ACTA SOCIETATIS
BOTANICORUM POLONIAE
Vol. 49, nr 3: 339—348
1980

Accumulation of heavy metals in an ecosystem influenced by zinc-plant emissions

ZUZANNA CZUCHAJOWSKA, ELŻBIETA LOREK, TERESA STRĄCZEK

Department of Plant Ecology, Institute of Botany, Silesian University, ul. Jagiellońska 24, 40-032 Katowice, Poland

(Received: September 25, 1979)

Abstract

Accumulation of Pb, Zn, Cd, Mn, Fe and Mg reaching the selected ecosystem in the dust emitted by a zinc-mill, was estimated in the leaves of *Pinus silvestris*, *Vaccinium myrtillus* and *Vaccinium vitis-idaea*, the main plant components of the system, and in the five upper soil layers. The values of metal concentration were different for the three considered species and showed — for each of them — dependence on the pollution degree of the stand. This regularity concerned Pb, Zn, Cd and Mn but not Fe and Mg. A significant positive correlation exists between the content of Pb, Zn and Cd in the soil and their concentration in leaves, the correlation for Mn is significant but negative. Manganese in leaves proved to be an antagonist in respect to the other metals.

INTRODUCTION

Zinc- and lead-mills are the source of intensive emissions, containing heavy metals which are particularly dangerous pollutants. It is the reason why this type of emissions was investigated in respect to their influence on soil (John et al., 1975), on the air (Dorn et al., 1976) and on plants (Kazimierczakowa, 1975). The present paper considers all these objects as components of an ecosystem, the main plant participants of which were the species *Pinus silvestris* predominating among the trees, and *Vaccinium myrtillus* and *Vaccinium vitis-idaea* — the two principal components of the herb layer. The content of Pb, Zn, Cd, Mn, Fe and Mg was estimated in the assimilating parts of these species. Vertical distribution of these elements in the five soil layers and in the dustfall at two altitudes was also determined.

The ability of metal accumulation by the investigated species in respect to the location of a stand was investigated. The second problem

was: how the accumulation of toxic metals in the soil and their concentration in the dustfall influence their uptake. Among these elements Zn, Mn, Fe and Mg are necessary for plant metabolism, while the necessity of Pb and Cd has not been considered so far.

MATERIAL AND METHODS

The investigations were carried out in four selected stands in 1977/ /78. Three of them, strongly influenced by a zinc-plant operating for many years at Miasteczko Śląskie, Upper Silesia, were situated at gradually increasing distances from the emitter, in the direction of prevailing winds; the K (Żyglinek), L (Brynica I) and M (Brynica II) stands — 0.9, 2.5 and 5.0 km from the zinc-plant. The fourth stand C (Kokotek) represented a control area in the forest district Lubliniec, relatively pollution-free, at a distance of 24 km from the center of emission. The polluted ecosystem represented a fresh pine forest in which the trees of *Pinus silvestris* were of equal age of about 20 years. In these stands there was a constant process (very advanced for the K stand) of thinning out owing to the influence of emissions. The cleared areas in which the intensity of light reaching the forest floor strongly increased, were becoming gradually dominated by both *Vaccinium* species, *Vaccinium myrtillus* being gradually ousted by *Vaccinium vitis-idaea*.

The soil samples were collected three-times during the whole research period, with the aid of a soil drill of 10 cm diameter, plunged to a depth of 25 cm, from different spots, rather uniformly distributed in the investigated area. Individual samples were divided into five layers: 0-5, 5-10, 10-15, 15-20 and 20-25 cm, and mixed samples were prepared, composed of 25-30 samples of any layer. The air-dry soil of every layer, sieved on a 2-mm sieve, was used to determine the pH values in H_2O and KCl and the buffer capacity in 0.025 N H_2SO_4 (bc_a) and 0.025 N NaOH (bc_b) in the way previously applied to aqueous homogenates of leaves (Czuchajowska, Przybylski, 1978). Soil dried at 105°C, sieved as before, was used for the estimation of organic matter content by Tiurin's method, nitrogen content — by that of Kjeldahl and metals content by means of atomic absorption spectroscopy (Baker, Smith, 1974) on a Perkin-Elmer 403 spectrometer. In the latter procedure acids extracts (50 ml) of 5-g samples of soil were applied: 1 N H_2SO_4 and 1 N HCl were used for Zn estimation, 0.1 N HCl for Mn and Fe, 0.05 N HCl for Mg and 1 N HNO_3 for Pb and Cd. Estimation of cadmium involved its concentration in the organic phase of methylisobutyl ketone.

