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Forest Leaf Litter Decomposition in the Vicinity of a Zinc Smelter

Carl L. Strojan*
Ecology Program, Rutgers – The State University, New Brunswick, NJ 08903, USA

Summary. Concentrations of about 26,000 ppm Zn, 10,000 ppm Fe, 2,300 ppm Pb, 900 ppm Cd, 340 ppm Cu, and 0.40% S were measured in the O_2 litter horizon about 1 km from a zinc smelter at Palmerton, Pennsylvania. Samples taken about 6 km east of the smelter had concentrations of about 15,000 ppm Zn, 6,500 ppm Fe, 970 ppm Pb, 250 ppm Cd, 170 ppm Cu, and 0.26% S. Samples from a control area about 40 km east of the smelter had concentrations of 2,800 ppm Fe, 650 ppm Zn, 260 ppm Pb, 50 ppm Cu, 9 ppm Cd, and 0.13% S.

Litter bags were used to estimate first-year weight loss in sassafras leaves and a mixture of chestnut oak/red oak leaves in the three sites. At the end of one year, average weight loss for sassafras was 39.3% in the control site, 21.8% at 6 km, and 17.5% at the 1 km site. For the chestnut oak/red oak mixture, average weight loss was 36.8% (40 km), 25.7% (6 km), and 19.1% (1 km). Numbers and diversity of soil microarthropods inhabiting the litter bags showed a corresponding decline at sites near the smelter. Concentrations of Ca, Cd, Cr, Cu, Fe, Mg, Mn, N, Na, Ni, P, Pb, S and Zn in the decomposing litter were also measured.

The average amount of organic matter on the forest floor was estimated to be 3.8 kg/m^2 in the control site, about 3.8 kg/m^2 at 6 km, and about 8.1 kg/m^2 1 km from the smelter. Average thickness of the litter horizons in these three sites was 6.0 cm (40 km), 7.0 cm (6 km), and 12.4 cm (1 km), suggesting a long-term depression of decomposition and mineral cycling near the smelter.

Introduction

As much as 90% of net production in temperate forests may eventually reach the forest floor as litter (Reiners, 1973). Leaves are the largest single source

* *Present address:* University of California, Laboratory of Nuclear Medicine and Radiation Biology, 900 Veteran Avenue, Los Angeles, CA 90024, USA

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of forest soil organic matter, and their annual contribution of mineral elements exceeds that of all other tree parts combined (Lutz and Chandler, 1946; Bray and Gorham, 1964; Gosz et al., 1972). In this context, the ecological importance of litter decomposition and mineral cycling becomes clear. Comparatively little is known about the effects of industrial pollutants on these two ecological processes. Reported here are the results of a study on leaf litter decomposition in the vicinity of a zinc smelter.

Background and Study Sites

A zinc smelter is located near the Lehigh Water Gap of Blue Mountain in Palmerton, Pennsylvania (40° 48′ N, 75° 36′ W). This smelter is the only significant source of industrial pollution in an otherwise rural region. Prior to construction of the smelter (1898–1911), the slopes of Blue Mountain at Lehigh Gap were covered with forests (Jordan, 1975). Today, however, an area of about 485 hectares around the smelter is either devoid of vegetation or only sparsely covered. Jordan (1975) concluded that the primary cause has been chronic emissions of metallic pollutants from the smelter. Nash (1975) concluded that abnormally high zinc levels are primarily responsible for the depauperate condition of the lichen flora near the smelter.

Primary smelter emissions are metal oxides, particularly of Cd, Cu, Fe, Pb and Zn. About 96% of the SO_2 produced in roasting the ores is recovered as sulfuric acid (Buchauer, 1973). Thus, the impact of heavy metals has not been masked by severe concomitant SO_2 pollution – as has been the case near other smelters (Costescu and Hutchinson, 1972).

