Plant and Soil 46, 251–257 (1977) Ms. 2912

SHORT COMMUNICATION

A comparative study of metal levels in plants from two contrasting lead-mine sites

Summary

An investigation into the levels of metals in plants growing on metalliferous soils was carried out. The exchangeable metal concentration of soils from Tyndrum and Trelogan was found to be extremely variable from sample to sample and the influence of soil pH on the exchangeable lead and zinc concentration is discussed. Large differences in heavy metal levels were found between species and may be indicative of different mechanisms of tolerance to lead and zinc excess. Large differences in calcium levels between plant tissues were also found. These may result from the use of calcium in ameliorating lead and zinc toxicity in some species.

Introduction

A number of studies have been made of lead tolerance in plants, *e.g.* Jowett[5] and Gregory and Bradshaw[3], but there is a lack of data concerning lead levels in a range of plant species. We decided to study metal levels in a number of species from two lead-mine spoil heaps of contrasting character at Trelogan in North Wales and at Tyndrum in Scotland. The Trelogan spoil is calcareous and the soils derived from it have a high pH. At Tyndrum the spoil bears acidic soils with a low calcium content. The sites have contrasting floras and few species in common.

Material and methods

1. Plant and soil collection. Plants and soil were collected from Tyndrum (G.R. NN 318304 and Trelogan (G.R. SJ127808). At each site three or occasionally two samples were taken from widely spaced areas of about 1m^2. The aerial plant parts of the sampled species were collected and soil samples were taken from around the roots of the sampled plants to a depth of 10 cm. At Trelogan a superficial wind blown drift material was not included in the sample since the plants were found rooting in the stable layers below. Collections were made at Tyndrum on 25 May, 1973 and Trelogan on 10 July, 1973.

2. Analysis. a. Plants. The required parts, after removal, were rinsed twice in deionized water until clean. Washing may result in some loss of absorbed ions, but this was not thought to be a serious source of error. The plant material was then oven dried at 60°C for 5 days and digested by wet ashing with

concentrated nitric acid. Analyses of the solutions were carried out using a Perkin-Elmer 103 atomic absorption spectrophotometer.

b. Soils. Soil samples were air dried in the laboratory and sieved through a 2 mm sieve. Subsequent analyses were carried out in duplicate on two sub-sampled replicates. Soil pH was measured in a 1:1 soil/deionized water mixture using a Beckmann zeromatic pH meter. The glass electrode was placed in the soil solid phase leaving the reference electrode in the clear supernatant.

For exchangeable metal extraction, each soil sample was leached with *M* ammonium acetate solution. Soil samples were grouped into pH ranges of 0.5 units from the results of the previous analyses and the pH of the ammonium acetate solution adjusted, using ammonia or hydrochloric acid, to fit the mean of each soil pH range. Consequently, soil extraction was carried out at the approximate pH of each soil sample.

Soil samples were dried at 80°C for 5 days to obtain an 'oven dry' reference weight and all results are expressed on this basis.

Results

The results of plant and soil analyses for lead, zinc and calcium are presented here. Analyses of the same samples for nickel, chromium, cobalt, iron, magnesium, sodium and potassium are given in Johnston[4].

TABLE 1

Tyndrum soil analysis

Plant growing on sample collected	Sample no.	pH	Metal concentration (ppm) Pb	Zn	Ca
Agrostis	1	5.2	3.844	23.3	23.8
canina ssp *montana*	2	5.1	5.982	33.5	44.1
	3	4.9	3.441	14.0	8.6
Calluna vulgaris	1	5.2	804	2.5	9.8
	2	4.4	4,221	33.0	30.0
	3	5.1	502	2.8	9.7
Cerastium holosteoides	1	7.0	805	21.7	704.8
	2	7.1	907	26.0	836.6
	3	6.8	979	54.8	113.4
Juncus squarrosus	1	5.3	8,120	91.3	253.7
	2	4.6	4,347	29.7	101.1
	3	5.6	3,923	34.2	171.0
Larix decidua	1	4.3	1,937	41.1	19.9
	2	4.3	3,345	91.2	27.4
	3	4.7	7,419	47.8	52.6
Pinus sylvestris	1	4.3	3,345	91.2	27.4
	2	4.6	4,086	42.1	17.9
	3	4.4	3.040	11.8	8.4
Saxifraga aizoides	1	7.1	202	3.0	24.1
	2	6.6	1,208	54.9	4.5
Thymus drucei	1	7.3	1,918	23.7	11.1
	2	7.1	1,522	37.4	8.1

a. Tyndrum. The soils (Table 1) were of pH 4.3–7.3. Exchangeable lead concentration ranged from 202 ppm—8,120 ppm with a mean of 2,995 ppm. The zinc levels were low (range 2.5 ppm —91.3 ppm; mean 36.9 ppm), compared to the Trelogan soils but most exceed values reported by Swaine[7] for 'normal' soils. Calcium levels were below 55.0 ppm except for those samples from under *Cerastium holosteoides* and *Juncus squarrosus* (plant names are those used in Clapham, Tutin and Warburg[2]).

