Polish Journal of Environmental Studies Vol. 13, No. 4 (2004), 367-374

Trace Elements Dynamics in the Upper Soil Horizons of the Puszcza Kampinoska Biosphere Reserve

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Received: 24 September 2003
Accepted: 11 December 2003

Abstract

This paper presents the results of a long-term study on trace elements content in the ectohumus horizons (O) and the mineral horizons (A or A/B) of the Puszcza Kampinoska Biosphere Reserve soils. Studied were the trace elements: Mn, Pb, Zn, Cu, Ni, Cr, Co. It was found that the mineral horizons of the soils contain natural amounts of the heavy metals; an increased concentration of Pb, Zn and Cu was found in ectohumus in some localities and dates. The observed years-long trend of the studied metals concentration has recently been diminishing. The recommended earlier critical values for forest ectohumus were confirmed.

Keywords: trace elements, ectohumus horizon, Biosphere Reserve

Introduction

The multi-year study on prognozing chemical soil properties in Puszcza Kampinoska Forest [1, 9, 11] gave the impulse to analyze the seasonal dynamics of trace elements concentration in the uppermost horizons of selected representative soil profiles, within the time span of a few growing periods. The earlier studies documented the elevated concentration of trace elements in the superficial horizons. Their content is insignificantly related to the poor, sandy parent rock; on the contrary, their actual concentration has been the result of biological accumulation and, also, to a large degree of atmospheric deposition [17]. The dynamics presented in this paper refer to the natural (undisturbed) condition of forest soils. The majority of soil dynamics papers deals with watered and fertilized soils [5] or they are focused on macroelements [4, 10]. The study leading to learning of distribution, dynamics and, in consequence, enabling the assessment of heavy metals concentration in forest litter and mineral-ectohumus horizons of soils has become even more important after the Kampinos National Park was included in the year 2000 to the worldwide network of biosphere reserves: Puszcza Kampinoska Forest Biosphere Reserve. Thus, it is necessary to monitor the state and dynamics of indicator components of its environment in order to protect and maintain the reserve's natural values.

The purpose of the present paper is to assess the soil's potential threats due to the activity of man, on the basis of distribution and dynamics of trace elements.

Material and Methods

The studied soils have originated and developed from the eolian loose sands on dunes (podzol soils), or at the feet of sandy dunes (degraded black earth). The black earth was characterized by a higher concentration of clay fraction compared with the soils present on dune slopes.

The spatial arrangement of soil profiles and the comprehensive description of the soils has earlier been published in a number of papers: their morphology, physicochemical and chemical properties [6, 9]. Table 1 presents the typology of soils under study, and their selected chemical properties, as well as the forest site types.

The studies were conducted during a 6-year period (1993-1998) in selected observational plots of an area of

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Table 1. Soil and site typology, pH and C organic in the soils of research plots.

Locality name and number of soil profile	Type and kind of soil	Forest community	Genetic horizon	pH_{KCl} median	Corg. [g/kg] mean
Piaski Duchowne	Proper rusty soil from dune sand	Peucedano Pinetum	O	3.45	278.00
			A	3.78	11.50
Lipków	Proper rusty soil from dune sand with admixture of silt	Tilio Carpinetum calamagrostietosum (initial stadium)	O	4,74	311.00
			A	3.36	16.00
Nart (21)	Proper rusty soil (dune sand)	Tilio Carpinetum calamagrostietosum	O	3.83	354.00
			A	3.20	13.80
Dąbrowa Stara	Podzolized rusty soil (dune sand)	Querco – roboris Pinetum	O	2.90	290.20
			A	3.30	18.70
Palmiry	Podzol soil (dune sand)	Peucedano Pinetum	O	2.82	361.00
			A	3.28	17.40
Nart (5)	Degraded black earth (dune sand with admixture of silt)	Communities at Arrhenatherion elatioris	O	4.34	322.20
			A	3.73	8.00

about 1000 m^2. Mixed soil samples consisting of a total of 20 subsamples each were collected from the organic horizon (O) and mineral horizon at the depth range 0-20 cm (horizons A or A/B, depending on actual soil type) in May, July and September, always during the first ten days of the month regardless of study year.