The dustfall on every area, ranging for the four investigated stands from 160 to 38 t per km^2 per year, and its metal content were measured by the sedimentation method (J u s t, 1963) at the level of 2 m above the surface and at 0.5 m, i.e. that of the dwarf shrub height, during the vegetation period from April to September 1977. The dustfall samples, collected in Weck jars placed under the canopy of three-tops on the mentioned altitudes, after transportation to the laboratory were evaporated to dryness. After estimation of the dry mass, the material was moistened with a few millilitres of the 1 : 1 mixture of concentrated HCl and 35% HNO_3, evaporated once more to dryness and calcinated in an electric oven at 450-500° during 3 hours (S t r u s i ń s k i, W y s z y ń s k a, 1971). Subsequent addition of the HCl-HNO_3 (3 : 1) mixture, followed by introduction of 10 ml H_2O, transformed the metals into soluble compounds. The solutions, acidified to pH = 1, were then used for estimation of metal content by atomic absorption spectroscopy (see above).

The leaves of *Vaccinium myrtillus* and *Vaccinium vitis-idaea* and the current year and biennial needles of *Pinus silvestris* were collected only once from the described stands in the following manner. From every dwarf shrub, taken out of a hundred specimens randomly chosen, one shoot was collected, containing leaves of all ages. In the case of *Pinus silvestris*, from every tree of the hundred randomly chosen individuals, one branch cut off from the middle part of the crown, containing current year and biennial needles, was collected. After transportation to the laboratory, the leaves and needles were picked off and thoroughly washed (to eliminate the metals superficially accumulated, the content of which could be easily influenced by disturbing factors, e.g. rainfall). Then the samples, dried to constant weight at 105° C, were powdered to a homogeneous material (properly protected against contamination by trace elements). It was subsequently heated at 500-550° C to constant weight. The ash obtained was dissolved in 1 N HNO_3 — only for Mn estimation 20% HCl was used — and the content of metals was estimated with an atomic absorption spectrometer (see above). In some cases the solutions had to be suitably diluted.

It should be mentioned that the content of Pb, Zn, Cd, Mn, Fe and Mg, expressed in ppm of dry material, was always estimated in 8 separate samples of soil, dustfall, leaves and needles. The results obtained by analysis were evaluated statistically, the correlation indices were calculated according to S n e d e c o r (1956).

RESULTS

The elements under consideration present in the dustfall (Table 1), accumulated mainly in the top soil layer (0-5 cm, Figs. 1, 2). Lead, zinc and cadmium were found in a particularly high percentage, their content in the deeper layers decreasing distinctly, e.g. for the K stand, closest to the emitter, the content of Pb decreased from 2800 ppm in the 0-5 cm layer to 75 ppm in the subsequent 5-10 cm layer and finally to 8 ppm in the lowest one. Only the soil from the L stand, characterised by a very high content of organic matter (ca 40%) showed appreciable concentration of metal in the second layer, 5-10 cm; this concerned Zn (the element known to form complexes with humic compounds), Cd and above all Pb, the latter element present in 1060 ppm concentration. The dependence of metal concentration in the polluted upper layer versus the distance to the emitter proved to be almost linear, e.g. the concentration of Pb decreased from 2800 ppm, through 1100 ppm to 130 ppm. The control stand showed a concentration of Pb, Zn and Cd of 75, 24 and 0.7 ppm, respectively. In the upper soil layer from the stand near the emitter (stand K, layer 0-5 cm) the pH increased, as a result of metal accumulation, from 5.4 to 5.8 in the period: April 1977 — November 1978. The two more distant stands did not show such a change, the pH values being contained in the range 4-5, as compared with the pH of the control area not exceeding pH = 4.

