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Effect of Physical Properties and Cation Exchange Capacity on Sorption of Heavy Metals onto Peats

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Abstract

Studies on sorption of heavy metal ions (Cr^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+}) onto peats of defined type, sort, and kind, as a function of their physical and chemical properties, as well as determination of adsorbent-adsorbate binding stability have been carried out. Among the tested peats the best sorption properties have been found for low-moor peats: Humus Peat and Rush Peat, characterized by high decomposition rates (DR). Among studied heavy metals, the greatest chemical affinity to sorption sites showed chromium ions, bound onto organic matter in insoluble forms, the lowest - zinc and cadmium ions, which mostly enriched mobile forms.

Keywords: cation exchange capacity, decomposition rate, heavy metals, peat, sorption

Introduction

Peat is young Quaternary, mainly Holocene, organogenic sedimentary rock at the first stage of coalification, formed by the decomposition of plant matter in the environment yielding weakly acidic humic substances. The main functional groups present in humic and fulvic acids are carboxylic and hydroxyl phenolic groups in which alkaline and alkaline earth cations may be substituted for H^+ ions, and which are able to interact with metal ions from solution.

The presence of these acidic groups, as well as its high specific surface area, suggest the potential ability of peat to be used as a low-cost and efficient natural adsorbent of metals from point- and non-point environmental pollution sources such as industrial effluents or solid waste dumps. Despite relatively long-lasting interest in peats as natural sorbents, knowledge concerning binding mechanisms of contaminants in this material is extremely limited.

In the present paper, batch experiments on adsorption and binding strength of metal ions (Cr^{3+}, Cu^{2+}, Cd^{2+} and Zn^{2+}) onto selected peats are presented.

Material and Methods

In the presented study, 4 low moor peat samples from Wizna peat bog (Poland) were examined.

The peats were characterized with respect to their botanical origin and major physical and physico-chemical properties. Peat classification was performed according to ASTM D 2607-69 [1] and the Polish Standard PN-85/G-02500 [2], which classify peats with respect to their botanical origin and fiber content adequate to the decomposition rate, and major peat-forming groups of plants specific to habitat. Major physico-chemical properties of the selected peats were evaluated by means of standard methods widely used for peat characterization [3] and respecting such parameters as decomposition rate (DR), natural moisture, bulk density, specific gravity, porosity, ash content, and pH.

Sorption and desorption experiments, and further investigations, were conducted with the use of material air-dried, homogenized, crushed and sieved through a ∅ 1 mm mesh sieve.

Peats were analysed for content of mineral constituents by using standard methods and for total initialcontent of the trace metals by using ICP-MS (Perkin Elmer Sciex Model 250 Elan). Evaluation of cation exchange capacity at pH 7 (CEC_{pH7}) and at pH 8.2 ($CEC_{pH8.2}$), as well as determination of main exchangeable cations of the studied peats, were carried out.

Functional groups in peats were identified by FTIR solid state transmission spectroscopy (Perkin Elmer System 2000) in pressed pellets of mixtures of samples and KBr.

Content of carboxyl and hydroxyl phenolic groups responsible for metal binding was determined in the studied peats by using potentiometric titrations.

Sorption onto selected peats in monometallic Me-Cl system was studied for Cr^{3+}, Cu^{2+}, Cd^{2+} and Zn^{2+}. In the batch experiment, particular metals were sorbed at initial concentrations (c_o) ranging from 1 to 7500 mg/dm^3, pH 4.0, liquid : solid ratio (L:S) 10:1, and contact time 12 h. After equilibration, the solution was separated from sediment through centrifugation and amount of metal (c_{eq}) was determined using flame atomic absorption spectroscopy (FAAS). Total amount of bound metals was calculated as the difference c_o-c_{eq} per mass unit of peat and the results were presented as isotherms.