In mineral samples the total (general forms) contents of particular elements were determined in 20%HCl extract after etching in about 500°C. Organic samples were ash-dried in about 500°C and dissolved under a hot environment in 10% HCl. In solutions prepared this way, the following elements were determined with use of the AAS technique: Mn, Pb, Zn, Cu, Ni, Cr, Co.

Results

No systematic differences in trace elements dynamics were observed in particular growing seasons, such that would be related to the sampling date (Fig. 1a, b, c); on the contrary, the differences were dependent on actual concentration of particular compounds in the ambient atmosphere [18].

The dynamics was, in the many years' perspective, higher concerning the organic horizons as compared with the mineral ones. The ectohumus samples contain higher amounts of Mn, Zn and Pb, Cu, Ni and Co compared with the mineral horizons. Particularly high differences were found in the case of manganese (with the exception of Dąbrowa Stara location), but even these differences have shown the diminishing trend within the last three years of study. Also, considering Cu, Ni and Co the pattern has been changing with time. In 1996-98, the content of nickel and copper in the mineral horizons usually exceeds that in the organic horizons (with the exception of Lipków), the differences being smaller in the case of copper. In Lipków, with relatively higher concentration of nickel, forest litter has uninterruptedly contained higher amounts of the element – perhaps as a result of increased emissions of nickel-rich dust. The content of cobalt is maintained higher in the O horizons, but the differences became smaller towards the end of study period in all studied horizons. At the same time, the content of Cu, Ni and Co has been on the increase in the mineral horizons (with one exception: Cu content in Lipków). The reason has been, most likely, the diminishing volume of trace elements fallen from the atmosphere, accompanied by the downward movement of the earlier sedimented soil resources of the elements.

The concentration of manganese in forest floor litter has been connected with the pH level dynamics of the studied soil horizons. The highest amounts of Mn are present in the horizons characteristic of the highest level of pH the rusty soils in Lipków and Nart (Table 2), while the lowest concentration of the element is accompanied by the lowest level of pH – the podzol soil in Palmiry, the podzol-rusty soil in Dąbrowa Stara (Table 2). The actual content may, however, be additionally modified by pollution, eg. in Lipków (2) and Nart (21).

Chrome concentration is higher in the A horizons, compared with the O horizons, in the majority of samples. A departure from the above-described pattern was observed at the early stage of study in Palmiry, the reason might have been the research plot location near the motor vehicle road and the resulting increased level of litter pollution with chrome.

A years-long diminishing tendency has been observed of trace elements concentration (Figs. 1a, 1b, 1c). The only exception has been the case of lead in Palmiry, Dąbrowa Stara and Piaski Duchowne.

