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SOME CONTROL OF AN AMPLIFIED HEAVY METAL DISTRIBUTION AT IMMISSION SITES OF DANUBE LOWLAND REFINERIES

The objective of this study was to investigate the effect of atmospheric immissions of both most significant industrial centres of Danube Lowland, Schwechat and Slovnaft refineries on environment. In this connection, the environmental pollution of immission zones with heavy metals should be evaluated on the basis of selected bioindicators (soil, lucerne, wheat, earthworms). Due to the orographic depression between Eastern Alps and Western Carpathians and characteristic atmospheric circulation with predominance of the winds blowing from the northwest, heavy metal aerosols from closed industrial activities are expected to influence the quality of the surrounding environment. However, most of 112 surface samples of soil taken from arable fields in the Schwechat District (Austria) showed natural levels of heavy metals. The uptake of heavy metals by wheat from soil was rather low, too. At the Slovakian monitoring site, bioaccumulation of heavy metals by lucerne, as a consequence of their availability in soil, had a slightly increased tendency. A considerably higher transfer coefficient was recorded for earthworm tissues, which was especially evident in cadmium content.

LIST OF SYMBOLS

FAAS	– Flame Atomic Absorption Spectrometry,
ETAAS	– Atomic Absorption Spectrometry with Electrothermal Atomization,
ICP AES	– Atomic Emission Spectrometry with Inductively Coupled Plasma,
IR	– Infrared Spectroscopy,
PE	– polyethylene,
PTFE	– teflon,
n.d.	– not determined,
<i>n</i>	– number of element determinations,
SD	– Standard Deviation,
RSD	– Relative Standard Deviation,
min.	– minimum concentration,

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max. – maximum concentration,
Var. coef. – variation coefficient.

1. INTRODUCTION

Heavy metals may be important trace elements in the nutrition of plants, animals or humans (e.g. Zn, Cu, Mn, Cr, Ni, V), the others are not known to have any positive nutrition effect (e.g. Pb, Cd, Hg). But all of these may produce toxic effects – some of them in very low concentrations – if they occur in excess. The bioaccumulation of heavy metals on large territories and over long periods, which may result in gradual damage of living organisms, necessitates careful monitoring of the input, mobility and effects of these pollutants [1].

The bioaccumulation of trace elements in living organisms and their biomagnification mean or describe the processes and pathways of these (possible) pollutants from one trophic level to another, thus exhibiting a higher bioaccumulation ability of organisms whose living status is higher. This increasing concentration due to food chain is caused by a longer retention time of toxic substances compared to the concentrations of macronutrients in organisms [2].

Heavy metals are emitted from a great number of sources which contribute to metal loads in the food chains of terrestrial and aquatic ecosystems. These elements are released to the environment as a result of a wide range of industrial activities and combustion of fossil fuels.

Cadmium enters the environment via three main routes: a) refining and use of cadmium, b) copper and nickel smelting and c) fuel combustion.

Vanadium compounds are widely distributed in the earth's crust and occur together with nickel in fossil fuels in the form of a porphyrin complex [3].

The increasing concentrations of heavy metals in the environment are assumed to result primarily from fly ash formed during burning of fossil fuels. Vegetation, airborne soil particles, volcanic aerosols and forest fires contribute considerably to natural emissions of trace elements. The current anthropogenic metal emissions are responsible for high concentrations of toxic elements in soil and water. They are up to several orders of magnitude higher than estimated natural concentrations. High levels of lead contamination occur near highways and cities due to the combustion of leaded gasoline [4].

Inputs of heavy metals into soils have gradually increased over the past decades as a consequence of agricultural practices (fertilizing, pesticides), disposal of sewage sludges, landfilling and atmospheric deposition. Unlike in other environments (i.e. atmosphere, aquatic bodies) heavy metals in soil are characterized by long residence times [5].

The objective of this publication was to investigate atmospheric immissions of both most significant industrial centres of Danube Lowland, Schwechat and Slovnaft

refineries, in order to evaluate the atmospheric impact of heavy metal aerosols on the food chain and their transfer in the model: soil-plants-terrestrial invertebrates [6]. Some other possible concentrations of heavy metal in the soil of the monitored south-east sites of refineries were evaluated as well. For this purpose the results of two different studies carried out in Slovakia and Austria were evaluated and summarised.

2. EXPERIMENTAL

2.1. STUDY AREA AND SAMPLING STRATEGY

The areas for monitoring heavy metals at various food chain levels, including soil substrates, are represented by a SE quadrant up to approximately 5 km distance from the both industrial refinery centres of Schwechat and Slovnaft.

