LANL Ref

2184

EFFECT OF HEAVY METALS AND MINERAL NUTRIENTS ON FOREST LITTER RESPIRATION RATE

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(Received 6 July 1992; accepted 17 November 1992)

Abstract

Two hypotheses were tested: (1) heavy metals such as Zn, Pb and Cd can suppress the respiration rate of forest litter at low–moderate pollution levels, and (2) mineral nutrients such as K, Ca and Mg can counteract the toxicity of heavy metals when applied onto the polluted litter. In a completely randomised design, three doses of heavy metals were used: Cd—10, 50, 250; Pb—100, 500, 2500; Zn—200, 1000, 5000 μg/g dwt litter, respectively. For Ca, Mg and K, the doses corresponded to 100, 500 and 2500 μg/g. A significant decrease in cumulated CO_2 evolution after 4 weeks of incubation was found for the litter samples treated with medium doses of Zn, Cd/Ca, Cd/Mg, Pb/Ca, Pb/Mg, Pb/K, Zn/Mg, Zn/Ca, Zn/K and for all the highest-dose treatments. The largest drop in respiration rate in both the medium and the highest doses was caused by additions of Zn either alone or in combination with K, Ca or Mg. The additions of mineral nutrients were found to decrease the litter respiration rate below the value measured for the respective heavy metal alone in the case of Cd/Ca, Cd/Mg, Pb/Ca, Pb/Mg and Pb/K in the medium-dose treatments, and for Cd/Ca, Cd/Mg, Cd/K, Pb/Ca and Pb/Mg in the highest-dose treatments. In all other cases, additions of the mineral nutrients did not influence the respiration rate significantly when compared to the effect of the respective heavy metal.

INTRODUCTION

The decomposition of litter is one of the most important processes in nutrient cycling in forest ecosystems. The recognition of its importance for the ecosystem functioning has stimulated numerous studies concerning litter decomposition rates (e.g. Meentemeyer, 1978; Berg *et al.*, 1987; Dziadowiec, 1987; McClaugherty & Berg, 1987; Blair, 1988) and nutrient dynamics in decomposing litter (e.g. Berg, 1986; Berg & Staaf, 1987; Maheswaran & Attiwill, 1987).

Because of its crucial importance for ecosystem functioning, litter decomposition was also a subject of many studies concerning the influence of industrial pollution at an ecosystem level. In the 1970s Rühling and Tyler (1973) studied litter decomposition rate in pine forests under the influence of emissions of Cu, Zn, Cd, Ni and Pb and suggested that litter decomposition rate can be retarded by heavy metals, at least in acidic stands. Babich and Stotzky (1974) have suggested that the accumulation of heavy metals in the litter layer can be toxic to microorganisms and that this phenomenon is responsible for the inhibition of decomposition of organic matter in heavily polluted forests. The toxicity of Cd to microorganisms was confirmed later in the laboratory experiments by Giesy (1978).

In heavily polluted regions the increased accumulation of organic matter on the forest floor was reported to be as high as 213% of the control (Strojan, 1978). The decreased litter decomposition rate in ecosystems under industrial pollution stress was found also by Killham and Wainwright (1981) and by Zieliński (1984). This led Grodziński and Yorks (1981) to recommend the measurements of the litter decomposition rate as a '...practical measure of system level pollution stress ...'.

In most of these studies the levels of heavy metals in litter were very high, exceeding the levels at undisturbed sites by up to three orders of magnitude. Thus, against the background of available data, Smith (1981) found evidence for the importance of heavy metals for litter decomposition rate only in situations of high air pollution load.

The experiments with artificial applications of various types of industrial dusts onto the forest floor suggested that their effect on organic matter accumulation is related not only to the concentration of heavy metals and other potentially toxic chemicals but also to some mineral nutrients commonly present in industrial emissions which can modify the toxic potential of heavy metals (Grodziński *et al.*, 1990).