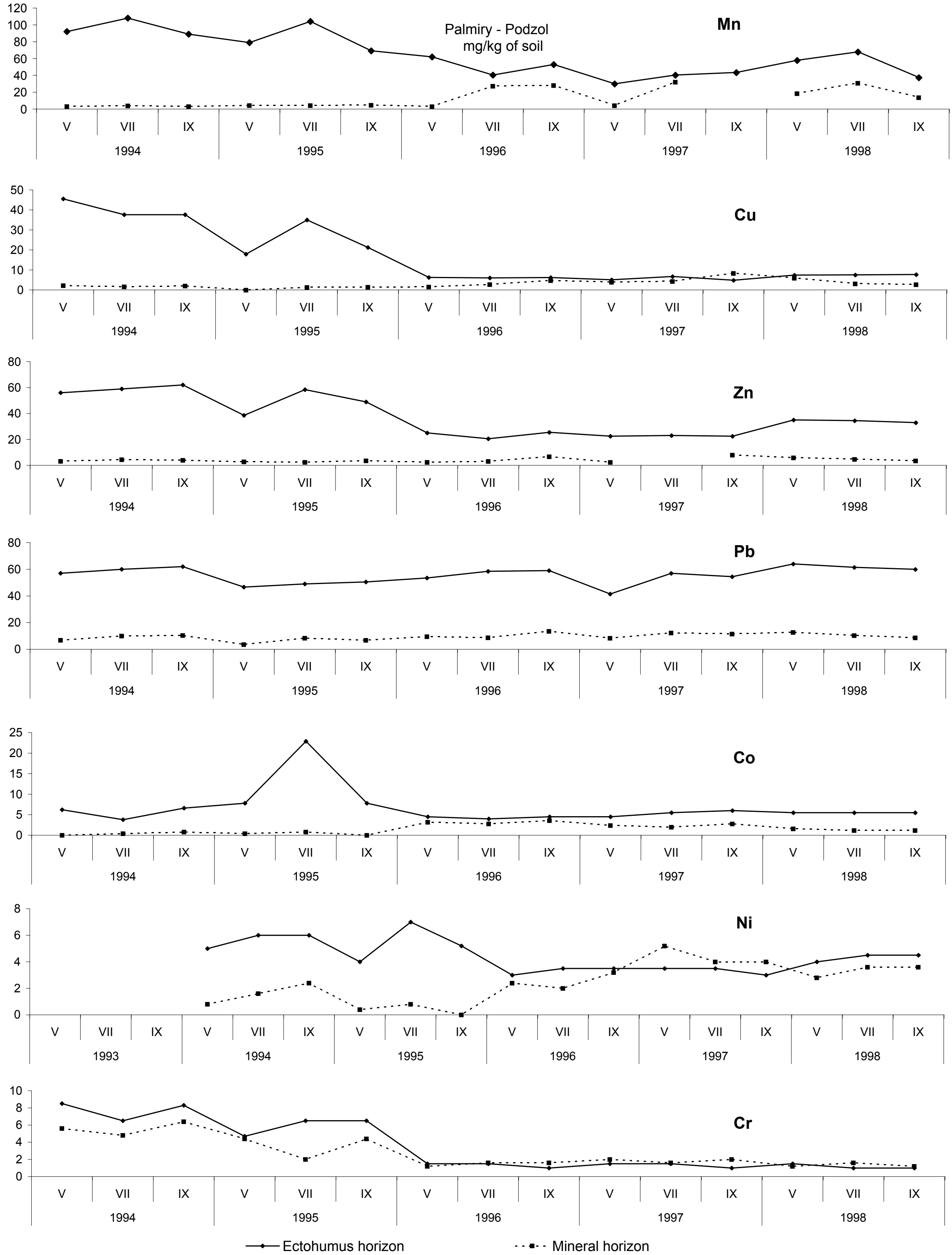

Fig.1a. Trace elements contents dynamics in podzol soil at Palmiry.

The upper horizons are enriched with trace elements, compared with the horizons of their bedrock C. The enrichment index (or, according to other authors, the distribution index) value was calculated as the ratio: element concentration in given horizon/mean concentration in the bedrock. The value of the index reaches a few units, considering Pb, Zn, Cu, Cr and Co in the organic horizons, while in the mineral horizons it varies from 1.2 to 3.0. In the case of Mn the index value equals about 40 in the O horizons, and