The continental climate with a mild zone typical of this area is determined by the wind conditions of the Danube Lowland and Low Carpathian Mountains. Due to orographic situation with its characteristic air circulation the winds in this area blow predominantly from the northwest at mean velocity of $5.2 \text{ m}\cdot\text{s}^{-1}$. A mean annual temperature is $9.8 \text{ }^\circ\text{C}$, the warmest month is July and the coldest – January. A long-term average annual precipitation in the area is 550 mm.

The Slovakian sampling zone may be characterized as an industrial-residential one, and the Austrian region – as predominantly agricultural. In terms of soil classification, both soil types are rich in carbonates (e.g. Calcaric Fluvisol).

In the Slovakian sampling zone, 10 localities for sampling were selected according to *Propositions for Sampling by Immissions Measurements STN 83 5511* [7]. Sampling of surface soil layer, vegetation and worms was done manually during a period of several months in summer (1996, 1997, 1998). Sample drawing in Schwechat is described in detail by SPIEGEL [6].

In the Schwechat district (Austrian region), soil samples were taken from 112 sampling sites on arable land which were evenly distributed all over the district with particular consideration of the soil types. 87 soil samples were taken from 0–25 cm soil depth, further 25 samples also from 25–50 cm and 50–75 cm depth. At each sampling site 24 soil samples were taken, which represented an area of ca. 1.5 ha.

On the basis of the industrial-residential nature of the Slovakian sampling zone, the most frequent plant bioindicator, lucerne (*Medicago sativa* L.), was collected about 2 cm over the soil horizon. At the Schwechat immission site, the plant samples were collected from 10 localities, the whole wheat plant (*Triticum aestivum*) just before flowering was taken according to methods reported in [8].

Lumbricid earthworms were collected at Slovnaft immission site from the soil by digging and handsorting, generally considered to be the most efficient sampling technique, and transferred in their native soil to the laboratory, where they were rinsed

with tap water in order to remove the adhering soil particles and maintained under moist conditions for several days in PE flasks to allow final gut emptying [9].

2.2. SAMPLES PRETREATMENT

Surface soil samples were taken from both immission sites, dried in laboratory drier at 40 °C for about 20 h, passed through a 2 mm mesh synthetic sieve and homogenized in an agate mill.

Plants and biota samples were dried for about 24 h at 105 °C in a laboratory drier and ground into fine, less than 0.06 mm, grain-size fraction in an agate ball mill.

2.3. ANALYTICAL PROCEDURES

2.3.1. DETERMINATION OF pH AND ORGANIC MATTER

The *soil pH* at Slovnaft site was determined in a suspension of air-dry soil in distilled water. Samples of 20 g of soil passed through a 1 mm mesh sieve to remove aggregates larger than 1 mm were allowed to equilibrate with 50 cm³ of distilled water for 5 minutes by continual mixing, and then pH was measured using MV 870 Digital pH Messgerät (Precitronic, Germany) with a glass-calomel electrode. In Austria, soil (< 2 mm grains) was mixed with 0.1 mol·dm⁻³ CaCl₂ solution (1:2.5 ratio), left overnight and mixed thoroughly before measuring with a glass-calomel electrode.

The *organic matter content* in the soils from Slovnaft site was determined by loss-on-ignition (1 g of soil ashed in muffle furnace at 600 °C to obtain its constant weight). The results were correlated with TOC (determined by IR method, measured with TOC analyser, DC-190, Dohrmann, U.S.A.) as well as with soil composition estimated manometrically. In Austria, the humus content was analysed by means of wet oxidation (0.5–10 g of soil was oxidized with 10 cm³ of potassium dichromate and 20 cm³ of H₂SO₄ and next titrated with Fe(II) sulfate) – table 1.