On the other hand, the concentrations of heavy metals are known to increase during litter decomposition, while many mineral nutrients tend to decrease in concentration as the decomposition proceeds (Berg *et al.*, 1991; Laskowski *et al.*, 1993*a*). Thus, even in moderately polluted ecosystems, heavy metals can achieve relatively high concentrations in more decomposed fractions of forest litter (Laskowski & Berg, 1993). This raises the question about the concentrations

Environ. Pollut. 0269-7491/94/$07.00 © 1994 Elsevier Science Ltd, England. Printed in Great Britain

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of particular heavy metals that can affect the decomposition rate of organic matter.

Against the background of the results mentioned above, two hypotheses are formulated:

(1) heavy metals suppress the respiration rate of forest litter also at low and moderate pollution levels (concentrations); and
(2) mineral nutrients such as K, Ca and Mg counteract the toxicity of heavy metals when applied to the polluted litter.

MATERIALS AND METHODS

Litter collection and preparation

Natural mixed forest litter was collected in August 1991 from the forest floor in a beech–pine forest in Ratanica watershed, approximately 40 km south of Cracow, Poland. Concentrations of some of the most important heavy metals and mineral nutrients in the litter are given in the Appendix. The soil is acidic, of a mor type; pH (H_2O) varying between 3·4 and 4·3 (Adamczyk, B., unpublished). More details on the Ratanica watershed are published elsewhere (Laskowski *et al.* 1993*b*; Różański *et al.* 1993).

Collected litter was sieved through a 0·5 cm mesh sieve and macro- and mesofauna was removed manually. The litter was thoroughly mixed and kept for 3 days at 4°C. Dry mass content was evaluated by drying five samples in an oven at 105°C until constant mass.

Experimental treatment and experiment design

Samples of 17·08 g fresh mass of litter (5·00 g dry mass) were placed into air-tight plexiglass jars of 462 cm^3 in volume. The experiment was given a completely randomized design with 38 different treatments. For experimental treatment the solutions of the following salts were used: $CdCl_2$, $Pb(NO_3)_2$, $ZnCl_2$, $CaCl_2$, $MgCl_2$ and KCl. Mixtures and doses used in the experiment are given in Table 1. All metals were applied as salt solutions in distilled water and the solution pH was adjusted in all experimental treatments to 3·5 using a few microlitres of 0·1 M HCl or 0·5 M NaOH. Solution pH was measured with a digital pH-meter of NESTER Instr., Model 49.

As the soil used in the experiment was naturally acidic and it was further treated with acidic solutions, some effect of the acidification itself could be expected. To assess the pH effect two kinds of control treatments were used: one sprayed with distilled water of pH 6·1, and the other one with distilled water acidified to pH 3·5 with 0·1 M HCl. All experimental treatments were duplicated and six control samples of each type were used. All litter samples were sprayed with 5 ml of experimental/control solutions.

After spraying, all jars were weighed and the recorded mass was used for supplementing the water content in litter during the experiment. The water content was adjusted every seventh day, before the respira-

Table 1. Average respiration rate of forest litter treated with heavy metals and heavy metal/mineral nutrient combinations