Leaf litter decomposition rates were measured in three forested sites on the ridge of Blue Mountain. One site was at Lehigh Gap, about 1 km from the East Plant smelter; the second was about 6 km to the east at Little Gap; and the third site, which served as a control, was about 40 km to the east at Fox Gap. These sites varied principally in distance from the smelter and, therefore, in the levels of airborne emissions to which they were exposed. They were otherwise selected to be comparable in major environmental factors which could influence soil organisms and decomposition, viz., parent rock, soil type, relief, vegetation, and climate (Table 1).

The pH of the O_2 litter horizon (partially decomposed litter) normally ranges from about 4.0 to 5.0. Near the smelter, however, pH levels are higher, possibly from the deposition of zinc oxides (Buchauer, 1971). A similar elevation in pH was reported by Paluch and Karweta (1970). This is unlike the situation near some smelters, where soil pH is very acidic from the precipitation of SO_2 as sulfuric acid (Gordon and Gorham, 1963; Costescu and Hutchinson, 1972). Although the observed pH differences at Palmerton may be biologically significant for soil organisms, these differences favor sites near the smelter, since a richer soil fauna and faster decomposition rate occur at pH values approaching neutrality (Bocock and Gilbert, 1957).

Rainfall and temperature were not measured in the study sites. Nash (1975) reported that mean annual precipitation (1938–1971) at six nearby U.S. Weather

Table 1. Comparison of study sites

	Lehigh Gap	Little Gap	Fox Gap
Bedrock[a]	sandstone, conglomerate	sandstone, conglomerate	sandstone, conglomerate
Soil type[a]	stony loam	stony loam	stony loam
Soil pH[b]	6.1 ± 0.1	5.3 ± 0.1	4.7 ± 0.1
Elevation above sea level (m)	456	325	437
Vegetation[c]	mixed oak	mixed oak	mixed oak
Annual leaf litter fall (g/m^2)[d]	307 ± 30	231 ± 15	388 ± 38
Soil metal levels	very high	high	normal

[a] From Fisher et al. (1962)
[b] Mean pH ($\pm$s.e.) of the O_2 litter horizon
[c] See Jordan (1975) for a more complete description
[d] Estimated mean dry weight ($\pm$s.e.) (Strojan, 1975)

Bureau stations ranged from 106–118 cm and mean annual temperatures ranged from 8.2–9.6° C.

Methods

Leaf Litter Decomposition. Litter bags (Bocock and Gilbert, 1957; Crossley and Hoglund, 1962) were used to estimate the first-year weight loss from leaves of *Sassafras albidum* (Nutt.) Nees and a 1/1 mixture by weight of *Quercus prinus* (L.)/*Quercus rubra* (L.). These species were selected because sassafras is common in the heavily polluted areas, while the oaks are dominant trees on the ridgetop. Freshly fallen leaves were gathered in autumn from both Lehigh Gap and from Fox Gap. After being oven-dried at 40° C to constant moisture, 4.00 g of polluted oak, clean oak, polluted sassafras, and clean sassafras leaves were each placed in separate litter bags to make a set. The bags were 18 cm × 18 cm and were constructed from fiberglass screen having an 18 × 14 mesh (approximately 1.5 mm^2 openings). In November 1972 thirty such sets were staked out in each of the three sites (360 total bags) and then lightly covered with some surface litter.

Every 2 months 20 litter bags (5 sets) were collected from each of the three sites, placed in individual plastic bags, returned to the laboratory, and placed in a modified Tullgren extractor for collection of soil arthropods. Afterwards the litter bags were carefully rinsed in tap water to remove adhering insect frass and other debris, oven-dried at 40° C to constant moisture, and finally the leaf material was reweighed. Percent loss of initial weight was used as a measure of decomposition rate.

Standing Litter Mass. Forest floor leaf litter was removed from 20 cm × 20 cm plots, separated according to horizon, oven-dried at 40° C to constant moisture, and weighed. The thickness of each horizon was also measured. Percent organic matter was determined by weight loss on ignition at 550° C (Ball, 1964). Five samples were collected 10 m apart along each of two transects in each site.