Table 1

Content of some metals in the dustfall in 1977

Stand	Altitude	Dustfall t/km²	Pb	Zn	Cd	Mn	Fe	Mg
			(ppm)					
K	2 m	124.47	9703	20131	198.9	810	22314	14067
	0.5 m	165.68	7412	14972	149.7	690	15713	12896
L	2 m	85.9	2977	5888	75.2	421	9388	6215
	0.5 m	64.4	3785	3955	67.8	305	15198	3955
M	2 m	62.78	2086	6519	97.8	600	11799	9126
	0.5 m	71.47	3230	8591	109.0	484	9106	7560
C (control)	2 m	37.67	273	709	27.3	500	7981	4775
	0.5 m	55.12	316	862	26.3	485	5997	4208

Accumulation of the investigated metals in the green parts of the plants depended for every considered stand on the plant species. The content of lead in the leaves collected from the most polluted stand K, showed drastic differences. For *Vaccinium vitis-idaea* Pb concentration, 2800 ppm, exceeded 30-times that in the leaves of *Vaccinium myrtillus* and 6-times the content in the biennial needles of *Pinus silvestris*. The

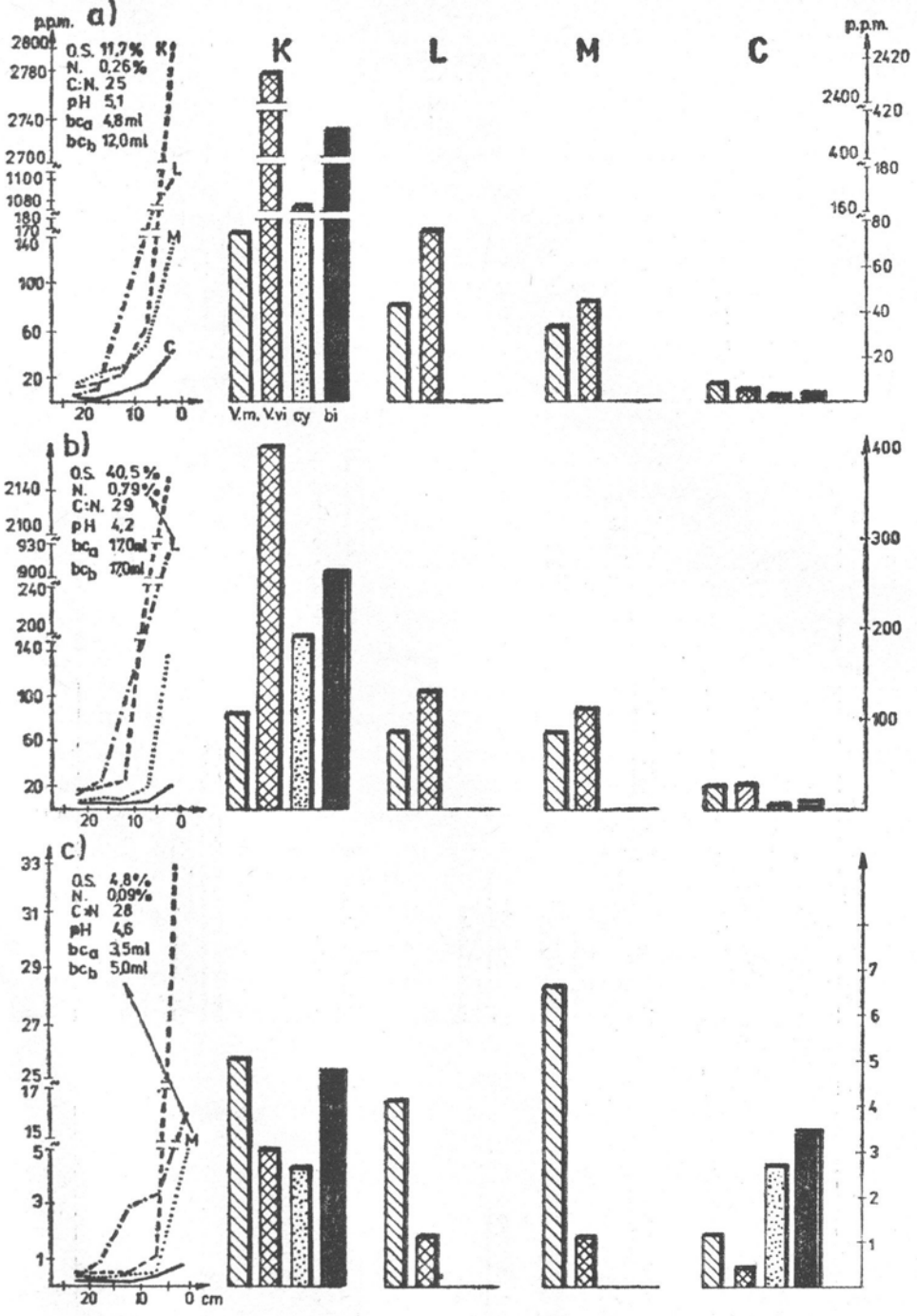

Fig. 1. Content of : (a) lead, (b) zinc, (c) cadmium (ppm) in five soil layers of the investigated stands (lines) and in the leaves of *Vaccinium myrtillus* (V.m.), *Vaccinium vitis-idaea* (V.vi) and the current year (cy) and biennial (bi) needles of *Pinus silvestris*, all collected in September 1978 (bars). The stands K, L and M are at a distance of 0.9, 2.5 and 5 km from the emitter, stand C is the control one. The values of metal concentration in the needles of *Pinus silvestris* are not given for stands L and M. The sets of numbers give the following parametres of the soil upper layer (0-5 cm) of the indicated stands: organic substance (O.s.), nitrogen content (N), C : N ratio, pH, buffer capacity against acid (bc_a), and against base (bc_b).

