^2 = 0.66$, $P \leq 0.05$) from a linear combination of the soil variables organic C content and effective cation exchange capacity following the equation: PC1 = 0.140 organic C + 0.002 ECEC. The PC2 can be predicted ($r^2 = 0.53$, $P \leq 0.05$) by the soil variables organic C content, pH, and concentrations of mobile Cd and Ni following the equation: PC2 = 0.137 organic C − 1.370 pH (H_2O) + 15.583 Cd + 1.234 Ni.

Microbial biomass C expressed on an organic matter basis was lowest in forest soils at site Ia in all soil depths, followed by Ib, and significantly increased ($P<0.05$) towards site III with decreasing deposition loads (Tab. 3). Differences between site Ia and Ib were not significant for organic and mineral soils studied. Differences in microbial

biomass C-to-organic C ratio between the four sites appeared to be due to higher concentrations of mobile Cd and Cr, and magnetic susceptibility (Fig. 1B).

((Figure 1))

3.3 Microbial respiration and metabolic quotient qCO$_2$

Microbial respiration was significantly lower in the Oh horizon at sites subjected to high deposition loads (i.e., sites Ia and Ib), compared to sites with moderate and low deposition loads (sites II and III, respectively) (Tab. 4). Respiration in the Oh horizon at site Ib was lower than at site Ia, although the results were not significant. In all other organic horizons and the mineral topsoil (0-10 cm), microbial respiration followed no consistent trend, or differences were slight. Respiration in the Of and Oh horizon was inversely correlated with magnetic susceptibility (X^2) values ($r \geq -0.49$, $P=0.000$) at the four forest sites.

The metabolic quotient (qCO$_2$-ratio of CO$_2$-C respiration to microbial biomass C) was significantly ($P<0.05$) higher in the forest soil at site Ia compared to site III (Tab. 4). The differences between the high-load and the low-load site were most pronounced in the L and Of horizon. Soil qCO$_2$ in the Oh horizon was inversely correlated with magnetic susceptibility (X^2) values ($r=-0.53$, $P=0.001$), and positively correlated with pH (H$_2$O) in the Of and Oh horizons ($r \geq 0.40$, $P=0.001$) at the four forest sites.

PCA revealed that soil differences in pH(H$_2$O) and concentration of mobile Ni contributed the most to the differentiation in microbial respirations, and that organic C appeared to largely control soil qCO$_2$ in the Oh horizon in the forest soils along the deposition gradient (Fig. 1B).

((Table 4))

3.4 Soil Enzyme Activities

The activities of L-asparaginase, L-glutaminase, β-glucosidase, acid phosphatase and arylsulfatase in the humus layer and mineral topsoil decreased with decreasing deposition loads. The β-glucosidase activity in the Oh horizon was negatively correlated with magnetic susceptibility X^2 ($r=-0.33$, $P=0.029$) at the four forest sites. The activities of all other enzymes in the Oh horizon were negatively correlated with magnetic susceptibility

(r≥-0.51, P≤0.002) (with exception of acid phosphatase activity), and positively correlated with pH (H$_2$O) (r≥0.47, P≤0.005) (with exception of L-asparaginase activity).

Specific activities (activity/kg^{-1} organic C) of selected soil enzymes were calculated for the humus and mineral soils because organic matter is known to affect enzyme activities (Table 5). The specific activities of L-asparaginase, L-asparaginase, β-glucosidase, acid phosphatase, and arylsulfatase in the humus samples (Of and Oh horizons) increased significantly with increasing deposition loads (P<0.05) (Tab. 5). In the L horizon and mineral topsoil (0-10 cm), no consistent trend was found for the specific enzyme activities. The specific activities of L-glutaminase, β-glucosidase, acid phosphatase and arylsulfatase were, in general, higher (P<0.05) in the Of and Oh horizons at forest site Ia compared to site Ib.