The plants (Table 2) showed large differences in lead levels. Two of the *Pinus sylvestris* samples contained only 5.0 ppm lead contrasting with 650.0 ppm in one of the samples of *Juncus squarrosus*. Zinc levels showed smaller variations and there were large differences in the calcium concentration which varied from 415 ppm in *Agrostis canina* ssp *montana* to 25,300 ppm in *Saxifraga aizoides*.

b. Trelogan. The soils at Trelogan (Table 3) were within the pH range 6.9–8.1. Exchangeable lead ranged from 36.0 ppm to 880.0 ppm with a mean of 567.8 ppm. There were high levels of zinc (range 200 ppm – 3,560 ppm; mean 1,999 ppm) which suggests that this metal may be important in influencing plant growth. The exchangeable calcium levels were also high (range 620 ppm – 10,900 ppm; mean 2,358 ppm).

TABLE 2

Tyndrum plant analysis

Species collected	Plant part	Sample no.	Metal concentration (ppm) Pb	Zn	Ca
Agrostis canina	Leaf	1	570	110	415
ssp *montana*	blades	2	290	85	800
		3	295	88	575
Calluna vulgaris	Young	1	60	65	2,450
	shoots	2	530	42	3,140
		3	120	28	1,245
Cerastium holosteoides	Leaves	1	280	205	11,000
		2	350	248	12,150
		3	135	340	10,750
Juncus squarrosus	Leaves	1	85	148	845
		2	650	375	555
		3	115	180	640
Larix decidua	Leaves	1	30	93	750
		2	40	88	1,085
		3	25	125	1,510
Pinus sylvestris	Leaves	1	15	183	515
		2	5	33	485
		3	5	35	705
Saxifraga aizoides	Leaves	1	205	65	25,300
		2	80	120	7,500
Thymus drucei	Leaves	1	495	105	11,000
		2	145	98	11,800

TABLE 3

Trelogan soil analysis

Plant growing on sample collected	Sample no.	pH	Metal concentration (ppm)		
			Pb	Zn	Ca
Acer pseudoplatanus	1	7.3	700	2,170	1,000
	2	7.3	880	2,640	6,250
	3	7.2	850	2,340	6,200
Agrostis stolonifera	1	7.5	800	2,700	1,250
	2	7.3	680	3,000	1,400
	3	7.4	600	3,560	3,700
Centranthus ruber	1	8.1	36	200	3,250
	2	8.1	140	300	3,500
	3	8.0	340	500	3,650
Cerastium holosteoides	1	7.4	270	1,500	4,150
	2	6.9	800	2,200	10,900
	3	7.3	400	2,050	3,550
Chamaenerion angustifolium	1	7.5	560	2,480	850
	2	7.6	340	960	1,450
	3	7.8	360	1,200	1,900
Festuca rubra	1	7.4	600	2,780	1,050
	2	7.5	800	2,850	1,170
	3	7.7	680	2,660	900
Hieracium sp.	1	7.6	330	1,470	1,870
	2	7.5	460	1,770	2,750
	3	7.5	500	1,520	1,200
Minuartia verna	1	7.5	460	2,150	620
	2	7.5	680	2,300	850
	3	7.6	740	1,930	950
Plantago lanceolata	1	7.3	700	2,100	1,300
	2	7.4	600	1,200	1,250
	3	7.5	700	1,700	1,170
Rumex acetosa	1	7.0	650	2,780	1,000
	2	7.1	700	2,640	950
	3	7.1	680	2,340	700

There were large differences in metal levels between plant species (Table 4). Many contain high concentrations of lead and zinc, *e.g. Rumex acetosa* (5,450 ppm lead and 11,000 ppm zinc, *Agrostis stolonifera* (1,965 ppm lead) and *Minuartia verna* (3,200 ppm zinc). High levels of calcium were also found in many species.

Discussion

The exchangeable levels of lead were higher in the Tyndrum soil compared with samples from Trelogan. This is probably associated with soil pH. Lead, which may occur as Pb (II), will remain in solution in Tyndrum soils (pH range 4.3–7.3) but will probably be precipitated as hydroxy compounds in