No. of treatment	Treatment	Dose (μg/g dwt)	Respiration rate μmoles CO_2 g dwt^{-1} $24h^{-1}$ average ± SE
1	contr–6·1[a]	0	64·84 ± 0·77
2	contr–3·5[b]	0	61·64 ± 1·04
3	Cd	10	59·51 ± 0·84
4	Pb	100	63·72 ± 0·27
5	Zn	200	59·13 ± 0·63
6	Cd/Ca	10/100	63·02 ± 0·55
7	Cd/Mg	10/100	62·03 ± 1·81
8	Cd/K	10/100	61·24 ± 2·43
9	Pb/Ca	100/100	59·08 ± 0·62
10	Pb/Mg	100/100	57·50 ± 2·67
11	Pb/K	100/100	59·81 ± 0·24
12	Zn/Ca	200/100	54·76 ± 2·19
13	Zn/Mg	200/100	54·70 ± 1·24
14	Zn/K	200/100	54·24 ± 2·09
15	Cd	50	62·76 ± 4·18
16	Pb	500	62·63 ± 0·71
17	Zn	1000	45·43 ± 1·35
18	Cd/Ca	50/500	50·94 ± 1·95
19	Cd/Mg	50/500	50·90 ± 1·97
20	Cd/K	50/500	56·82 ± 0·85
21	Pb/Ca	500/500	51·12 ± 1·68
22	Pb/Mg	500/500	49·28 ± 0·39
23	Pb/K	500/500	52·41 ± 1·68
24	Zn/Ca	1000/500	42·48 ± 1·87
25	Zn/Mg	1000/500	44·53 ± 0·64
26	Zn/K	1000/500	46·32 ± 1·02
27	Cd	250	53·16 ± 2·04
28	Pb	2500	50·09 ± 2·78
29	Zn	5000	32·10 ± 1·04
30	Cd/Ca	250/2500	39·01 ± 0·77
31	Cd/Mg	250/2500	35·88 ± 1·34
32	Cd/K	250/2500	43·21 ± 0·10
33	Pb/Ca	2500/2500	38·03 ± 2·72
34	Pb/Mg	2500/2500	34·05 ± 0·17
35	Pb/K	2500/2500	45·89 ± 0·38
36	Zn/Ca	5000/2500	32·80 ± 1·74
37	Zn/Mg	5000/2500	32·29 ± 1·26
38	Zn/K	5000/2500	30·31 ± 0·37

[a] Contr–6·1—control treated with distilled water of pH 6·1.
[b] Contr–3·5—control treated with distilled water acidified to pH 3·5.

The sprayed and weighed samples in the open jars were placed in climatic chambers at random and were incubated at 20°C and relative humidity of 97 ± 3%. The climatic chambers were flushed during the experiment with ambient air.

Respiration measurements

The respiration rate was measured using the NaOH CO_2-absorption method (Rühling & Tyler, 1973). Five ml of 0·2 M NaOH were placed in small (15 cm^3) plexiglass containers fastened to the jar lids. All jars were flushed with fresh air and then tightly closed with lids. Twelve empty jars, distributed at random among experimental jars, were incubated for each respiration measurement as blanks. After an incubation period of approximately 12 h, 2 ml of 1 M $BaCl_2$ were added to

0·1 M HCl in the presence of phenolphthalein as an indicator. The accuracy of titration was 0·05 ml and the incubation time was recorded with the accuracy of 1 min.

For the first 5 days, respiration rate was measured daily, and from the tenth day weekly. The experiment was finished after 1 month.

Calculations and statistical analysis

The litter respiration rate was calculated as μ mols CO_2 g dwt^{-1} per 24 h. Cumulative CO_2 evolution was calculated by summarising results from the first 5 days of measurements and the values for the periods between weekly measurements were interpolated based on the two consecutive measurements.

Statistical significance of differences between the treatments was tested with one-way analysis of variance (ANOVA). Means were separated with Tukey test with 95% confidence intervals (Sokal & Rohlf, 1981).

RESULTS

The rates of litter respiration were compared on each day when the respiration was measured and for the cumulated CO_2 evolution. No significant difference was found between the two types of control litter (pH 3·5 and pH 6·1) throughout the whole experimental period (Fig. 1).

