

Study of Cd, Cu, Ni, Pb, and Zn Mobile Forms in Gravitation Dust Sediment Particles*

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In order to separate water-soluble compounds of hazardous elements, a single-step extraction process was carried out and gravitation dust sediment was extracted with distilled and snow water. For the isolation of ion-exchangeable forms, 0.1 mol dm^{-3} CaCl_2 and 0.1 mol dm^{-3} NaNO_3 were used. The determination of the elements content in extracts was carried out with flame atomic absorption spectrometer, the Perkin—Elmer model 3030 equipped with a deuterium lamp for background correction and air/acetylene flame. The total content of selected elements in the sample of the gravitation dust sediment decreases in the order Cu, Zn, Pb, Ni, Cd. From selected elements as water-soluble forms are presented only Cd, Cu, and Zn. Cd, Cu, Pb, and Zn were determined in the solution of CaCl_2 and Cd, Cu, and Zn in the solution of NH_4NO_3 and NaNO_3 .

The toxicity of gravitation dust sediment, represented by particles, which are capable of spontaneous sedimentation, and its effect on living organisms is minimal. These particles can contaminate the soil by those element forms, which are able of transport from dust sediment particles to the soil. From the standpoint of mobility in soil, the mobile forms constitute the highest danger. Mobile forms, which have the greatest importance from the point of view of their biotoxicity, include nonspecific sorbed, easily changeable and water-soluble compounds [1]. Many of heavy metals are more soluble in the acid soil environment than in neutral one. In such environmental conditions the reception of toxic elements from soil by the root system of plants will be more intensive [2]. Water-soluble forms can directly enter the plant [3].

The identification of mobile element forms according to their various physical (solubility) or chemical (bonding) properties is part of fractionation [4]. The extraction is a method suitable for the determination of the separate fractions. For the isolation of forms, which are able to mobile from gravitation dust sediment particles to the soil it is possible to use reagents, which are used for extraction of soils. For the extraction of ion-exchangeable forms, solutions of alkaline, alkaline earth, and ammonium salts ($0.05\text{--}0.1 \text{ mol dm}^{-3}$ CaCl_2 , 0.1 mol dm^{-3} NaNO_3 , 0.1 mol dm^{-3} $\text{Mg}(\text{NO}_3)_2$, 1 mol dm^{-3} NH_4NO_3) are often used [1, 5, 6]. Water-soluble forms of elements are extractable

with ion-exchangeable forms, too [5].

In case of evaluation of possible bonding form of elements in dust particles it is appropriate to use values of the standard Gibbs energy of assumed reactions among element forms in dust particles and selected extracting reagents.

EXPERIMENTAL

Individual single-step extraction procedures applied on a gravitation dust sediment sample were carried out by techniques used on a soil sample. The ratio value of the sample mass to volume of extracting solution (m/V) was constant, $0.5 \text{ g}/75 \text{ cm}^3$ for all experiments. This ratio was adapting in accordance with the mass ratio of the deposited dust sediment to contaminated soil.

In order to obtain bigger amount of a sample for all experiments, a sample has not been collected by validated technique. The time of sampling was elongated and the sampling area was enlarged. A sample of the gravitation dust sediment from the locality Košice-Železníky was applied in experiments. It was adapted by drying, grinding, and homogenizing and then it was weighed and extracted.

For single-step extraction procedures extracting reagents were used: distilled water ($\text{pH} = 4.87$), snow water ($\text{pH} = 5.18$), 0.1 mol dm^{-3} NaNO_3 ($\text{pH} = 5.57$), and 0.1 mol dm^{-3} CaCl_2 ($\text{pH} = 5.65$). All used

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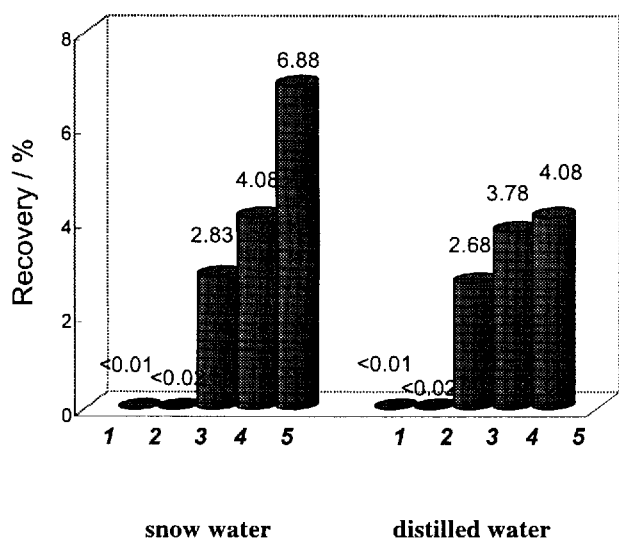
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Table 1. The Content of Characteristic Ions and Selected Elements in Snow Water