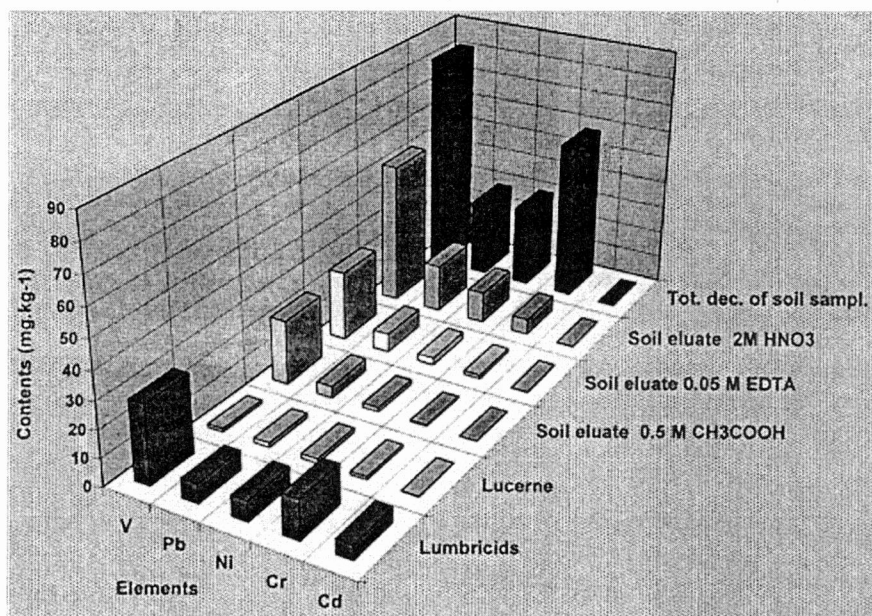
Table 1

Some characteristic data on the soils in the areas studied

Austrian immission zone (Schwechat District – agricultural area)			Slovakian immission zone (industrial-residential area close to Slovnaft)		
pH		7.2	pH		7.4
CaCO ₃	(%)	15.1	Humus	(%)	0.3
Clays	(%)	27	Silica, clays, mica, limonite	(%)	70
Sand	(%)	24	Dolomite	(%)	27
Humus	(%)	3.2	Loss-on-ignition	(%)	11.8
			TOC	(mg·kg ⁻¹)	4534.5

2.3.2. HEAVY METAL EXTRACTIONS

The procedures of soil extraction were accomplished using various extraction agents, e.g. HNO_3 , EDTA, CH_3COOH , BaCl_2 and aqua regia (the figure).



Mean contents of element in various environmental samples

HNO₃ extraction. A 10 g soil sample was shaken with 100 cm³ of HNO_3 extractant in a horizontal LT2 Shaker (200 cycles per minute) during 6 hr in a polyethylene vessel at a room temperature. After shaking, the sample was centrifuged (5 min, 3000 rpm) and the supernatant was analysed.

Aqua regia extraction. 3 g soil samples were put together with 21 cm³ of HCl and 7 cm³ of HNO_3 , left overnight at a room temperature, boiled for 2 hours at 200 °C and poured into 100 cm³ vessels.

BaCl₂ extraction. 20 g of soil and 50 cm³ of 0.1 mol·dm⁻³ BaCl_2 solution were shaken and filtered according to BLUM [10].

Acid decomposition of the lucerne samples was performed in a mixture of 10 cm³ of 65% HNO_3 (suprapure) and 10 cm³ of D.I. water in closed PTFE vessels for 50 minutes using a microwave oven (CEM, MSD-2000, U.S.A.) by 5 stages set and 80% power. Mineralized solutes were transferred into 100 cm³ flasks and filled up to the mark with D.I. water. Wheat samples (0.8 g) were decomposed in 8 cm³ of acid mixture ($\text{HNO}_3:\text{HClO}_4 = 5:1$) for 4–5 hours.

The heavy metal concentrations were analysed using an ICP-AES 2070 (Baird, USA), ETAAS Varian GTA-95 (Victoria, Australia) and FAAS-Perkin Elmer 1100 equipped with deuterium arc background corrector (USA) as well as with AAS with Zeemann background correction HITACHI Z-8000. The analytical accuracy of measurements was checked by means of Certified Reference Materials; CRM B 184 – bovine muscle (Belgium) for lumbricidae and CRM 12-2-03 Lucerne P-ALFALFA, SIM (Slovakia) for plants.