The PCA for the Oh horizon was chosen to represent the pattern of specific enzyme activities in the forest soils along the fly ash deposition gradient (Fig. 2). The first component of the PCA accounted for 42%, the second PC accounted for another 27% of the variation in the specific enzyme activity data (Fig. 2A). PCA did not lead to a clear spatial separation of this data set, and thus, interpretation of the two components of this PCA remains unclear. Nevertheless, plotting the factor scores of the first two PC's of the specific enzyme activities in relation to physical and chemical soil properties for the Oh horizon of the four forest sites allowed to explain some underlying ecologically concepts between enzyme activities and abiotic soil properties in fly ash-affected forest soils. Data sets which are clustered in the same data swarm in a PCA are believed to be correlated.   The specific activity values of L-asparaginase appeared in the same data swarm as base saturation and concentrations of NH$_4$Cl extractable Mg, while specific L-glutaminase activity values were clustered with soil pH (Fig. 2B). Specific β-glucosidase activity appeared in the same data swarm as effective cation exchange capacity, C-to-N ratio of the organic material, and concentrations of mobile Ni in the soils. Specific acid phosphatase and arylsulfatase activities were clustered with concentrations of mobile Cr, magnetic susceptibility and with concentrations of mobile Cd, respectively.

4. Discussion

Typical features indicating long-term emissions from coal-fired power plants to forest soils in the studied forest area in eastern Germany were high values of magnetic susceptibility, pH, base saturations and effective cation exchange capacities in the forest floor. Magnetic susceptibility was chosen as an indirect measure to reflect the fly ash pollution gradient along the transect of four forest sites, because a significant relationship between increased magnetic susceptibility, industrial emission and dust deposition in topsoil has been reported in many studies (Strzyszcz, 1993; Kapicka et al., 1999; Klose et al., 2001; Klose et al., 2003a). Magnetic susceptibility values were higher at a pure conifer stand compared to a site where chronic alkaline depositions lead to drastically changes in the vegetation structure from a-priori conifer into a dominantly (70% coverage index) deciduous stand. These results indicate that the amounts of deposited ferromagnetic particles were, in part, controlled by the forest stand type. However, the effect of other factors such as location of site relative to the power plant and/or to the prevailing wind direction cannot be excluded.

The observed alterations in chemical properties of the studied forest soils suggest that alkaline components dominated the emissions at sites with high and moderate deposition loads. The increase in the pH of the humus layer and mineral topsoil of a-priori spruce stands from high and moderate deposition loads decreased the mobile fractions (e.g., water-soluble, exchangeable and readily exchangeable heavy metals bound to metal-organic complexes) of Pb (Table 2), Cu and Hg (data not shown), while those of Cd, Cr, Ni (Table 2), Zn and Co (data not shown) were increased.

Microbial biomass C and N decreased in forest soils with high and moderate deposition loads relative to a low-load site. This trend became most evident in the Of and Oh horizons, which accumulated a large proportion of the persistent fly ash components (Klose et al., 2001; 2003a). Therefore, it is possible that the effects of fly ash deposition on the mineral soil are minimal. Because studies on the effects of the fly ash deposition on the soil microbial biomass, respiration, and enzyme activities are limited, we have made comparisons with wood ash-fertilized and limed soils. Fritze et al. (1994) observed no change in the soil microbial biomass C, while others reported lower microbial biomass values for wood ash-treated soils relative to ash-free soils (Bååth et al., 1995). Liming

increased (Wolters et al., 1995) or decreased soil microbial biomass (Lorenz et al., 2001). Besides the soil pH, water, temperature, the C-to-N ratio of the soil, the substrate quantity and availability have been shown to affect the biological response to liming and ash treatment (Bååth et al., 1995; Lorenz et al., 2001).

The microbial biomass C-to-N ratio is often used to describe the structure and the state of the microbial community. Some studies hypothesized that a high microbial C-to-N ratio reflects a higher proportion of fungi in the microbial biomass, whereas, a low value suggests that bacteria predominate the microbial populations (Pichtel and Hayes, 1990; Joergensen, 1995). Assuming this hypothesis is true, the microbial C-to-N ratio in humus horizons of forest soils along the deposition gradient could imply that the microbial biomass at sites with high deposition loads (i.e., with higher pH) was dominated by bacteria, while fungi were predominant in the low-load coniferous forest sites (i.e., with lower pH). Several studies documented that after lime application bacteria became dominant over fungi (Wolters et al., 1995).