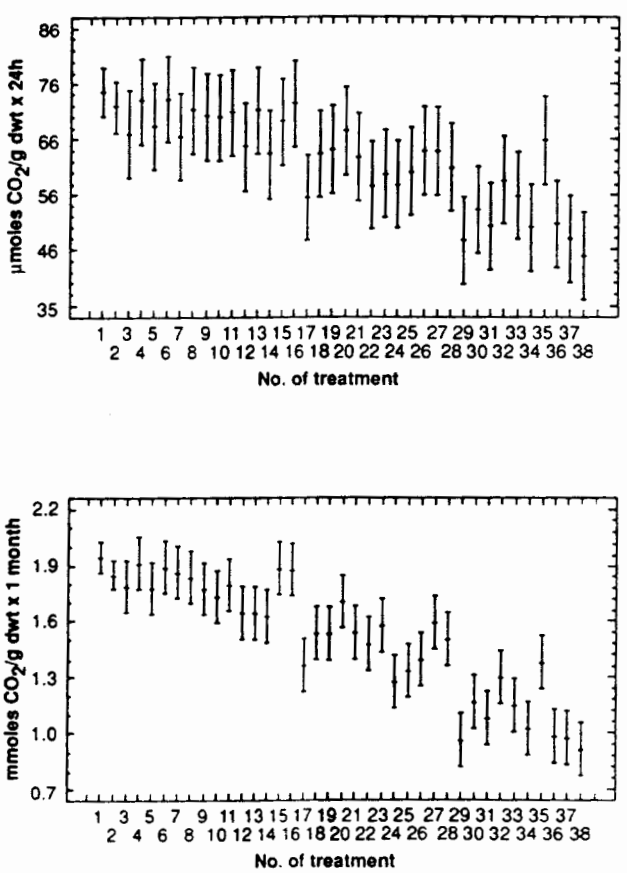

Fig. 1. (Top) Respiration rate on the third day after experimental treatment, and (bottom) the cumulative CO_2 evolution for a 1-month incubation: means and 95% Tukey HSD intervals (for details, see Table 1).

Highly significant differences in respiration rates ($P < 0·0001$) were detected between the treatments for all measurement days from the beginning of incubation. In the course of the experiment the differences between treatments increased with time: for the first day after treatment $F = 3·59$, on the fifteenth day $F = 28·42$ and at the end of the experiment $F = 44·49$ (ANOVA). The number of treatments differing significantly from the control of pH 3·5 increased from two at the start of the experiment to 21 after a 1-month incubation. Already on the third day 12 treatments showed a significant decrease in respiration rate. Nine of them were those given the highest doses of Zn, Zn/Ca, Zn/Mg, Zn/K, Cd/Ca, Cd/Mg, Cd/K, Pb/Ca and Pb/Mg, and three were those treated with the medium doses of Zn, Zn/Ca and Pb/Mg (Fig. 1). After a 1-month incubation all the highest-dose treatments gave a significant reduction in respiration rate. In the medium-dose treatments the following samples differed significantly from the control of pH 3·5: Zn, Cd/Ca, Cd/Mg, Pb/Ca, Pb/Mg, Zn/Ca, Zn/Mg and Zn/K. No significant difference was found between the control treatment and any of the experimental treatments in the lowest doses.

The average respiration rate for the whole experimental period ranged from 30·3 μmols CO_2/g dwt per 24 h for litter treated with the highest dose of Zn/K combination (treatment no. 38) to 64·8 μmols CO_2/g dwt per 24 h for the control of pH 6·1 (treatment no. 1; Table 1).

As the effect of experimental treatments on litter respiration rates was consistent throughout the whole experiment, highly significant differences between the treatments ($P < 0·0001$) were also found in cumulated CO_2 evolution calculated for the whole incubation period. All the highest-dose treatments and all medium-dose treatments with the exception of Cd, Pb and Cd/K decreased the CO_2 evolution from litter (Fig. 1). The lowest cumulated CO_2 evolution was found for samples treated with the highest doses of Zn, Zn/Ca, Zn/Mg and Zn/K.

Additions of mineral nutrients caused significant decreases in a cumulated CO_2 production as compared to the respective heavy metals alone at medium doses of Cd/Ca, Cd/Mg, Pb/Ca, Pb/Mg and Pb/K, and at the highest doses of Cd/Ca, Cd/Mg, Cd/K, Pb/Ca and Pb/Mg (Fig. 1).