Sequential extraction of bound metals, its particular stages, the methods applied at each of the stages, listed below in the order of increasing binding strength [4 modified by 5], look as follows:

F0 (PS) – pore solution (distilled water, S:L 1:10, 2h),
F1 (EXC) – exchangeable cations (1M CH_3COONH_4 at pH 7, S:L 1:20, 2h),
F2 (CARB) – carbonatic (1M CH_3COONa+1M CH_3COOH at pH 5, S:L 1:20, 5 h),
F3 (ERO) - easily reducible phases (hydrous Mn-oxides, 0.1 M $NH_2OH{\cdot}HCl$+0.1M HNO_3 at pH 2, S:L 1:50, 12 h),
F4 (MRO) – moderately reducible phases (amorphous Fe-oxides, 0.1 M $(COONH_4)_2$+0.1M $(COOH)_2$ at pH 3, S:L 1:50, 24 h),
F5 (OR) – oxidizable phases (sulphidic and organic phases, 30%H_2O_2 at pH 2, temp. 90^{0}C, and extraction 1M CH_3COONH_4 at pH 7, S:L 1:20, 2h)
F6 – residue, metals bound in the lithogenic crystallites of the mineral fraction (65%HNO_3, temp. 130^{0}C).

This sequential fractionation is appropriated mainly for identification of chemical forms of metal bindings onto heterogeneous mineral matrices. In studies on peats, this scheme has been used to distinguish forms of sorbed metals and it displays the strength of bonds defining metal mobility and potential for remobilisation - and the binding mechanisms themselves [6]. Three forms of metal bindings can be distinguished: mobile (exchangeable), mobilizable, and immobile (strongly bound).

Fractions F0-F2 belong to mobile forms, F3 and F4 to mobilizable forms, and fraction F5 to immobile forms. In the studied peats fraction F6 did not occur.

Results and Discussion

Samples representing low-moor peat were: Alder Humus Peat (W1), Brushwood Humus Peat (W9b), Rush Peat (W9c) and Hypnum Moss Peat (W8). Sample W1 represented Alnioni kind, Alneti class. Peat-forming vegetation was Carici elongatae - Alnetum, major species was alder (*Alnus glutinosa*). The sample W9b represented Alnioni kind, Saliceti class, peat-forming plant groups were Betuletum humilis. Peat-forming species were willow (*Salix cinerea*) and birch (*Betula humilia*) with admixture of reed (*Phragmites communis*) and sedge (*Carex*). The sample W9c represented Limno-Phragmationi kind of Rush Peat, belonging to Reed-Sedgeous class (*Carici Phragmitetii*), peat-forming plant groups were Caricetum rostratae phragmitosum. The dominating species were reed (*Phragmites communits*) and, in smaller amounts, sedge (*Carex*). The sample W8 represented Hypnum Moss Peat, Bryalo-Parvicaricioni kind, Bryaletii class, peat-forming plant group was *Caricetum*. Dominating species were green mosses of low-moor peat bog (*Musci*) with minor admixture of Sphagnum.

Physico-chemical characteristics of investigated samples of W1, W9b and W9c peats displayed considerable similarity (Table1). Brushwood Peat Humus (W9b) and Rush (Reed-Sedge) Peat (W9c) were equally of relatively high decomposition (DR-55%), slightly acidic (pH 6.32 and 6.21), of ash content close to 10% (AC – 10.40% and 9.50%, respectively). Alder Peat Humus, taken from a depth similar to this for W9b (below 28 cm), displayed a higher degree of decomposition (DR – 70%), somewhat higher pH (pH 6.45) and ash content (AC – 12.22%). Physico-chemical properties of Moss Peat (W8) were substantially different. This peat was weakly decomposed (DR -18%), clearly acidic (pH 5.76) and of lower ash content (AC – 7.20%). Peats which were more decomposed were also characterized by higher ash contend and bulk density.

Low contents of mineral fractions suggest that the organic matter decides on the capacity for sorption of metals onto peats.