3. RESULTS AND DISCUSSION

Most of 112 surface soil samples taken from the agricultural fields in the District of Schwechat (Lower Austria) show quite natural levels of heavy metals [6]. However, we should stress that immitted heavy metals in arable soils are subjected to a considerable dilution due to ploughing. Measurable enrichment of soil with metals caused by a widespread anthropogenic pollution, predominantly by atmospheric aerosols of heavy metals, was observed only in a few cases. One sampling spot at the sampling network was enriched with Pb and Cr whose concentrations exceeded their admissible levels [11]. Anthropogenic impact of the metal accumulation in surface soil horizon was confirmed by determination of Pb, Cd as well as Cu, Zn and Cr the concentrations of which decreased with the soil depth [6]. The fixation/mobilization potential of the soil in respect of heavy metals depends on pH, organic matter and clay content in soil. In Schwechat, these characteristics favour immobilization of (toxic) metals to a great extent. Table 1 presents some characteristic parameters of the tested soils in the Austrian and Slovakian immission

Table 2

Mean heavy metal contents in environmental samples
from impacted south-eastern sites of Schwechat and Slovnaft refineries

Metal (mean content)	Austrian region				Slovakian region					
	Surface soil (mg·kg ⁻¹)	Wheat (mg·kg ⁻¹)	Soil eluate in BaCl ₂ (mg·kg ⁻¹)	K ₁	Surface soil (mg·kg ⁻¹)	Lucerne (mg·kg ⁻¹)	Earth- worms (mg·kg ⁻¹)	K ₁	K ₂	K ₃
Cd	0.27	0.04	<0.01	0.16	0.39	0.22	5.30	0.56	24.09	13.58
Cr	38.70	0.23	<0.05	0.01	58.10	1.09	14.10	0.02	12.93	0.24
Ni	28.0	0.20	<0.10	0.01	29.60	1.63	7.20	0.05	4.42	0.24
Pb	31.50	0.95	<0.20	0.03	28.30	1.60	7.0	0.06	4.37	0.25
V	–	–	–	–	81.40	1.25	28.80	0.02	23.04	0.35

K₁ – metal content in plant/metal content in soil,

K₂ – metal content in earthworms/metal content in plant,

K₃ – metal content in earthworms/metal content in soil.

zones. pH of soil is slightly alkaline. In Austria, the content of humus in the soil tested (agricultural area) is considered to be medium, while in Slovakia it can be classified as deficient (humus content less than 1%).

An assessment of total contents of selected heavy metals in the soils allows the statement that their levels in the soil extracts obtained using aqua regia are different, but the metal concentrations in 0.1 mol·dm⁻³ BaCl₂ extractant are mostly below the detection limit (tables 2, 3, 4; figure). The latter phenomenon was the reason for any other comments as well as any detailed statistical evaluations.

The transfer coefficient for a soil–plant system is quite low and the heavy metal uptake by wheat via the soil is rather low as well. At the Slovakian monitoring site the bioaccumulation of heavy metals by lucerne, as a consequence of their availability in soil and atmospheric aerosols as well, showed a slightly increased tendency. A considerably higher, multiple bioaccumulation coefficient was recorded in related earthworm tissues (table 2).

Table 3

Mean element contents in soil, various soil extractants, plant and biota at Slovnaft site

Elements	Total decomposition of soil samples	Mean contents (mg·kg ⁻¹), n = 10				Lucerne	Earthworms
		Soil extractants in					
		2M HNO ₃	0.05M EDTA	0.43M CH ₃ COOH			
Cd	0.39±0.18	0.21±0.05	0.17±0.03	0.15±0.03	0.22±0.06	5.30±1.70	
Cr	58.10±3.20	5.60±1.0	1.25±0.39	0.60±0.22	1.09±0.25	14.10±2.70	
Ni	29.60±3.40	11.30±2.20	2.59±0.60	1.62±0.38	1.63±0.41	7.20±2.10	
Pb	28.30±3.02	17.30±2.40	6.60±0.80	4.30±1.04	1.60±1.20	7.0±2.0	
V	81.40±9.93	52.0±6.10	25.30±1.70	22.90±1.80	1.25±0.6	28.80±4.10	

Based on the results obtained for a plant bioindicator, lucerne, it can be concluded that the concentrations of metals in the plant are below total admissible levels for agricultural feed in Slovakia, except the vanadium, whose concentration in plant tissue slightly exceeded this limit (table 2).

Table 4

Medians, means, concentration range and variation coefficients for heavy metals at Schwechat site

Element	Surface layer of soil (mg·kg ⁻¹)					Wheat (mg·kg ⁻¹)			
	Min	Max	Median	Mean	Var. coef.	Min	Max	Mean	Var. coef.
Cd	0.15	0.55	0.26	0.27	23.80	0.03	0.06	0.04	20.90
Cr	7.60	101.90	37.30	38.70	39.20	0.18	0.32	0.23	16.60
Ni	6.60	46.60	28.90	20.0	24.70	0.09	0.31	0.20	35.40
Pb	15.10	116.30	27.70	31.5	43.0	0.79	1.18	0.95	11.10

The amount of heavy metal contaminants assimilated by organisms is not well known yet. Since the mobility of soil organisms may have significant implications for e.g. food chain transfer and the use of accumulation model in establishing environmental quality criteria, it was of importance to investigate the interactions of accessible heavy metals of soil matrix with lumbricids. In this study, within the Slovakian industrial-residential area, average bioaccumulation factors for vanadium (23.04) and for cadmium (24.09) were recorded in related earthworms/plants, however they were not confirmed in related soils/earthworms. These enhanced metal concentrations in the monitored area may result from numerous dumps and industrial activities. As mentioned above, vanadium and nickel emissions may be due to Russian crude oil burning processes.