Component	NH_4^+	Cl^-	HCO_3^-	NO_3^-	Ca^{2+}	Mg^{2+}	CO_2	Cu	Zn	Pb	Ni	Cd
$\rho/(\text{mg dm}^{-3})$	2.76	4.43	6.10	2.10	5.01	0.61	17.60	0.021	0.091	< LoD	< LoD	0.003

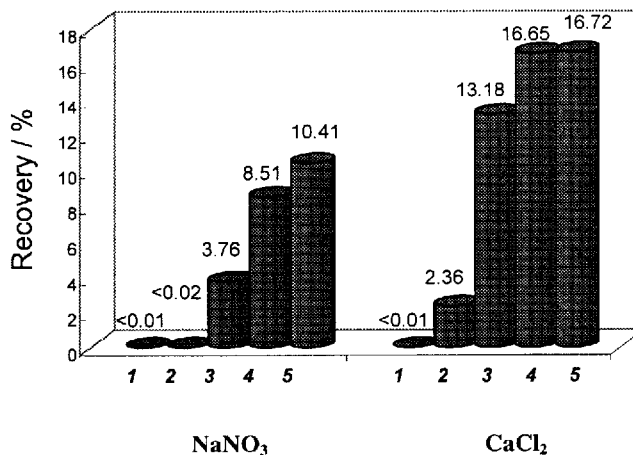
Table 2. Gravitation Dust Sediment – Content of Selected Elements

Element	Cu	Zn	Pb	Ni	Cd
w/%	0.5500	0.2015	0.0446	0.01470	0.0012

**Fig. 1.** The recovery of selected elements using snow and distilled water. 1. Ni, 2. Pb, 3. Cu, 4. Cd, 5. Zn.

reagents represent the slightly acid soil environment. The composition of used snow water is listed in Table 1.

For all selected extracting reagents similar extraction procedures were used. To 0.5 g sample placed in 250 cm³ polyethylene extracting vessel 75 cm³ of extracting reagent was added. The extracting vessel together with its content was immediately shaken in mechanical shaker, which operated at approximately 240 min⁻¹ for the duration of 1 hour at room temperature of (20 ± 2) °C. The extract was immediately filtered through a filter paper (ø = 18.5 cm, with narrow pores). The filtrate was collected in the 100 cm³ glass measure bottle for analysis by flame atomic absorption spectrometry. A blank extract (*i.e.* without dust) was analyzed along with each batch of three samples. The determination of the Cd, Cu, Ni, Pb, and Zn content in extracts and snow water was carried out with flame atomic absorption spectrometer, the Perkin—Elmer model 3030 equipped with a deuterium lamp for background correction and air/acetylene flame.

**Fig. 2.** The recovery of selected elements using NaNO₃ and CaCl₂. 1. Ni, 2. Pb, 3. Cu, 4. Cd, 5. Zn.

RESULTS AND DISCUSSION

The total content of selected elements in the gravitation dust sediment sample is on the level of minor or trace elements, respectively, as shown in Table 2. From the results in Figs. 1 and 2, illustrating the recovery of elements depending on individual extracting reagents used, it can be seen that the mobility of selected elements is different; it is connected with different binding forms of elements in dust particles. The content of Ni in all extracts was below the limit of detection of used analytical detection method. Lead acted in the same way as nickel, with the exception of extraction to 0.1 mol dm⁻³ CaCl₂. All other elements are extractable to all used extracting reagents and their content in individual extracts is in average 4–17 % of Zn, 3.8–17 % of Cd, and 2.7–13 % of Cu.

In the case of evaluation of water-soluble forms it is appropriate to use values of the solubility of some defined compounds in water, which are shown in Table 3 [7, 8].