The FTIR spectra of the studied peats are shown in Fig.1. The region corresponding to high frequencies shows broad band centred on 3300 cm^{-1}. This band is generally attributed to the ν(O-H) vibrations of carboxylic and alcoholic groups. Bands at around 2930 and 2850 cm^{-1} are assigned to asymmetric and symmetric C-H stretching motions of aliphatic groups. The band at around 1600 cm^{-1} is attributed to vibrations corresponding to aromatic C=C stretchings and to the asymmetric COO^- stretching vibrations. The band at around 1400 cm^{-1} is assigned to symmetric COO^- stretching motions and to the bending vibrations of aliphatic groups. A less intense band, attributed to $\delta(CH_2)$ and $\delta(CH_3)$ vibrations of aliphatic groups, appears in these spectra at 1459 cm^{-1}, another (at 1515 cm^{-1}) may be assigned to aromatic ring vibrations and to in-plane δ(NH) vibrations. The band at 1647 cm^{-1} is assigned to aromatic carbonyl, and the one at approximately 1720 cm^{-1} - to ν(C=O) motions in carboxyl groups. The band appearing at approximately

1270 cm^{-1} may be assigned to the C-O stretching vibrations of phenolic groups [7].

Similarity of these spectra shows that products of humification processes of organic matter have a similar chemical structure.

Content of acidic groups in the investigated peats is as follows:

W1 - 117.4 cmol(+)/kg of COOH and 197.0 cmol(+)/kg OH,
W9b – 119.5 cmol(+)/kg COOH and 130.0 cmol(+)/kg OH,
W9c – 115 cmol(+)/kg COOH and 168 cmol(+)/kg OH,
W8 – 80.9 cmol(+)/kg COOH and 147.3 cmol(+)/kg OH.

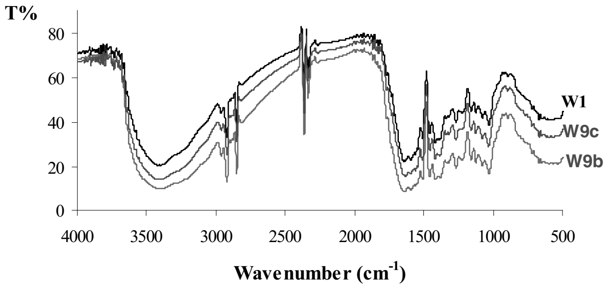

Fig.1. FTIR spectra of selected peats. W1 - Alder Peat Humus, W9b - Brushwood Peat Humus, W9c - Rush (Reed-Sedge) Peat.

In general, mineral fractions of peats W1, W9b and W9c are similar as far as their chemical composition is concerned (Table 2). The most abundant component is CaO (5.80-7.51% wt.). Al_2O_3 (1.22-2.09% wt.) and Fe_2O_3 (0.75-2.11% wt.) occur in accessory amounts . The content of SiO_2 and MgO is minor, while alkalis are present in trace amounts. Content of background trace elements in the samples also shows similarity (Table 2). Sample W9b, taken from 20-60 cm below the surface, displayed higher metal content than sample W9c taken from below 60 cm, what reflects the trend of metal content in peat to decline with increased depth. Background metal content in peat W1 generally falls within a rather narrow range. In general, metal concentrations were typical for pristine areas and reflected natural concentrations of these elements in unpolluted soils.

Total cation and base cation exchange capacities ($CEC_{pH8.2}$ and CEC_{pH7}, respectively), as well as main exchangeable cations, of Peat Humus W1 and W9b and Rush Peat W9c are almost identical (Table 3). It proves an absolute domination of Ca^{2+} ions in all the cation exchange, while the portion of other exchangeable ions is negligible. Exchangeable Ca^{2+}'s are about a half of the total content of these ions in peats. Of the other accessory ions, most of Mg^{2+} and Na^{+} cations in peats also occupy exchange sites, while exchangeable Mn^{3+}, Al^{3+}, Fe^{3+} occur there in insignificant or negligible proportions. These peats show also a high degree of base saturation (90-97%) that correlates with slightly acidic pH. Cation exchange capacity of Moss Peat W8 is more than two times lower, and shows much lesser saturation (63.5%) corresponding to acidic pH.

Comparison of cation exchange capacity with content of the acidic groups in the studied peats suggests that mainly carboxylic groups take part in exchange of ions during sorption.