Chemical Analyses. Total nitrogen was determined by the standard Kjeldahl method; total phosphorus was determined colorimetrically as reduced phosphomolybdate; total sulfur was determined gravimetrically by precipitation as barium sulfate; and organic matter was determined by loss on ignition at 550° C. All other elements were analyzed by atomic absorption spectrophotometry (Perkin-Elmer Model 303) following a nitric-perchloric acid digestion.

Results

In all cases, concentrations of soil contaminants (Cd, Cu, Fe, Pb, S, Zn) decreased as distance from the smelter increased (Table 2). Concentrations also decreased sharply with profile depth, indicative of aerial deposition. For example, near the smelter over 90% of total metal concent occurred in the uppermost 15 cm of the soil profile (Buchauer, 1973; Strojan, 1975). Concentrations of Cu, Pb and Zn in the control site were somewhat higher than those reported from other deciduous forests (Reiners et al., 1975; Gosz et al., 1976), which may indicate some pollution in the Fox Gap area. The significance of the various Fe concentrations is difficult to evaluate, since some mineral soil, high in iron, invariably becomes mixed with the organic matter. Soil contamination may also account for the unusually high Mn concentrations measured at Lehigh Gap and Fox Gap.

With few exceptions, soil concentrations of other elements were comparable in the three study sites (Table 2). The major exception was the lower value for Ca near the smelter, which may have resulted from its replacement on cation exchange sites by metal contaminants (Rühling and Tyler, 1973). Other loosely bound cations, however, such as K and Na, did not show a similar trend. An alternative possibility is that Ca levels are unusually high in the control site and normal near the smelter. Calcium concentrations in forest litter reported by Gosz et al. (1976) were in fact more similar to those near the smelter.

Several observations are apparent from differences in the chemical composition of fallen leaves collected near the smelter and the control site (Table 3). First, both sassafras and oak leaves collected near the smelter had much higher concentrations of pollutants than leaves collected in the control site. Second, levels of pollutants were higher in sassafras than in oak. Third, separation

Table 2. Mean dry weight concentrations (±s.e.) of 15 elements in the O_2 litter horizon based on 10 samples from each site

Element	Lehigh Gap	Little Gap	Fox Gap
Ca (%)	0.41±0.07	0.81±0.06	1.39±0.15
K	0.10±0.02	0.06±0.01	0.07±0.00
Mg	0.08±0.01	0.07±0.01	0.07±0.01
N	1.86±0.03	1.83±0.03	1.96±0.03
P	0.19±0.01	0.18±0.01	0.25±0.01
S	0.38±0.08	0.26±0.01	0.13±0.01
Cd (ppm)	885 ±47	256 ±10	8.8±0.5
Cr	24.3±1.6	14.9±1.5	15.7±1.2
Cu	340 ±28	172 ±4	47 ±3
Fe	10,300 ±716	6,500 ±224	2.785 ±172
Mn	3,900 ±180	757 ±77	4,195 ±282
Na	75 ±3	60 ±1	61 ±2
Ni	20.6±1.4	19.8±0.6	19.7±1.3
Pb	2,333 ±237	971 ±19	258 ±10
Zn	25,750 ±351	14,600 ±618	676 ±83

Table 3. Organic matter and elemental concentrations in freshly fallen leaves collected at Fox Gap (clean) and Lehigh Gap (polluted). Values are the averages of two samples