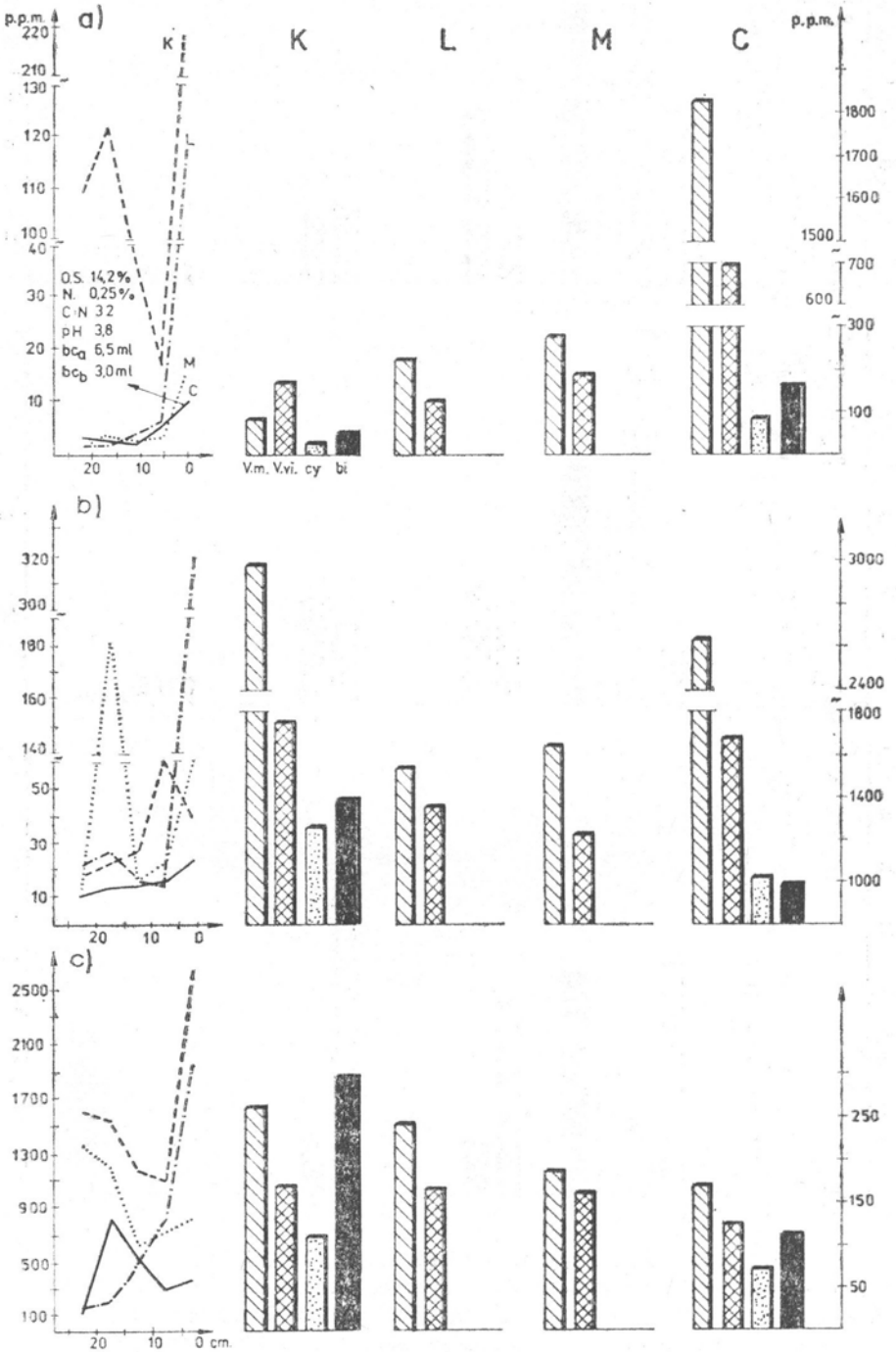

Fig. 2. Content of: (a) manganese, (b) iron, (c) magnesium (ppm) in five soil layers and in the leaves of the investigated species. For other explanations see Fig. 1.

concentration of zinc was lower, however, *Vaccinium vitis-idaea* accumulated 4-times more of this element than did *Vaccinium myrtillus*. Cadmium was accumulated to the highest degree by *Vaccinium myrtillus* (7 ppm) growing in the stand near the emitter. It is characteristic that the predominance of some heavy metals concentration in *Vaccinium vitis-idaea* over *Vaccinium myrtillus* (Figs. 1, 2) diminishes with increasing distance from the emitter, this concerning Pb, Zn and Mn. Concentration of Cd, Mg and Fe was always higher in *Vaccinium myrtillus* than in *Vaccinium vitis-idaea,* however, the content of the latter metal showed only limited difference for the three investigated species in respect to the distance.

A significant positive correlation was found between the content of Pb, Zn and Cd in the soil and their concentration in the leaves of both *Vaccinium* species. The respective values for *Vaccinium myrtillus* are as follows: Zn 0.86**, Pb 0.94**, Cd 0.65**; for *Vaccinium vitis-idaea:* Zn 0.90**, Pb 0.98**, Cd 0.91** (the index ** denotes the level of significance equal to 0.01). Manganese behaved differently from all other metals. Its uptake by the three species was independent of Mn concentration in the soil and in the dustfall. The lowest concentration of manganese was found in the soil of the control stand, in which all species accumulated many times more manganese than in the three polluted