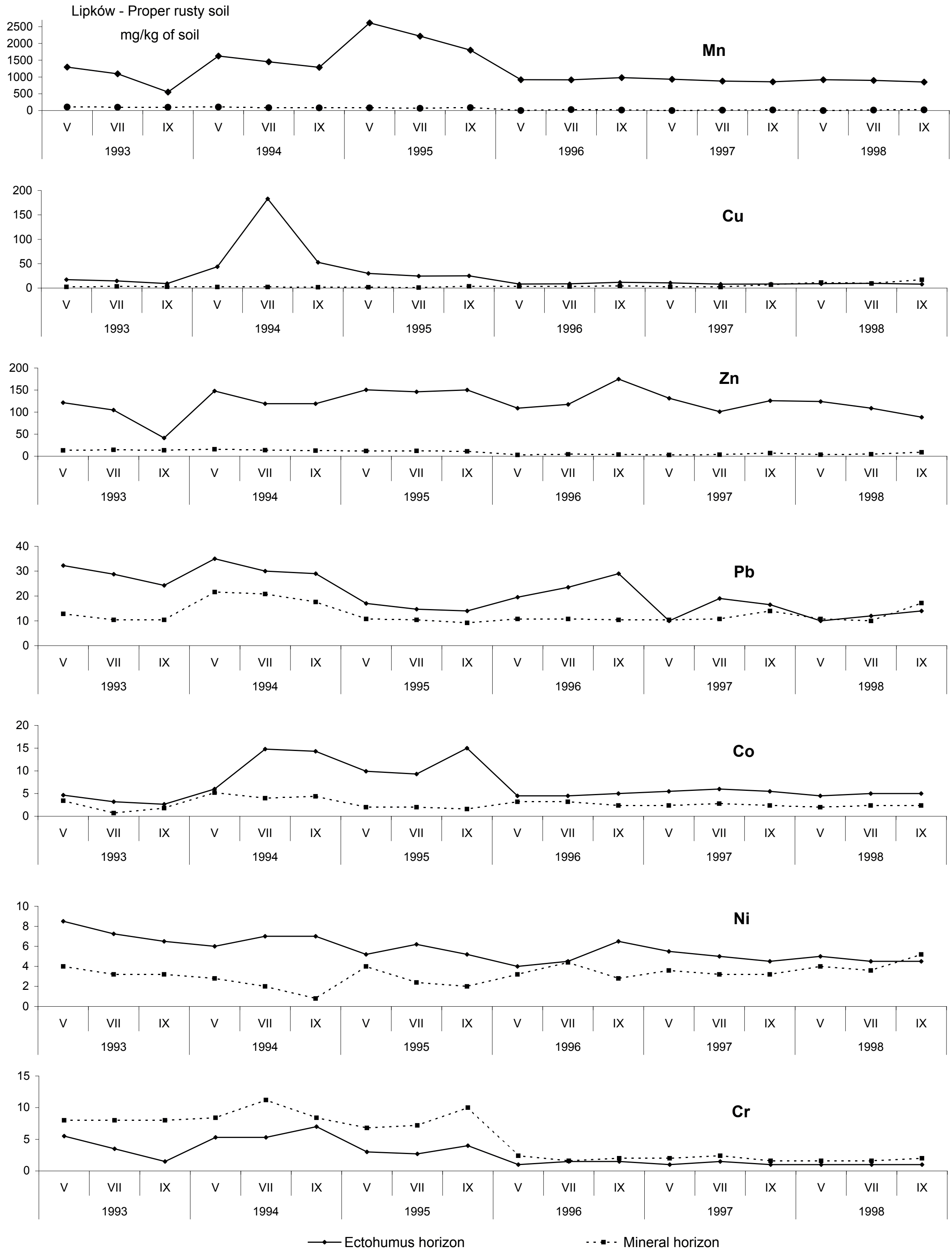

Fig.1b. Trace elements contents dynamics in rusty soil at Lipków.

only some 1.5 in the A horizons. Some departures from the above-stated general pattern were observed in some sampling plots, considering Mn, Pb, Zn and Cr. Abnormally high enrichment with trace elements in some localities gives evidence for the growing local pollution. This last statement is true considering Mn concentration in the O horizons in Lipków and Nart (21) as well as the A horizons of black earth in Nart and Piaski Duchowne. An increased value shows the enrichment index for Pb in horizons O and A in