TABLE 4

Trelogan plant analysis

Species collected	Plant part	Sample no.	Metal concentration (ppm)		
			Pb	Zn	Ca
Acer pseudoplatanus	Seedling leaves	1	1,790	2,900	8,000
		2	1,715	2,500	8,500
		3	1,955	3,500	8,750
Agrostis stolonifera	Leaf blades	1	1,965	2,500	6,500
		2	1,480	2,000	4,500
		3	1,760	2,500	4,000
Centranthus ruber	Leaves	1	50	102	11,250
		2	45	92	12,000
		3	45	75	8,000
Cerastium holosteoides	Leaves	1	960	2,900	28,500
		2	530	1,750	12,000
		3	938	2,763	34,180
Chamaenerion angustifolium	Leaves	1	45	178	11,250
		2	60	192	12,500
		3	55	138	16,000
Festuca rubra	Leaf blades	1	720	1,900	5,000
		2	670	800	2,500
		3	570	1,600	4,500
Hieracium sp.	Leaves	1	120	1,000	18,000
		2	140	1,200	19,750
		3	100	1,200	17,750
Minuartia verna	Leaves	1	1,580	3,200	12,000
		2	1,575	2,200	11,000
		3	700	2,500	12,500
Plantago lanceolata	Leaves	1	430	1,500	18,750
		2	420	1,750	15,000
		3	455	1,200	11,250
Rumex acetosa	Leaves	1	2,580	5,000	5,000
		2	2,200	5,000	35,000
		3	5,450	11,000	20,000

Trelogan soils since the pH of most samples from this site is nearer the pKa value for the equilibrium shown in (1).

$$[Pb(H_2O)_4]^{2+} \overset{Ka}{\rightleftharpoons} [Pb(H_2O)_3OH]^+ + H^+ \; (pKa = 7.9) \qquad (1)$$

(pKa valve taken from Cotton and Wilkinson[1]).

Progressive ionization of aquo ligands will lead to insoluble polymeric hydroxy complexes and this may account for the lower availability of this metal at Trelogan.

In spite of the lower exchangeable soil lead, many plants from Trelogan contained higher levels of lead than species from Tyndrum. The plant response to lead varies also between species from the same site. For example, at Trelogan *Plantago lanceolata* has an average lead concentration in its leaves of 438 ppm when growing in a soil with an average exchangeable lead content of 666 ppm whereas *Rumex acetosa* contains an average of 3,410 ppm lead in its leaves when growing in soil of mean lead concentration 676 ppm. The different levels of lead within the plants may be a manifestation of different means of lead tolerance by the plants concerned.

The high calcium levels in the Trelogan spoil is reflected in the generally higher plant calcium content from this site compared with plants from Tyndrum. This may account for the higher plant lead levels at Trelogan since calcium is known to often have an ameliorative influence on heavy metal toxicity. Thus some plants from Trelogan may counteract lead toxicity by maintaining high internal calcium levels. It is noteworthy however that the plant levels of calcium vary from species to species and in some plants the role of calcium may be less important. Compare, for example, *Festuca rubra* with *Cerastium holosteoides*. Whilst both have comparatively small differences in mean lead levels (*Festuca rubra* contained 653 ppm compared to 807 ppm in *Cerastium holosteroides*), calcium concentrations are very different (4,000 ppm in *Festuca rubra* compared with 24,893 ppm in *Cerastium holosteoides*).

Trelogan soils contained high levels of exchangeable zinc. This was unexpected since the pH range of soils from this site exceed the pKa for the equilibrium (2) leading to the formation of insoluble hydroxy complexes.

$$[Zn(H_2O)_4]^{2+} \overset{Ka}{\rightleftharpoons} [Zn(H_2O)_3OH]^{+} + H^{+} \ (pKa = 5.4) \qquad (2)$$

(pKa value taken from Cotton and Wilkinson[1]). The pH of the soils are not high enough to promote formation of soluble zincates (which occurs at $\sim$ pH 13.0). One possible explanation for the higher exchangeable zinc at Trelogan compared to Tyndrum, is a very high total zinc in the solid phase, the slight solvolysis of which would result in a comparatively large exchangeable fraction. This gains some support since Smith and Bradshaw[6] estimated the total zinc level in samples from Trelogan to be 35,940 ppm.

W. R. Johnston and John Proctor

Biology Dept., University of Stirling,
Stirling, FK9 4LA, Scotland

Received 25 July, 1975

References

1 Cotton, F. A. and Wilkinson, G., Advanced Inorganic Chemistry. John Wiley and Sons. New York, (1966).

2 Clapham, A. R., Tutin, T. G. and Warburg, E. F., Flora of the British Isles. University Press, Cambridge, (1962).

3 Gregory, R. P. G. and Bradshaw, A. D., Heavy metal tolerance in populations of *Agrostis tenuis* and other grasses. New Phytol. **64**, 131–43 (1965).

4 Johnston, W. R., Mineral uptake of plants of serpentine and lead-mine soils. B.A. (Hons) thesis. University of Stirling (1974).

5 Jowett, D., Populations of *Agrostis* spp. tolerant of heavy metals. Nature, Lond. **182**, 816 (1958).

6 Smith, R. A. H. and Bradshaw, A. D., Stabilization of toxic mine wastes by the use of tolerant plant populations. Trans. sec. A. Inst. Mining and Metallurgy. **81**, A230–A237 (1972).

7 Swaine, D. J., The trace element content of soils. Tech. Commun. Commonw. Bur. Soils No. **48**. (1955).