The biomass of lumbricids is rich in nutrients and proteins and therefore may be used for feeding the poultry, birds, fish and other animals. However, the cadmium concentration in the earthworm tissues exceeded the limit fixed for agricultural feed and from this point of view may cause gradual intoxication of higher species of trophic chain of naturally living organisms. The correlation between the individual heavy metals and some selected soil parameters for the Schwechat District was statistically evaluated using linear regression analysis. The influence of close settlement, industrial emitter as well as of sewage sludge application were partially confirmed.

Lead and cadmium concentrations increased with an organic matter content, but not with clay content increase in the soil. An inverse correlation was found for chromium and nickel. The concentrations of these two metals are positively correlated with the content of the pedogenic Fe- and Mn-oxides [6].

To sum up, total decomposition of soils may not indicate external (antropogenic) contamination, but may be the result of geological metal content. In the Schwechat area, very low metal concentrations in the soil eluate in BaCl_2 are correlated adequately with the metals whose concentrations in the wheat are below the admissible levels.

While FAAS and ICP AES spectrometry were generally faster and operationally easier for the higher concentration range, the ETAAS was more appropriate for the low metal concentration range. The accuracy of measurements was verified by determination of the elements being studied in certified reference materials (CRM), whereas the analytical results were in a good agreement with each other for all methods applied as well as with CRM.

4. CONCLUSIONS

In natural systems, the bioavailability, toxicity and transport of heavy metals depend on the specification of heavy metals. Possible chemical forms of heavy metals in a natural system are hydrated metal ions, soluble metal complexes, metal precipitates,

metal ions adsorbed to organic matter and bacterial residues and metal ions adsorbed to the surface and interstices of minerals. From this point of view various analytical and modelling approaches can be used to determine the specification of heavy metals in a natural system. Together with analytical methods, modelling approaches can provide an additional understanding of the environmental factors controlling metal distribution in natural systems, including soil. For the same reasons, the extractability of heavy metals from the soils can be better interpreted and predicted if a deeper insight into the metal binding properties of soil particles is available.

This study presents some of such approaches and describes the factors that contribute to bioaccumulation of toxic heavy metals in higher naturally living organisms. Nevertheless, this phenomenon may gradually endanger the entire trophic system.

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KONTROLA INTENSYWNEGO ROZPRZESTRZENIANIA SIĘ METALI CIĘŻKICH W STREFACH IMISJI RAFINERII NA TERENIE NIZINY NADDUNAJSKIEJ

Badano, jaki jest wpływ imisji atmosferycznej na środowisko na terenie dwóch ważnych ośrodków przemysłowych, rafinerii Schwechat i Slovnaft, położonych na Nizinie Naddunajskiej. W tym celu należało określić zanieczyszczenie środowiska metalami ciężkimi w strefach imisji na podstawie wybranych bioindykatorów (gleba, lucerna, pszenica, dżdżownice). Ze względu na orograficzne obniżenie pomiędzy Alpami Wschodnimi a Karpatami Zachodnimi i charakterystyczną cyrkulację powietrza z przewagą wiatrów z północnego zachodu można spodziewać się, że aerozole metali ciężkich pochodzą-

ce z działalności przemysłowej będą wpływać na jakość okolicznego środowiska. Jednakże w większości ze 112 próbek gleby pobranych z powierzchni pól uprawnych w rejonie Schwechnat (Austria) stwierdzono naturalny poziom metali ciężkich. Asymilacja metali ciężkich przez pszenicę była również mała. Na monitorowanym obszarze w Słowacji bioakumulacja metali ciężkich z gleby przez lucernę wykazywała nieznaczną tendencję wzrostową. Zaobserwowano natomiast znacznie wyższe współczynniki przenoszenia (akumulacji) w komórkach dżdżownic, co było szczególnie widoczne w przypadku kadmu.