The microbial biomass C-to-total organic C ratio, which shows the importance of soil microorganisms as a sink for mobile C in soils, was decreased in high deposition-load sites compared to low load sites. Fritze et al. (1996) reported that microbial biomass C contributed between 1.19 and 1.38% to the total organic C content in undisturbed humus layers from boreal coniferous forest ecosystems. The values from the less fly ash influenced soils were slightly below this range. The decrease of this ratio at the heavily and moderately influenced forest sites (i.e., sites Ia, Ib and II) may also indicate a disturbance in the C turnover in these soils. The reduction of the microbial biomass, the microbial biomass C-to-N ratio, and the microbial biomass C-to-total organic C ratio in forest soils that chronic received high loads of atmospheric depositions was potentially the result of the following factors: (i) a significant increase in soil pH as documented by Koch et al. (2002) and Klose and Makeschin (2003a; b), which may have caused a decrease in soil fungi-to-bacteria ratio, as indicated in this study and others (Bååth et al., 1995; Wolters et al., 1995), (ii) a decrease in substrate availability caused by an accumulation of persistent lignite-derived organic C compounds, as shown by Rumpel et al. (1998), and/or (iii) an increase in the concentrations of mobile fractions of Cd, Cr, Ni, Zn and Co.

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Decreased respiration rates in the Oh horizon of forest sites receiving high deposition loads compared to sites with moderate and low deposition loads may be attributed to increased concentrations of selected mobile heavy metals, that have accumulated in these horizons as a result of long-term atmospheric deposition. Klose et al. (2001; 2003b) showed, using ferromagnetic susceptibility measurements and scanning electron microscopy, that persistent fly ash components were mainly accumulated in the Of and Oh horizons of coniferous forest soils. A decrease in the respiration rate from site-specific litter collected from three forest sites along the same transect (i.e., sites Ia, II and III) due to fly ash pollution from a power plant was shown previously (Klose et al., submitted for publication). The addition of fly ash to sandy soils severely inhibited microbial respiration (Pichtel and Hayes, 1990), while increases in respiration rates in limed and ash-treated forest soils have been found (Fritze et al., 1994; Wong and Wong, 1986). Microbial respiration in forest soils subjected to power plant emission was strongly affected by the pH, concentration of mobile Cr and the C-to-N ratio of the soil. Similar results were reported by Bååth et al. (1995) on the effect of liming and ash treatment on soil respiration.

Higher soil qCO_2 in forest soils receiving high deposition loads relative to less affected sites could be related to an alteration in the energy requirements of soil microorganisms as suggested by Anderson and Domsch (1990), or to shifts in the microbial community structure as hypothesized by Bååth et al. (1992). Increasing soil qCO_2 with increasing application rates of wood-ash were reported by Fritze et al. (1994). Any type of disturbance will increase the qCO_2-ratios of soils (Fritze et al., 1996). Consequently, lower qCO_2-ratios at the forest sites with low deposition loads in this study would imply a relatively undisturbed soil biological functioning. Further it could suggest that organic matter mineralization at less affected sites was controlled by highly competitive fungal populations as reported by Fritze et al. (1994).

Enzyme activities and specific enzyme activities (activity rates on an organic C basis) were higher in the high deposition-load forest sites compared to the moderate and low-load sites. Specific enzyme activity values give an estimate of how suitable the organic matter is to degradation by enzymatic reactions, and thus are believed to be measures of organic matter quality (Boerner et al., 2000). Higher deposition-induced activities of L-

asparaginase, L-glutaminase, β-glucosidase, acid phosphatase, and arylsulfatase on an organic C basis would indicate an increased input of organic substances or a higher availability of these substances, and thus an increased turnover of organic N, S and P compounds in the mineral topsoil and forest floor as a result of past fly ash deposition. These results are in contrast to macro-morphological humus characteristics (i.e., humus type and thickness of organic horizons) found at the four sites along the deposition gradient (Klose and Makeschin, 2003b). The weak correlation structure of specific enzyme activity data in the PCA suggests that a larger sample size is needed for these parameters to reliably describe the underlying ecological factors in fly ash-affected forest soils.