DISCUSSION

Doses of heavy metals used in the experiment

Many of the studies describing the inhibition of litter decomposition rates by industrial pollution were conducted in regions polluted with extremely high doses of various heavy metals. Thus, Strojan (1978) reported concentrations of Cd, Pb and Zn in litter layers in the vicinity of a zinc smelter being as high as 900, 2300 and 26 000 μg/g dwt, respectively. In the region of a lead smelter, Watson (1975) found concentrations of Cd, Pb and Zn in litter of 100, 60 000 and 2000 μg/g dwt,

respectively. The highest concentrations of the same three metals measured by Coughtrey *et al.* (1979) in the neighbourhood of a smelter in Avonmouth (UK) were 98, 2179 and 2814 μg/g dwt, respectively. Ranges reported by Kabata-Pendias and Pendias (1979) for soils contaminated with industrial emissions were 10–290, 300–3800 and 200–3400 μg/g dwt for Cd, Pb and Zn, respectively. In contrast, Laskowski and Berg (1993) in their studies on heavy-metal dynamics in decomposing unpolluted forest litter found that after 60–80% mass loss the concentrations of Cd, Pb and Zn in remaining litter can reach up to ca. 2, 80 and 300 μg/g dwt, respectively.

In this experiment the doses used corresponded to (in μg/g dwt): Cd, 10–250; Pb, 100–2500 and Zn, 200–5000. Thus, the lowest doses of heavy metals used in the experiment were close to the natural levels of heavy metals in more decomposed litter fractions, while the medium and highest doses covered the ranges of concentrations typical for moderately to highly polluted forest ecosystems and were below the extreme values reported. It should be mentioned, however, that the additions were of soluble salts and therefore the effective concentrations of available metals could have been higher than environmental levels at similar total concentrations. This relates particularly to soils of high pH where large part of metal ions can be immobilised by clay minerals and soil organic matter.

Effect of heavy metals on litter respiration

In field studies, when a litter is contaminated simultaneously by various heavy metals and other toxic elements, some statistical methods must be applied to distinguish which ones are predominately responsible for changes in the organic matter decomposition rate. Thus, using a multiple regression model and a partial correlation analysis Coughtrey *et al.* (1979) suggested that increased litter accumulation in forests contaminated with emissions from a metal smelter was caused mainly by high concentration of Zn and Cd in the litter layer. Grodziński *et al.* (1990) used a correlation analysis and a principal components analysis to show that litter decomposition rate can be decreased by high levels of Mn, Cd, Pb and Zn, and increased by some major nutrients. However, as heavy metals and other elements are usually highly interrelated with each other in industrial emissions (Ebregt & Boldewijn, 1977), this gives a high level of uncertainty to such a statistical inference. Controlled experiments give the possibility of separating the effect of various pollutants on litter decomposition.

It has been observed in various studies that the contamination of soil with Cd alone can give very different responses. Thus, Bewley and Stotzky (1983) did not notice any significant difference in the respiration rate of soil samples treated with 1000 μg Cd/g dwt. This low sensitivity of soil biota to Cd contamination can be explained however, to some extent by the high clay content in soil and by the fact that the soil used in that substrate-addition experiment by Hattori (1991) only the highest concentration of Cd used (1120 μg/g) delayed the degradation of glucose and cellulose in soil. On the other hand, Chang and Broadbent (1981) found a significant decrease in the respiration rate of the soil samples treated with only 50 μg/g of Cd.

In this study, an approximately 14% decrease in cumulated CO_2 production was noted at the end of experiment only in samples treated with 250 μg/g dwt, whereas lower concentrations had no effect. This suggests that Cd, which is usually considered to be one of the most toxic heavy metals, affects litter respiration rate only at very high concentrations.