Element	Oak mixture		Sassafras		*Q. prinus* clean	*Q. rubra* clean
	clean	polluted	clean	polluted		
Organic matter (%)	95.4	95.9	96.4	94.1	94.9	96.5
Ca	0.95	0.83	1.03	1.10	1.15	0.65
K	0.75	0.58	0.30	0.31	0.65	0.90
Mg	0.05	0.05	0.07	0.05	0.04	0.04
N	1.04	1.46	1.42	1.32	1.00	1.16
P	0.14	0.14	0.13	0.13	0.15	0.15
S	0.18	0.18	0.11	0.26	0.19	0.13
Cd (ppm)	3	73	10	335	3	3
Cr	3	>1	5	3	8	>1
Cu	18	37	34	115	15	15
Fe	90	435	305	2,500	100	95
Mn	1,250	1,075	485	640	1,250	1,125
Na	100	70	50	70	80	120
Ni	16	12	12	20	15	14
Pb	30	265	39	820	22	42
Zn	115	2,313	158	9,125	75	165

of clean oak leaves into their chestnut oak and red oak components indicated that these species were chemically similar except for some differences in Ca, Pb and Zn concentrations. Since these leaves were not washed prior to analysis, estimates of contaminants included particles adhering to the leaf surface as well as those physically within the leaf. Buchauer (1973) reported that metal levels in unwashed leaves collected near the smelter were from 2 to 6 times as high as in leaves washed with soap and water.

A one-way analysis of variance indicated that no significant difference in weight loss occurred between leaves originally collected in the control site and leaves collected near the smelter ($F \sim 0$, $P \gg 0.05$). When the data were analyzed by species, however, differences became apparent. For example, weight loss in clean sassafras leaves was slightly higher than in polluted sassafras leaves ($F = 3.10$, $0.10 < P > 0.05$), whereas polluted oak leaves decomposed somewhat faster than clean oak leaves ($F = 4.45$, $0.05 < P > 0.025$).

Figure 1 shows first-year weight loss of the leaves in the three sites. Data from the clean and polluted leaves were pooled. After one year an average of 36.8% of the oak mixture had decomposed at Fox Gap, 25.7% at Little Gap, while only 19.1% had decomposed at Lehigh Gap. During this time chestnut oak and red oak decomposed at nearly identical rates. Average first-year decomposition of sassafras was 39.3% at Fox Gap, 21.8% at Little Gap, and only 17.5% at Lehigh Gap.

Qualitative differences in decomposition were also apparent. Leaves decomposing at Fox Gap became increasingly bleached and fragmented as the year progressed. Litter arthropods and fungal hyphae were also observed in the

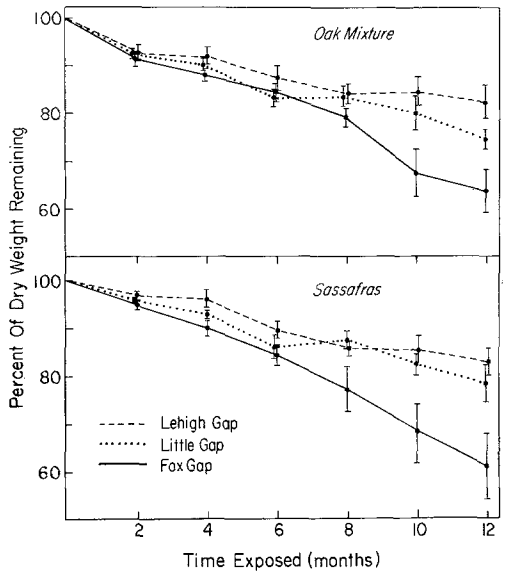

Fig. 1. First-year weight loss of sassafras leaves and a 1/1 mixture of chestnut oak/red oak leaves. Data are plotted as mean percentages (±95% confidence limits) of 10 litter bags

decaying leaves. Leaves decomposing at Little Gap, and to an even lesser extent at Lehigh Gap, did not show these same characteristics.

No significant differences were found in total numbers of arthropods extracted from originally clean versus polluted leaves in any of the three sites. Significant site differences, however, were found. Both density and diversity of arthropods inhabiting the litter bags were consistently and significantly lower near the smelter. The total arthropod fauna extracted from bags at Little Gap represented 55.1% of the total extracted at Fox Gap, while the total from Lehigh Gap was only 18.1% of that at Fox Gap. Particularly striking was the decline in numbers of mites (Acari) near the smelter, many of which are known to feed on decaying leaf litter (Wallwork, 1967). Reduction of soil microarthropod density has been experimentally shown to result in a slower rate of plant litter decomposition (Kurcheva, 1960; Edwards and Heath, 1963; Witkamp and Crossley, 1966).