stands. Mn concentration in the leaves of *Vaccinium myrtillus* (1900 ppm), exceeded almost 3-times that found in the leaves of *Vaccinium vitis-idaea* and 20-times that in the current year needles of *Pinus silvestris* (Fig. 2a). Along with the gradually decreasing distance from the emitter, the uptake of Mn by the same species decreased, reaching very low values near the zinc-plant. Statistical calculations showed a significant, negative correlation between Mn content in the soil and leaves of both *Vaccinium* species: —0.42* and —0.35* for *myrtillus* and *vitis-idaea,* respectively (the level of significance equal to 0.05). Although analysis on manganese content in *Pinus silvestris* leaves was performed only for the most polluted stand K, and the control one C, it seems obvious that the negative correlation is also typical for this species.

DISCUSSION

Confrontation of the results presented above with a few literature data is really difficult because of the differences, or even neglection in some papers of such parameters as soil characteristics, the amount of industrial emission, etc. The obtained data concerning the content of Fe and Mg in the leaves of *Vaccinium* species and *Pinus silvestris,* are in general similar to the mean values calculated from the data of W i e l-

golaski et al., (1975) and Huttunen (1975), for the same species grown in the forests of Norway and Finland. This leads to the conclusion that the content of Mg in plants, and particularly that of Fe remains at a constant level for any particular species, even in different climatic-edaphic conditions (see also Eaton, Mechan, 1971).