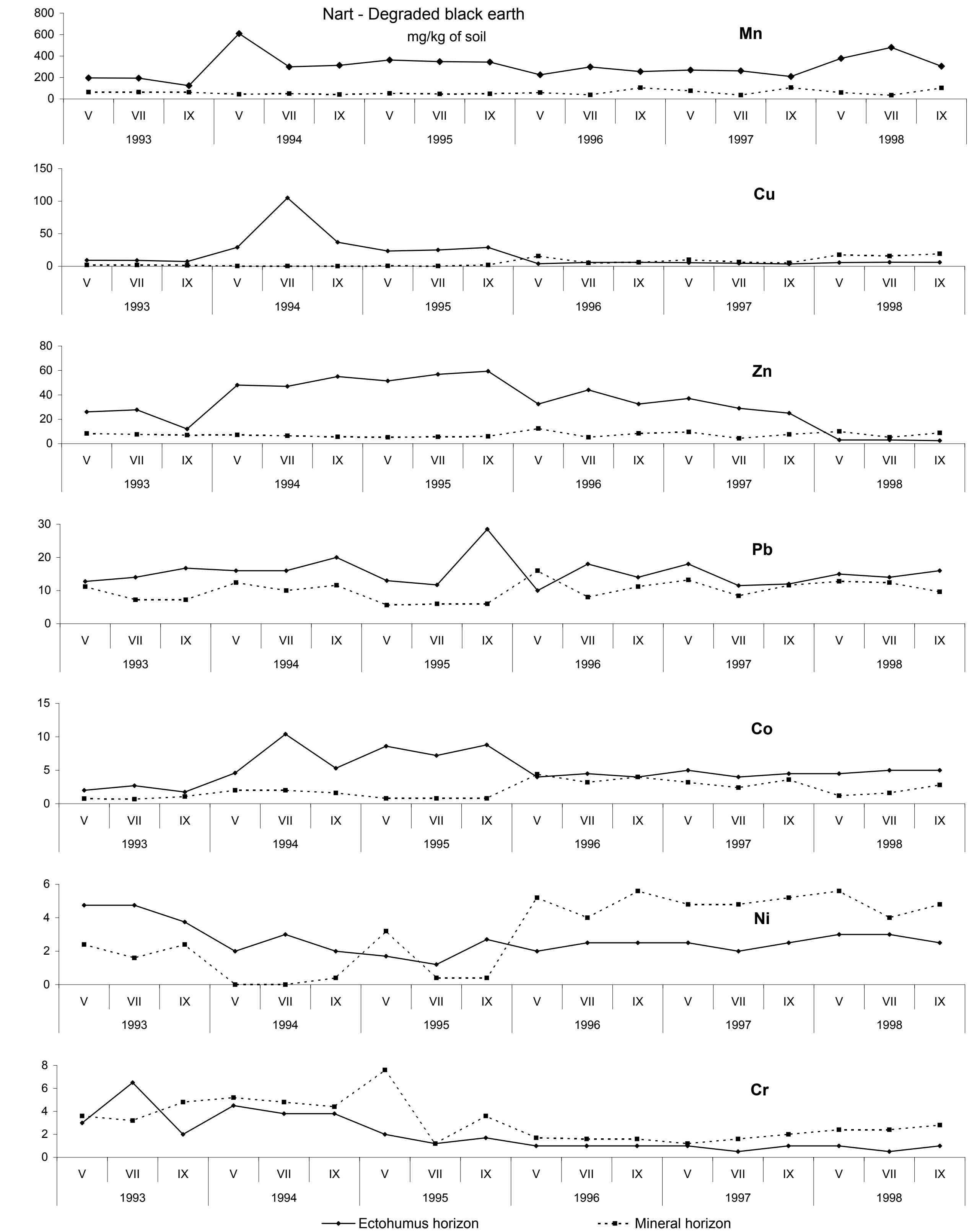

Fig.1c. Trace elements contents dynamics in blackearth at Nart.

Palmiry, while considering Zn – in O horizons in Nart (21) and Lipków, and finally – all A horizons of the studied soils; in the case of Cr – more than half of all the samples had elevated enrichment index value for the A horizons.

Discussion

The seasonal (considering the growing season) dynamics of particular elements depends on the sorption capacity of soils and plant intake intensity; this has been

Table 2. Trace elements content in soils [mg/kg]; med. median; SD – standard deviation.

Element	Genetic horizon	Palmiry				Dąbrowa St.			
		min.	max.	med.	SD	min.	max.	med.	SD
Mn	O	30.0	108.0	62.0	25.0	64.0	299.0	124.0	67.5
	A	3.2	32.4	4.6	11.9	19.2	118.8	36.4	27.8
Cu	O	4.9	45.5	7.6	14.7	4.5	52.2	8.1	13.3
	A	0.0	8.4	2.8	2.1	0.0	25.6	2.6	7.1
Zn	O	20.5	62.0	34.5	15.3	12.5	57.2	30.9	11.7
	A	2.4	8.0	3.6	1.7	4.0	11.2	5.6	2.3
Pb	O	41.5	64.0	57.0	6.3	27.5	67.0	50.5	11.0
	A	3.6	13.6	9.6	2.6	5.2	16.0	11.4	2.9
Co	O	3.8	22.9	5.5	4.6	1.3	10.4	4.6	2.5
	A	0.0	3.6	1.2	1.2	0.0	4.4	1.7	1.2
Ni	O	3.0	7.0	4.0	1.2	3.0	8.3	4.4	1.3
	A	0.0	5.2	2.4	1.5	0.0	5.6	3.0	1.8
Cr	O	1.0	8.5	1.5	2.9	1.0	7.5	1.5	2.3
	A	1.2	6.4	2.0	1.8	1.2	7.6	3.2	1.9