In addition to weight loss, chemical changes in the decomposing litter were also measured (Tables 4 and 5). Loss of most nutrient elements followed patterns known to occur in decaying litter (Remezov, 1961; Attiwill, 1968; Gosz et al., 1973). For example, K was almost entirely removed from the leaves during early stages of decomposition. Other cations, such as Ca, Cr, Mg, Ni, P and S showed little change in concentration during decomposition, so that their loss paralleled overall weight loss. A third class of elements increased in concentration as the leaves decomposed. The greatest increases occurred among those elements emitted as smelter pollutants. For example, Zn concentrations in initially clean leaves decomposing at Lehigh Gap increased almost 100-fold during the year, while Cd, Fe and Pb concentrations increased 10–100 times. Only Cu showed an increase of less than 10-fold.

Field measurements of forest litter horizons also indicated significant reductions in decomposition rates and increases in standing leaf litter near the smelter.

Table 4. Organic matter and elemental concentrations of initially clean oak leaves following litter bag exposures of 4, 8 and 12 months in each of the three sites. Values are the averages of two samples

Element	Initial conc.	Lehigh Gap			Little Gap			Fox Gap		
		4	8	12	4	8	12	4	8	12
Organic matter(%)	95.4	94.8	92.7	93.7	96.9	94.5	93.0	91.7	92.2	94.8
Ca	0.95	1.05	1.10	0.90	1.12	1.20	1.23	0.90	1.57	1.33
K	0.75	0.23	0.03	0.06	0.09	0.03	0.04	0.06	0.02	0.04
Mg	0.05	0.04	0.05	0.05	0.05	0.07	0.06	0.04	0.06	0.08
N	1.04	1.26	1.37	1.42	1.20	1.37	1.48	1.27	1.47	2.06
P	0.14	0.10	0.13	0.10	0.12	0.13	0.12	0.12	0.12	0.15
S	0.18	0.16	0.21	0.21	0.16	0.17	0.19	0.19	0.18	0.19
Cd (ppm)	3	182	260	270	22	49	118	7	13	15
Cr	3	3	7	5	7	3	8	3	5	6
Cu	18	58	95	92	49	52	54	24	62	64
Fe	90	650	1,350	2,075	810	480	1,125	195	465	773
Mn	1,250	1,250	910	1,225	1,085	1,000	1,125	960	1,160	1,463
Na	100	80	130	120	100	140	140	140	150	140
Ni	16	10	23	19	13	17	19	19	22	21
Pb	30	400	905	850	112	90	355	50	92	141
Zn	115	3,688	6,938	9,500	1,335	1,625	4,375	195	310	435

Table 5. Organic matter and elemental concentrations of initially clean sassafras leaves following litter bag exposures of 4, 8 and 12 months in each of the three sites. Values for the unexposed leaves are the averages of two samples; values for exposed leaves are based on single determinations

Element	Initial conc.	Lehigh Gap			Little Gap			Fox Gap		
		4	8	12	4	8	12	4	8	12
Organic matter (%)	96.4	94.0	93.3	90.3	94.8	94.5	93.0	95.1	93.3	93.2
Ca	1.03	1.05	1.05	0.09	1.20	1.20	1.00	1.05	1.25	1.53
K	0.30	0.31	0.31	0.08	0.20	0.04	0.06	0.17	0.03	0.04
Mg	0.07	0.07	0.07	0.07	0.07	0.09	0.07	0.06	0.09	0.11
N	1.42	1.80	1.96	2.17	1.73	1.73	2.33	1.94	2.35	2.72
P	0.13	0.13	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.16
S	0.11	0.20	0.22	0.30	0.09	0.07	0.30	0.17	0.12	0.12
Cd (ppm)	10	300	405	250	35	95	265	5	10	11
Cr	5	3	3	3	3	3	5	3	3	2
Cu	34	135	265	290	80	190	180	65	170	53
Fe	305	2,500	3,000	6,500	850	1,450	4,500	715	1,250	825
Mn	485	700	740	1,750	550	440	610	600	1,500	1,230
Na	50	100	130	150	70	130	120	80	120	130
Ni	12	10	15	25	10	25	15	15	15	19
Pb	39	550	1,170	2,050	120	270	820	90	125	90
Zn	158	7,125	11,000	10,500	1,625	3,250	9,750	375	500	360