This is not true in respect to Pb, Zn and Cd. For instance the concentration of Pb in the two *Vaccinium species* exceeded several times that found by Lâg and Bolviken (1974) in *Vaccinium* species grown in natural galena soils, Zn content also appeared to be two-times higher than that found by Kazimierczakowa (1975) for *Vaccinium vitis-idaea* growing on a pollution-free area. The amounts of Cd found in the leaves of *Vaccinium myrtillus* and *Pinus silvestris* were also several times higher than those estimated by Lâg and Bolviken (1974). The distinct differences in leaf morphology of the two investigated *Vaccinium* species (apart from those of *Pinus silvestris*) cannot be considered as the only important reason of different ability of heavy metal accumulation, because the ratio of a considered metal concentration in *Vaccinium vitis-idaea* to that in *Vaccinium myrtillus* showed distinct changes depending on the distance from the source of emission, i.e. on metal content in the dustfall and in the soil (this concerned, first of all, Pb, Zn, Cd and Mn). To what degree an assimilating organ shows a different ability of accumulating different metals over a longer period of time, is clearly shown by comparison of the current year and biennial needles of *Pinus silvestris*. The needles older by one year accumulated 250% and 200% more lead and iron, respectively, than did the youngest ones, however, only 20-50% more Zn, Cd and Mg.

It is necessary to point out that heavy metals contamination of a plant is not always reflected in changes of its life activity, as shown by Czuchajowska, Strączek (1979) in respect to the germination viability of *Vaccinium* species seeds, and by Buszman (1979) — as regards the flowering phenomenon of these species.

Manganese seems to a large extent an antagonist in respect to the other metal elements considered in this paper. The individual features of the species strongly influenced its accumulation. It is remarkable that the leaves of *Vaccinium myrtillus* grown in the relatively pollution-free stand C accumulated 20-times more of Mn than the leaves collected from the stands influenced by the zinc-plant. These amounts are 5-times higher than those observed by Wielgolaski et al. (1975). On the other hand, the data for *Vaccinium vitis-idaea* growing in the control stand do not deviate from those obtained by the mentioned authors. The substantial differences in manganese accumulation in the green parts of plants originating from the same stand make it necessary to consider whether the data concerning the values of pH and the buffer

capacity of homogenates of leaves (Czuchajowska, Przybylski, 1978; Czuchajowska, 1979) are responsible among other factors for the high degree of Mn accumulation in *Vaccinium myrtillus* leaves as compared with those of *Pinus silvestris* (Fig. 2a), because of the well known dependence of manganese mobility on the pH of the medium. One should mention here that the latter factors are related to the redox potentials which influence manganese binding to chloroplasts previously treated with some chemicals, as Takahashi and Asada (1977) have noticed recently.

Less manganese accumulation in *Vaccinium* plants in heavily polluted stands may result from the difficulty of its transport to the aerial parts from the roots. This may be caused by the antagonistic character of Mn in respect to Pb and Cd. The latter two metals occur in high concentration in *Vaccinium* roots (Lorek, 1978), for which a highly positive correlation between the content of Mn and that of Pb, Zn and Cd has already been found.

Acknowledgment

The authors are grateful to Doc. Dr hab. T. Przybylski from the Silesian University, for helpful discussions.

REFERENCES

Buszman B., 1979. Phenological changes of *Vaccinium myrtillus* L. and *Vaccinium vitis-idaea* L. caused by industrial emissions, Materials of the IVth Scientific Session of the Naturalists of Silesia. Katowice, October 1979 (in Polish, in print).

Baker A. S., Smith R. L., 1974. Preparation of solution for atomic absorption analyses of iron, manganese, zinc and copper in plant tissue. J. Agr. Food Chem. 22: 103.

Czuchajowska Z., 1979. Seasonal changes of pH and buffer capacity of aqueous homogenates of *Vaccinium vitis-idaea* and *Vaccinium myrtillus* leaves. Acta Soc. Bot. Pol. 48: 35-46.

Czuchajowska Z., Przybylski T., 1978. Seasonal changes of acidity and buffer capacity of aqueous homogenates of *Pinus silvestris* needles and the influence of zinc-plant immisions. Bull. Acad. Pol. Sci. Cl. 2 26: 361-368.

Czuchajowska Z., Strączek T., 1979. The influence of zinc-plant emissions on germination viability and survival rates of the seeds of *Vaccinium* species. Materials of the IVth Scientific Session of the Naturalists of Silesia. Katowice, October 1979 (in Polish, in print).

Dorn C. R., Pierce J. O., Phillips P. E., Chase G. R., 1976. Airborn Pb, Cd and Cu concentration by particle size near a Pb smelter. Atmosph. Envir. 10: 443-446.