It seems likely that such large differences in the effect of Cd on soil respiration rate can be explained by the organic matter content in soil. In contrast to organic matter-rich litter used here, the soil used in the experiment by Chang and Broadbent (1981) contained only 1·31% organic carbon. They noticed that even in their low-organic-matter soil most of the metal ions added were almost immediately bound into insoluble compounds. This interpretation seems to be confirmed by the data of Doelman and Haanstra (1979) who compared the effect of Pb on the respiration rate of four different soils. In the samples with Pb concentrations in the range of 375–7500 μg/g they found significant reduction in respiration rate for soils with organic matter content of 2·8–6·7%, while the respiration of the peat soil with 46% organic matter was not affected even by the highest Pb concentration.

It thus seems likely that in organic-matter-rich soils Cd alone cannot be responsible for a significant decrease in litter decomposition rate in low to moderately polluted areas.

In the present experiment Zn was the heavy metal which caused the largest decrease in litter respiration rate, even if the highest Zn concentration used by us was considerably below those from the most heavily polluted forests. This suggests that for litter decomposition processes Zn pollution can be the most important among the heavy metals studied. In many industrial emissions Zn is the heavy metal which reaches the highest concentrations (Strojan, 1978; Grodziński *et al.*, 1990) and is strongly interrelated to Cd, and this may be a reason why Cd is frequently judged to be one of the most important metals responsible for retardation of organic matter decomposition in polluted ecosystems (*cf.* Coughtrey *et al.*, 1979; Grodziński *et al.*, 1990).

Effect of mineral nutrients on respiration of contaminated litter

The addition of mineral nutrients did not counteract the effect of heavy metals on respiration rate. Moreover, in a few cases it provoked an additional decrease in respiration rate as compared to treatments with the respective heavy metals alone. This may be interpreted as a synergistic effect of heavy metals and mineral nutrients in toxicity to decomposers. A possible explanation could be the observation by Sperl *et al.* (1986)

Pb and Cu ions in the soil solution as a consequence of an experimental liming in Norway spruce stands. A competition between heavy- and alkaline-metal ions for binding sites in the litter organic matter can result in increased solubility of some heavy metals and, as a consequence, their toxicity.

This finding seems to be contradictory to earlier suggestions by Grodziński *et al.* (1990) that a considerable content of some mineral nutrients in industrial dusts can buffer the negative effect of heavy metals. The latter conclusion, however, was derived from a statistical analysis of data obtained from an experiment with chemically complex industrial dusts. Thus, in that study a whole group of nutritional ions (Na, K, Mg, Cl, SO_4 and PO_4) positively correlated with litter decomposition rate was found. Rühling and Tyler (1973) suggested that the inhibition of litter decomposition by heavy metals can be caused by the blocking of organic colloids by heavy-metal ions substituting for K, Mg and Ca. The present results indicate, however, that the latter three nutrients probably do not counteract heavy metal toxicity to decomposers.

This finding emphasises possible side-effects of liming in forest ecosystems, usually made with Ca alone or with additions of K and Mg (e.g. Beese, 1985; Huettl & Wisniewski, 1987). All these nutrients caused considerable decrease in respiration rate when combined with some heavy metals in our experiment. Nihlgård (1988) also emphasised a possible negative effect of liming, used in southern Sweden to counter soil acidification, on the humus layer and on soil biota.

ACKNOWLEDGEMENTS

The authors wish to express their thanks to Drs Björn Berg and January Weiner for critical reading of the manuscript and for helpful discussions. This study was supported by the Polish Ministry of National Education, grant no. IBS-14/91.

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Appendix: Chemical composition of the forest litter used in the experiment: average values, standard deviations (SD) and standard errors (SE); $n = 5$

	K (mg/g)	Na (mg/g)	Ca (mg/g)	Mg (mg/g)	Fe (mg/g)
Average	1·220	0·176	1·380	0·558	4·120
SD	0·217	0·046	0·471	0·018	1·684
SE	0·097	0·021	0·211	0·008	0·753

	Mn (μg/g)	Zn (μg/g)	Cu (μg/g)	Pb (μg/g)	Cd (μg/g)
Average	336·40	147·52	35·36	100·88	2·41
SD	21·11	7·07	5·29	21·83	0·10
SE	9·44	3·16	2·37	9·76	0·05