For example, just after autumn leaf fall, average accumulation ($\pm$s.e.) of old organic matter on the forest floor (O_2+A_1 horizons) was estimated to be 3.8 ± 0.3 kg/m^2 in the control area, 3.8 ± 0.2 kg/m^2 at Little Gap, and 8.1 ± 0.5 kg/m^2 at Lehigh Gap. The average thickness ($\pm$s.e.) of these same horizons was estimated to be 6.0 ± 0.4 cm (Fox Gap), 7.0 ± 0.6 cm (Little Gap), and 12.4 ± 1.2 cm (Lehigh Gap), suggesting a significant long-term depression of decomposition and mineral cycling near the smelter. This accumulation of organic matter was present in spite of the fact that annual leaf litter input to the forest floor was somewhat lower near the smelter (Table 1). Thus, the net accumulation must result from lowered decomposition rather than increased litter production.

Discussion

The 1.5 mm mesh size used for litter bags allowed entry of the smaller members of the soil biota, but excluded larger organisms such as ground beetles. Witkamp and Olson (1963) concluded that litter bag methods tend to underestimate "true total decomposition" due to confinement and subsequent protection of the litter, while methods using non-confined litter tend to overestimate this rate because of the unknown weight loss from leaf fragments that have broken off but not yet decomposed. In view of this, the experimentally determined decomposition rates are best used comparatively between sites rather than as absolute rates.

It seems reasonable that lower decomposition rates near the smelter were due to fewer soil organisms and lower biological activity, which in turn were due to high levels of soil pollutants. The work of Jordan and Lechevalier (1976), along with other data (Strojan, 1975), clearly indicates that both the soil microfauna and microflora have been adversely affected near the smelter. The possibility exists that some factor other than smelter pollutants may have caused the observed differences in decomposition. This appears highly unlikely, however, in view of the magnitude of the differences observed and the high levels of pollutants measured.

The findings reported here are consistent with those from other studies in similar areas. For example, Watson et al. (1976) reported lower total arthropod density and biomass, and an accumulation of undecomposed O_2 litter near a lead mining-smelting complex with high concentrations of litter heavy metals. Rühling and Tyler (1973) found that the CO_2 evolution rate from spruce needle litter contaminated by Cd, Cu, Ni, Pb and Zn was only one-half the rate of non-contaminated areas. Bhuiya and Cornfield (1972) found that 1000 ppm Cu, Ni, Pb and Zn all significantly decreased CO_2 evolution when added to soil. Bond et al. (1976) reported an inhibition of O_2 uptake and a reduction in CO_2 evolution following the addition of 10 ppm Cd to coniferous forest litter microcosms.

The mechanism of the toxicity discussed here is unknown but may involve enzyme inhibition. Tyler (1974) reported significant negative regressions of

urease activity, acid phosphatase activity, and soil respiration rate on the logs of Cu + Zn concentrations.

The long-term consequences of reduced litter decomposition are unclear. Tyler (1972) suggested that in highly polluted terrestrial ecosystems organic matter may accumulate to the point where it effectively removes much of the mineral pool from circulation, thereby reducing primary production. On the basis of a theoretical study, Dudzik et al. (1976) concluded that damage to decomposers or nutrient pools is a potential source of instability to the entire ecosystem.

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