It has been shown that various soil enzyme activities react differently to soil pollution with fly ash from coal-fired power plants. Pichtel and Hayes (1990) reported that the activities of dehydrogenase, phosphatase, arylsulfatase and invertase were significantly inhibited after treatments of soils with alkaline power plant fly ash, whereas catalase activity was not affected. Lai et al. (1999) reported that dehydrogenase activity was generally decreased in a sandy soil when alkaline coal fly ash was applied in combination with sewage sludge. Compensatory liming of a spruce forest in Germany increased protease activity in the forest floor and mineral topsoil, while catalase activity followed no distinct pattern (Lorenz et al., 2001).

In addition to the marked changes in soil properties along this deposition gradient, emission-induced differences in the vegetation structure and, thus, variations in amounts and quality of the litter produced by each stand could have contributed to the responses of microbial and biochemical properties of the four studied forest sites. Severe damage of spruce stands in the *St. Marienthal* forest area with up to 52% foliage damage was observed in 1989 (Klose and Klose, 1997). Due to improved light conditions in a sparsely foliated canopy, higher pH and improved nutrient status in soils, deciduous tree species in the second tree story became dominant (coverage index of 70%) over the spruce stands at the high deposition-load site. This vegetation structure would suggest a higher litter quality at high deposition-load sites, which in turn should increase microbial and soil enzyme activities. However, in this study microbial biomass, soil respiration and

microbial biomass C-to-organic C ratio were decreased in coniferous forests by chronic alkaline depositions, while enzyme activities were increased.

5. Conclusions

Forest soils along the fly ash deposition gradient differed in several important environmental parameters that influence size and activity of soil microorganisms and soil enzymes. These changes in soil properties mainly occurred in the organic layers and were caused by the accumulation of emission-derived alkaline compounds, organic C sources, and heavy metals, or by changes in vegetation structure towards a nutrient-rich litter. Chronic fly ash depositions decreased microbial biomass, soil respiration and microbial biomass C-to-organic C ratio in a-priori old spruce stands in Upper Lusatia, eastern Germany, while enzyme activities and the qCO_2 were increased. Moreover, the study demonstrated that decreases in the size and activity of microbial biomass are not necessarily accompanied by decreases in specific enzyme reactions.

The actual mechanisms by which some biological parameters responded negatively to the effects of alkaline depositions on soil chemical properties and plant growth remain unknown. At the beginning, atmospheric deposition from coal-fired power plants probably had a positive effect on microbial and biochemical processes due to increases in pH and concentrations of nutrients in soil, similar to the effects reported for compensatory forest liming practices. However, we hypothesize that with increasing deposition loads selected microbial soil processes were severely inhibited due to the accumulation of heavy metals and almost inert organic C compounds derived from lignite and deposited with the fly ash. Due to a general reduction of alkaline air pollution, decreasing soil pH values in future will increase nutrient imbalances and the mobility of accumulated heavy metals and, as a consequence, reduce organic matter decomposition and element cycling in fly ash-affected forest stands in the Upper Lusatian region.

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Figure Captions

Figure 1. Scores of the first two principal components (PCs) of the microbial biomass and respiration (A) and scores and loadings of the microbial biomass and respiration data in relation to soil physical and chemical properties (B) in the Oh horizon of coniferous forest sites along a deposition gradient in eastern Germany. Abbreviations: X^2: magnetic susceptibility, BS: base saturation, ECEC: effective cation exchange capacity, org.C: organic C, C/N: C-to-N ratio of the organic material, Mg: contents of NH_4Cl-extractable Mg, Cd, Cr, Ni, Pb: concentrations of NH_4NO_3-extractable heavy metals, cmic: microbial biomass C, nmic: microbial biomass N, cmic_corg: microbial biomass C-to-organic C ratio, cnmic: C-to-N ratio in the microbial biomass, respir.: microbial respiration, qco2-c: metabolic quotient.