Eaton G. W., Mechan C. N., 1971. Effects of leaf position and sampling data on leaf nutrient composition of eleven highbush bluberry cultivars. J. Am. Soc. Hort. Sci. 96: 379-380.

Huttunen S., 1975. The influence of air pollution on the forest vegetation

around Oulu. Acta Univ. Oulensis, ser. A no. 33, Biologica 2; (I) 1-18, (II) 1-37, (III) 1-24.

John M. K., van Laerhoven C. J., Cross C. H., 1975. Cadmium, lead and zinc accumulation in soils near a smelter complex. Environ. Lett. 10: 25-30.

Just J., 1963. Methodics of sanitary investigation of the atmospheric air. Biuletyn SANEPID no. 1 (in Polish).

Kazimierczakowa R., 1975. Correlation between the amount of industrial dust fall and the lead and zinc accumulation in some plant species. Bull. Acad. Pol. Sci. Cl. 2 23: 611-621.

Lâg J., Bolviken I., 1974. Some naturally heavy metal poisoned areas of interest in prospecting, soil chemistry and geomedicine. Jordungerskelsens Saertrykk, Norges geologiske inderskelse 202: 73-96.

Lorek E., 1978. Investigations of chemical composition of the fruits of bilberry *Vaccinium myrtillus* L., and *Vaccinium vitis-idaea* L. as indicator of the degree of environment pollution in a highly industrialized region. Ph. D. Thesis, Library of Uniwersytet Śląski, Katowice (in Polish).

Snedecor G. W., 1956. Statistical methods. Iowa State University Press, Iowa, p. 535.

Strusiński A., Wyszyńska H., 1971. Estimation of iron, copper, zinc and lead in atmospheric air. Roczniki PZH 22: 649-656 (in Polish).

Takahashi M., Asada K., 1977. Manganese binding to sodium cyanide-treated chloroplasts: Effects of light and redoxpotentials on the binding. Plant Cell Physiol. 18: 807-814.

Wielgolaski F. E., Kjelvik S., Kallio P., 1975. Mineral content of tundra and forest tundra plants in Fennoscandia. Analysis and synthesis. Fennoscandia Tundra Ecosystems Part 1, 16: 317-332.

Kumulowanie się metali ciężkich w ekosystemie pozostającym pod wpływem emisji huty cynku

Streszczenie

Zbadano zawartość Pb, Zn, Cd, Mn, Fe i Mg w liściach *Pinus silvestris*, *Vaccinium myrtillus* i *Vaccinium vitis-idaea*, stanowiących główne składniki wybranego ekosystemu znajdującego się w bezpośrednim sąsiedztwie huty cynku w Miasteczku Śląskim (stanowiska K, L i M odległe w kierunku przeważających wiatrów, odpowiednio, o 0,9 2,5 i 5,0 km; stanowisko kontrolne C — w odległości 24 km). Oznaczono także zawartość wymienionych metali w pięciu warstwach gleby o podanej charakterystyce, a także w pyłach przemysłowych na poziomie 0,5 i 2 m (tab. 1). Gromadzenie się metali w liściach okazało się dla każdego badanego stanowiska zależne od gatunku rośliny, np. stężenie Pb w *Vaccinium vitis-idaea* (K), 2800 ppm, przekraczało 30-to krotnie stężenie w *Vaccinium myrtillus* i 6-cio krotnie w jednorocznych szpilkach *Pinus silvestris*. Przewaga stężenia Pb, Zn i Mn w liściach *Vaccinium vitis-idaea* nad ich zawartością w *Vaccinium myrtillus* zmniejszała się w miarę oddalania od emitora. Znaleziono znaczącą dodatnią korelację pomiędzy zawartością Pb, Zn i Cd w glebie, a ich stężeniem w liściach; korelacja taka dla Mn okazała się ujemna. Antagonistyczny charakter Mn w stosunku do innych badanych pierwiastków znalazł także odbicie w zmniejszającej się kumulacji tego metalu w liściach w miarę zbliżania się do emitora (rys. 2a), co prawdopodobnie wynika z utrudnienia jego przewodzenia z korzeni do liści, związanego z dużym stężeniem Pb i Cd w korzeniach *Vaccinium* species.