Thermodynamic data [9] were used for the calculation of standard Gibbs energy of assumed ion-exchangeable reactions between considered bound forms (carbonate and sulfate) and extracting reagents (CaCl₂ and NaNO₃). Standard Gibbs energy values were calculated for the following type of ion-exchangeable reactions

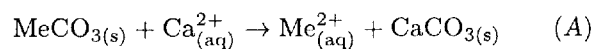


Table 3. The Solubility of Some Defined Compounds in Water

Compound	(Solubility in 100 g H ₂ O)/g		Compound	(Solubility in 100 g H ₂ O)/g	
CdCO ₃	is (0 °C)	is (100 °C)	ZnCO ₃	is (0 °C)	–
CdSO ₄	75 (0 °C)	60.8 (100 °C)	ZnSO ₄	s (0 °C)	53.8 (20 °C)
CuSO ₄	14.3 (0 °C)	75.4 (100 °C)	NiCO ₃	is (0 °C)	is (100 °C)
PbCO ₃	is (0 °C)	is (100 °C)	NiSO ₄	38.9 (20 °C)	77 (100 °C)
PbSO ₄	is (0 °C)	vls (100 °C)			

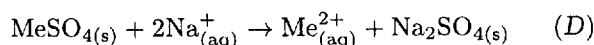
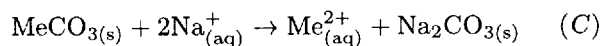
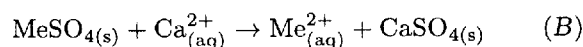
is – insoluble, s – soluble, vls – very little soluble.

Table 4. Standard Gibbs Energy Values of Ion-Exchangeable Reactions among Considered Defined Compounds of Selected Elements and NaNO₃

Element	Type of the reaction	$\Delta G_{298}^{\circ}/(\text{kJ mol}^{-1})$	Element	Type of the reaction	$\Delta G_{298}^{\circ}/(\text{kJ mol}^{-1})$
Cd	A	+72.9	Zn	B	–19.62
Cd	B	+3.64	Pb	A	+77.57
Cu	A	–70.7	Pb	B	+46.82
Cu	B	–145.74	Ni	A	+48.48
Zn	A	+65.36	Ni	B	–24.35

Table 5. Standard Gibbs Energy Values of Ion-Exchangeable Reactions among Considered Defined Compounds of Selected Elements and CaCl₂

Element	Type of the reaction	$\Delta G_{298}^{\circ}/(\text{kJ mol}^{-1})$	Element	Type of the reaction	$\Delta G_{298}^{\circ}/(\text{kJ mol}^{-1})$
Cd	C	–9.27	Zn	D	–74.61
Cd	D	–51.36	Pb	C	–4.59
Cu	C	–123.04	Pb	D	–8.18
Cu	D	–170.73	Ni	C	–33.68
Zn	C	–16.8	Ni	D	–79.34



where Me = Cd, Cu, Zn, Pb, and Ni. Results of these calculations are shown in Tables 4 and 5.

The total content of selected elements in the gravitation dust sediment sample decreases in the order Cu, Zn, Pb, Ni, Cd. The recovery (w) of these elements in distilled and snow water extracts decreases in the order Zn, Cd, Cu; $w(\text{Pb}) = w(\text{Ni})$. The content of Pb and Ni was below the limit of detection (LoD) of the FAAS method. From these results and values of solubility of some compounds in water it is possible to assume that part of Zn, Cd, Cu, and Pb is binding in sulfate forms and part of Pb and Ni in carbonate forms.

The 0.1 mol dm^{–3} NaNO₃-extractable content of elements decreases in the order Zn, Cd, Cu, Pb; $w(\text{Pb}) = w(\text{Ni})$ (contents of Pb and Ni < LoD). From these results and standard Gibbs energy values of ion-exchangeable reactions among element forms and the extracting reagent it is possible to assume the exis-

tence of Zn, Cu, and Pb in sulfate forms and of Cu, Pb, and Ni in carbonate forms. On the basis of thermodynamic calculations and results of extraction it is possible to allege that Cd is not present in the dust sample either in carbonate form or in sulfate form.

Recoveries of selected elements in 0.1 mol dm^{–3} CaCl₂ extract decrease in the order Zn, Cd, Cu, Pb, Ni (the content of Ni < LoD). Zn, Cd, Cu, and Pb can occur in dust particles in both forms, *e.g.* in sulfate or carbonate forms.

By comparison of thermodynamic calculations results and elements recoveries to all extraction reagents it is possible to predict that part of Cu, Pb, and Zn is bound as sulfate and part of Pb as carbonate. Cd in these two forms is not bound. Nickel is not extractable to applied extracting reagents.

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