Figure 2. Scores of the first two principal components (PCs) of soil enzyme activities (A) and scores and loadings of the enzyme activity data in relation to soil physical and chemical properties (B) in the Oh horizon of coniferous forest sites along a deposition gradient in eastern Germany. Abbreviations, l-asp.: L-asparaginase activity, l-glu: L-glutaminase activity, beta-gluc: β-glucosidase activity, acid p.: acid phosphatase activity, and sulf.: arylsulfatase activity. For further abbreviations, see Figure 1.

Table 1. Location and vegetation structure of coniferous forest sites along a deposition gradient in the Upper Lusatian district, southeast Germany.

Site characteristics	Site			
	Ia	Ib	II	III
Description	-------------------- Forest area St. Marienthal --------------------			Forest area Kleiner Nonnenwald
Distance from Turów (km)	3	3	6	15
Geographical location	51°57'36''N, 14°53'35''E	51°57'36''N, 14°53'35''E	51°57'36''N, 14°53'35''E	51°58'16''N, 14°50'10''E
1th tree storey[a]	Picea abies (< 5%)	P. abies (50%)	*P. abies* (15%)	P. abies, Pinus sylvestris (60%)
2nd tree storey[a]	Fagus sylvatica, Betula pendula, Acer pseudoplatanus (70%)	Sorbus aucuparia (5%)	B. pendula (25%)	
Bush storey[a]	Rubus idaeus, Vaccinium myrtillus (< 5%)	Frangula alnus, F. sylvatica (< 5%)	R. idaeus, V. myrtillus (75%)	V. myrtillus (25%, patchy pattern)
Ground vegetation[a]	Melica uniflora, Calamagrostis epigejos, Eupatorium cannabinum, Rubus idaeus (10%)	Avenella flexuosa, C. epigejos V. myrtillus, R. idaeus (20%)	C. epigejos (60%)	C. arundinacea (<10%)
Total species number	45	38	24	23
Site index	----------------------------- WM2[b]-----------------------------			

[a] Vegetation structure was determined in Spring 2000. Numbers in parentheses represent the total coverage index for the vegetation in the storey specified according to Braun-Blanquet (1964).
[b] WM2 = slightly stagnic soil with moderate nutrient supply (Ecological Forest Site Classification for Eastern Germany, Kopp and Schwanecke, 1994).

Table 2. Physical and chemical properties of coniferous forest soils along a deposition gradient in the Upper Lusatian district, southeast Germany.[a]

		Physical soil properties	Chemical soil properties									
										Heavy metals		
		χ^2	pH	Org. C	Total N	C/N	ECEC[c]	BS[d]	Cd	Cr	Ni	Pb
Site	Horizon	$(10^{-8} \text{ m}^3 \text{ kg}^{-1})$[b]	H_2O	(g kg^{-1})			(cmol kg^{-1})	(%)		(mg kg^{-1})[e]		
Ia	L	20	5.7	357	14.2	25	514	93	0.30	0.37	1.52	1.21
	Of	224	5.6	159	7.1	22	258	72	0.25	0.38	3.12	1.23
	Oh	265	5.6	149	6.0	25	240	66	0.20	0.33	3.57	1.09
	0-10 cm	32	5.2	36	1.4	25	93	45	0.08	0.27	1.01	5.74
Ib	L	32	5.2	409	16.1	25	465	86	0.31	0.35	2.27	1.93
	Of	298	5.3	191	7.6	25	262	45	0.18	0.59	1.98	1.64
	Oh	316	5.2	146	5.1	29	258	46	0.22	0.39	3.07	1.07
	0-10 cm	79	4.7	46	1.9	24	136	36	0.10	0.26	1.97	3.76
II	L	16	5.2	404	16.3	25	409	90	0.32	0.28	1.13	1.84
	Of	167	5.2	248	11.4	22	251	73	0.21	0.34	1.56	2.37
	Oh	159	4.7	224	9.0	25	224	24	0.19	0.36	1.60	4.44
	0-10 cm	10	4.2	22	1.1	21	77	18	0.05	0.32	0.50	9.22
III	L	25	4.5	450	18.2	25	236	64	0.29	0.17	2.00	4.64
	Of	111	4.3	326	14.9	22	215	14	0.17	0.25	1.55	11.68
	Oh	92	4.2	255	10.8	24	193	9	0.16	0.16	1.60	19.35
	0-10 cm	13	3.9	47	2.0	24	89	7	0.05	0.17	0.50	10.23