Element	Genetic horizon	Nart 21				Nart 5			
		min.	max.	med.	SD	min.	max.	med.	SD
Mn	O	89.0	1938.0	881.0	499.4	124.0	609.0	298.5	112.1
	A	3.2	40.8	22.0	10.9	34.4	106.0	55.6	23.0
Cu	O	6.4	64.5	9.4	18.1	3.6	105.1	6.7	24.3
	A	0.0	18.0	2.8	5.5	0.2	19.2	3.6	6.6
Zn	O	29.0	92.9	61.0	20.8	2.5	59.4	32.5	18.7
	A	2.8	8.8	7.2	2.1	4.4	12.4	7.12	2.1
Pb	O	21.0	45.0	30.5	8.0	10.0	28.5	14.5	4.2
	A	6.4	19.6	12.0	3.1	5.6	16.0	10.6	2.9
Co	O	4.5	9.4	5.5	1.8	1.8	10.4	4.6	2.3
	A	0.4	3.6	2.0	1.0	0.7	4.4	1.8	1.2
Ni	O	3.5	7.0	4.5	1.1	1.2	4.8	2.5	0.9
	A	0.0	4.4	2.8	1.3	0.0	5.6	3.6	2.1
Cr	O	1.0	8.3	1.5	2.6	0.5	6.5	1.1	1.6
	A	0.8	7.6	2.4	2.2	1.2	7.6	2.6	1.7

Element	Genetic horizon	Piaski Duchowne				Lipków			
		min.	max.	med.	SD	min.	max.	med.	SD
Mn	O	153.7	497.0	218.5	98.7	551.5	2612.5	957.5	534.8
	A	31.2	160.0	120.8	39.5	3.2	107.2	51.4	40.6
Cu	O	5.2	125.0	10.0	35.8	8.1	183.0	11.2	41.1
	A	0.2	13.6	3.0	4.2	1.2	17.2	3.1	4.2
Zn	O	20.0	57.0	38.0	12.1	41.3	175.0	120.3	29.2
	A	4.4	13.4	9.3	2.8	3.2	16.0	10.2	4.7
Pb	O	21.0	58.5	46.0	8.8	10.0	35.0	19.3	8.1
	A	7.2	17.6	10.6	3.3	9.2	21.6	10.8	3.9
Co	O	1.6	19.7	5.5	6.1	2.7	15.0	5.3	4.0
	A	0.7	3.6	2.4	1.0	0.7	5.2	2.4	1.1
Ni	O	2.5	8.0	5.0	1.4	4.0	8.5	5.4	1.2
	A	0.8	6.0	3.2	1.4	0.8	5.2	3.2	1.0
Cr	O	1.0	7.5	1.5	2.2	1.0	7.0	1.5	2.0
	A	1.6	10.0	3.8	2.9	1.6	11.2	4.6	3.5

observed in the case of macroelements of the studied plant communities [4]. The seasonal dynamics of trace elements pattern is affected by pollution fall, while the annual and long-term fluctuations depend on the periodic changes in dust deposition [16, 18].

In the long-term it is to state that there has been a general diminishing trend of the concentration of the studied trace elements over the period of 1996 through 1998. This conclusion is in agreement with the last decade's observed improvement in the air-sanitary condition, both in the urban terrain and non-urban terrain, including also the area under protection by law, the latter has been characterized by even more positive parameters [16]. The Biosphere Reserve Puszcza Kampinoska has been subjected to a number of versatile anthropogenic influences. It is surrounded from the east by the Warsaw agglomeration, and from the west it borders with the industrialized area of Sochaczew – Chodaków; from the south the Kampinos Forest is close to the intensively growing large dwelling districts of Lipków, Truskaw, Izabelin. The Puszcza Kampinoska Forest is an extremely attractive area for tourism. The earlier study [3] finding was confirmed that the increased concentrations of trace elements are only locally present in the forest litter of the area subjected to elevated impact of anthropogenic factors. The years-long dynamics study revealed no occurrence of extreme concentrations during the entire research period (Tab. 2).