[a] Values shown are means of 4 observations and 4 sampling dates (n = 16) in 1999 and 2000.

[b] Magnetic susceptibility = (Ferromagnetic analyzer (FMA) value (mHz) $*$ (0.7 $*$ 10^{-5})) / bulk density (Klose et al. 2003a).

[c] ECEC = effective cation exchange capacity.

[d] BS = base saturation.

[e] Concentrations of NH_4NO_3 extractable ("mobile") heavy metals.

Table 3. Microbial biomass C and N in organic horizons and mineral soils (0-10cm) of coniferous forest sites along a deposition gradient in southeast Germany.[a]

Site	Horizon	C_{mic}	S_E[b]	N_{mic}	S_E	C_{mic}/N_{mic}[d]	C_{mic}/C_{org}[e]	S_E
		(mg kg^{-1} soil)[c]					%[c]	
Ia	L	3014a	240	591a	96	5a	0.70a	0.04
	Of	1273a	125	179a	35	7a	0.64a	0.06
	Oh	716a	28	80a	10	9a	0.51a	0.01
	0-10 cm	216a	11	24a	10	9a	0.69a	0.03
Ib	L	3331ab	278	499b	95	7b	0.78ab	0.06
	Of	1555b	79	281ab	67	6a	0.76ab	0.02
	Oh	860a	79	139b	23	6b	0.61a	0.06
	0-10 cm	227a	24	60bc	11	4b	0.63a	0.03
II	L	4547b	547	499b	93	9c	1.03b	0.13
	Of	2052c	117	218a	13	9b	0.78b	0.03
	Oh	1826b	101	128b	10	14c	0.80b	0.05
	0-10 cm	357b	26	31ab	6	12c	1.55b	0.08
III	L	3710b	369	464b	56	8bc	0.97b	0.10
	Of	3756d	169	294b	26	13c	1.13c	0.01
	Oh	2585c	153	252c	19	10d	1.08c	0.04
	0-10 cm	629c	57	72c	8	9a	1.41b	0.12

[a] Values shown are means of 4 observations and 4 sampling dates (n = 16) in 1999 and 2000.

[b] Standard error.

[c] Within each horizon, column means followed by the same letter are not statistically significant at P<0.05.

[d] Microbial biomass C-to-microbial biomass N ratio.

[e] Microbial biomass C expressed on an organic matter basis. Calculation as follows: (Cmic/organic C) * 100.

Table 4. Microbial respiration and metabolic quotient (qCO_2) in organic horizons and mineral soils (0-10 cm) of coniferous forest sites along a deposition gradient in southeast Germany.[a]

Site	Horizon	Respiration[b] (mg CO_2-C kg^{-1} h^{-1})		qCO_2[b] (mg CO_2-C g^{-1} C_{mic})	
		mean	S_E[c]	mean	S_E
Ia	L	58.9a	4.8	20.3a	0.8
	Of	7.8a	1.0	6.3a	0.7
	Oh	3.1a	0.2	4.3a	0.1
	0-10 cm	0.8a	0.1	3.9a	0.2
Ib	L	71.8b	2.8	14.0b	0.2
	Of	5.8b	0.8	3.6b	0.4
	Oh	2.6a	0.3	3.6b	0.5
	0-10 cm	0.7a	0.0	2.8ab	0.2
II	L	41.5c	2.9	11.6c	1.3
	Of	6.0b	0.3	2.9b	0.1
	Oh	4.3b	0.3	2.4b	0.1
	0-10 cm	0.6a	0.0	1.8c	0.1
III	L	48.1ac	3.7	12.1c	0.8
	Of	9.8ab	1.0	2.8b	0.1
	Oh	8.1c	0.8	2.9b	0.3
	0-10 cm	0.6a	0.0	1.1c	0.1

[a] Values shown are means of 4 observations and 4 sampling dates (n = 16) in 1999 and 2000.

[b] Within each horizon, column means followed by the same letter are not statistically significant at $P<0.05$.

[c] Standard error.

Table 5. Soil enzyme activities relative to soil organic C content in organic horizons and mineral soils (0-10 cm) of coniferous forest sites along a deposition gradient in southeast Germany.[a]

Site	Horizon	Specific enzyme activity[b]									
		L-asparaginase		L-glutaminase		β-glucosidase		Acid phosphatase		Arylsulfatase	
		--- (mg NH$_4$-N kg^{-1} organic C h^{-1}) ---				----------- (mg PN kg^{-1} organic C h^{-1}) -----------					
		mean	S$_E$[c]	mean	S$_E$	mean	S$_E$	mean	S$_E$	mean	S$_E$
Ia	L	0.21a	0.02	1.47a	0.04	2.44a	0.32	2.04a	0.15	0.25a	0.03
	Of	0.15a	0.02	2.00a	0.17	2.46a	0.14	4.41a	0.23	0.28a	0.04
	Oh	0.11a	0.01	0.61a	0.01	2.25a	0.15	3.62a	0.34	0.13a	0.01
	0-10 cm	0.16a	0.02	1.32a	0.10	1.98a	0.19	7.81a	0.36	0.62a	0.07
Ib	L	0.13ab	0.01	0.94b	0.05	2.32a	0.31	1.97a	0.07	0.08b	0.01
	Of	0.11ab	0.01	0.79b	0.04	2.12a	0.18	3.00b	0.18	0.15a	0.02
	Oh	0.10a	0.00	0.44b	0.01	1.55b	0.12	2.57b	0.23	0.08b	0.01
	0-10 cm	0.11b	0.01	1.02ab	0.16	1.47b	0.13	3.44b	0.19	0.45b	0.04
II	L	0.19ab	0.04	1.36ac	0.08	1.24b	0.24	3.10b	0.18	0.13b	0.02
	Of	0.10b	0.01	0.89b	0.09	1.25b	0.24	2.80b	0.26	0.07b	0.00
	Oh	0.07b	0.01	0.23c	0.02	0.96b	0.18	1.67c	0.20	0.04c	0.00
	0-10 cm	0.23c	0.02	0.97b	0.04	1.79ab	0.22	7.09a	0.97	0.58a	0.03
III	L	0.21a	0.02	1.24c	0.12	1.14b	0.18	0.99c	0.04	0.04c	0.01
	Of	0.08b	0.01	0.29c	0.02	1.75ab	0.24	0.66c	0.08	0.02c	0.00
	Oh	0.09ab	0.01	0.18d	0.02	1.40b	0.20	0.76d	0.05	0.03c	0.00
	0-10 cm	0.17a	0.02	0.39c	0.03	2.28a	0.04	5.01b	0.11	0.63a	0.05

[a] Values shown are means of 4 observations and 4 sampling dates (n = 16) in 1999 and 2000.

[b] Within each horizon, column means followed by the same letter are not statistically significant at P <0.05.

[c] Standard error.

A

PC 2 (21%)

3
2
1
0
-1
-2
-3

-2   -1   0   1   2   3

PC 1 (57%)

SITE

▲ III
● II
□ Ib
■ Ia

B

PC 2

1.0

cnmic
BS   Mg
ECEC   C/N
Ni
qco2-c   pH(H$_2$O)
respir.
org. C   cmic
Pb   cmic_cor
Cd
total N   X^2 Cr
nmic

-1.5   -1.0   -.5   0.0   .5   1.0   1.5

PC 1