An increased level of trace elements has been maintained in the ectohumus horizons in some localities and sampling dates: in as much as 49.0%, 17.6% and 19.4% of all samples, concerning Pb, Zn and Cu, respectively. An elevated concentration of Pb was stated in the years 1994 and 1995 in sample plots of Piaski Duchowne, Dąbrowa Stara, Palmiry and Nart (in the last mentioned case in a dune). Increased values of Zn were found in the forest litter during the entire research period in Lipków. Copper concentration was increased in all the researched plots in 1994, and only in some of them also in 1995 (Piaski Duchowne, Palmiry and Dąbrowa Stara). Nevertheless, even those elevated values prove the studied soils need to be included to the group of uncontaminated soils. Ni, Cr and Co concentrations in forest litter were maintained within the normal range. The mineral horizons of the studied soils contain the normal concentration of all the trace elements of interest. Each time, when evaluating the actual concentrations of particular elements, the tentative crucial limits were used as elaborated in 1999 by Konecka-Betley et al. [11] for the forest floor litter, and the crucial limits for the arable soils: mineral and organic, as proposed by Kabata and coworkers in 1993 [8]. The recommended critical values mentioned above were established to guarantee the sustainable development of the natural environment. Considering the present paper's dynamic study results as well as those presented by Czępińska-Kamińska and Janowska in 2000 [3] one should confirm the correctness of the critical limits as worked out for the forest ectohumus by Konecka -Betley et al. in 1999 [11]: Cu – 30.0 ppm; Zn – 75.0 ppm; Pb – 40.0 ppm; Cr – 25.0 ppm; Ni – 35.0 ppm; Co – 20.0 ppm. The presence of ectohumus is usually connected with environments characteristic of low or even very low pH index values. Any higher concentration of trace elements than the above-quoted means some degree of soil pollution. The clear dependency between manganese content and litter pH suggests the need for a more detailed study in order to determine the manganese critical concentrations [14, 15].

Also, the same time accomplished study on plants [6] and somewhat younger investigations of soils in other catenas of Puszcza Kampinoska Forest [12], confirm the assumption of the natural (undisturbed) level of trace elements in the soils of PK Forest. Locally present increased values warn of the danger of anthropopressure.

It is commonly accepted that plant and animal species that are especially sensitive to environmental changes may be used as bioindicators. This results from the present study that also forest litters may serve an excellent biological indicators of environmental alterations, due to their ability to collect, in the course of biological accumulation, those elements from the direct fall from the atmosphere as well as those sedimented because of the beneath-crown fall and washed-off from tree stems [7]. The litter samples subjected to the present study are characterized by significantly higher concentrations of Mn, Pb, Zn (for medians and maximum values see Table 2) as well as increased maximum content of Cu and Co, comparing with plants from the same area [6].

The soils of PK Forest resemble those rusty and podzol soils from the other regions of Poland, in respect with the content of trace elements. The organic soil horizons of PK Forest contain similar amounts of trace elements as comparable, unpolluted soils of Puszcza Biała Forest, and even somewhat smaller concentrations in the mineral horizons [13]. Similar results were obtained comparing the values of the enrichment index for trace elements between the two forest complexes. In the latter comparison, some exceptions were only found for Mn, Pb and Zn, that have probably been the result of the locally elevated fall of the metals. Considering the general character of soils representing the easternmost regions of Poland [19], it is to conclude that the soils of the PK Forest collect similar amounts of Zn, Cu, Pb, Ni; smaller amounts of Cr; and – in more than half samples – higher amounts of Mn and Co in organic horizons. The concentration of nearly all of the trace elements (with the exception of Co) was smaller in PK Forest soils, compared to the eastern Poland. Another comparison made: with PK Forest soils studied 20 years ago [2], shows that at present the soils contain smaller amounts of Mn, Pb, Zn, Cr, similar or slightly larger loads of Ni and larger amounts of Co, in the litter horizon.

Conclusions

1. The years-long dynamic study has revealed the diminishing trend of trace elements concentration in the upper soil horizons of forest soils in the Biosphere Reserve "Puszcza Kampinoska".

2. The dynamics observed within the growing season depend mainly on the actual atmospheric air dust deposition volume.
3. Puszcza Kampinoska Forest soils are characterized by the natural level of trace elements concentrations.
4. The locally or temporarily observed elevated concentrations of Pb, Zn and Cu in ectohumus are warning signs showing possible anthropopressure hazards.

Acknowledgement

The study was carried out under grants 4S 40108804 and 6PO4G 05612 of the State Committee of Scientific Research.

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