On one hand, capacity of the studied peats for sorption of metals strongly depends on the sorbed metals. The maximum capacity of each peat (in mass units) for the 4 metals followed the order: $Cr^{3+}>Cu^{2+}>Cd^{2+}=Zn^{2+}$. This series is in agreement with the well known ordered sequence: monovalent alkali metal cations < H_3O^+ < alkaline earth cations < transitional group monovalent cations < transitional group divalent cations (among them Cu^{2+} and Zn^{2+}) < trivalent cations, which grows with growing sorption capacity of organic matter for the cations [8]. Also, results obtained by Wieder [9] confirm this conclusion. Sorption depends on ionic radius, ion charge, electron structure, and hydration of bound metals. Higher capacity for sorbing Cu^{2+} than Zn^{2+} is an effect for the electron structure of Cu^{2+}. Cu^{2+} has one unpaired electron on its 3d orbital and has more active polarization and higher affinity to anionic sites [10].

On the other hand, physico-chemical properties dependent on the botanic origin of peat appear to exert a definite effect on its sorption capacity for metal ions. Due to similarity of the physico-chemical properties of Humus

Table 1. Physicochemical properties of investigated peats.

Type of peat	Depth, (cm)	Decomposition rate (DR), (%)	pH (H_2O)	Natural moisture content (%)	Bulk density (g/cm^3)	Specific gravity (g/cm^3)	Porosity (%)	Ash content (AC), (%)
Alder Peat Humus - W1	<28	70	6.45	73.60	0.310	1.609	80.73	12.55
Brushwood Peat Humus - W9b	20-60	55	6.32	79.67	0.295	1.587	81.88	10.40
Rush (Reed-Sedge) Peat - W9c	<60	55	6.21	75.11	0.247	1.597	85.54	9.50
Hypnum Moss Peat - W8	<33	18	5.76	92.80	0.156	1.551	89.94	7.20

Peats W1 and W9b, and Rush Peat W9c (decomposition rate, ash content, ion exchange capacity and main exchangeable ions) sorption capacities of these peats from synthetic, monometallic Me-Cl solution appeared to be similar for studied metals and fell into a very narrow range. For Cd^{2+} they are 33200 - 37520 mg/kg and for Zn^{2+} – 32050 - 32700 mg/kg (Fig.3). The sorption capacity for Cu^{2+} was estimated to be between 47100 and 49300 mg/kg. Cr^{3+} was the most susceptible to binding onto peat: sorption capacity of peats for this cation ranged from 51880 to 52800 mg/kg.

Compared to Peat Humus and Rush Peat, weakly decomposed acidic Hypnum Moss Peat, with more than two times lesser ion exchange and low buffering capacities, shows also significantly lower binding capacity with respect to all studied metals (Fig.2).

The pattern of pH changes of equilibrium solution in batch system with Humus and Rush Peat showed increase to alkaline pH values 7.42 - 7.90 at the lowest initial Cd^{2+}, Zn^{2+}, Cu^{2+} and Cr^{3+} concentrations, which reflects buffering capacity of material, and moderate decrease of pH of equilibrium solution of Cd^{2+} and Zn^{2+} to values 5.4 - 5.7 for Cd^{2+} and 5.1-5.2 for Zn^{2+}. Small changes of pH of the equilibrium solutions of Zn^{2+} and Cd^{2+} suggest that these metals are mainly bound by replacing Ca^{2+}, dominant in sorption complex of peats.

Also, the sorption capacities of these peats for Cd^{2+} and Zn^{2+} (in equivalent units), similar to their CECs, suggest the ion exchange being a major binding mechanism for these ions. Simple retention of Me-containing pore solution in peat pores and electrostatic attraction between the negatively charged peat surface and positively charged metal ions may be considered as other mechanisms of weak metal binding.

The pH patterns for Cu-Cl system and sorption capacities of peats for Cu^{2+} (in equivalent units), about 1.5 times higher than their CECs, definitely reflect higher role of H_3O^+ displacement by Cu^{2+} ions than by Cd^{2+} and Zn^{2+}.

For Cr^{3+} sorption onto peats, the highest pH decrease of equilibrium solution – falling within the range 2.55-3.01

Table 2. Content of mineral components constituents and trace metals in the selected peat matter (Peat Humus W1, W9b, and Rush Peat W9c).

Peat	Content of mineral constituents (%)								
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	Mn_2O_3	CaO	MgO	Na_2O	K_2O
Alder Peat Humus -W1	0.51	2.09	0.01	1.73	0.038	7.51	0.24	0.029	<.05
Brushwood Peat Humus - W9b	0.35	1.50	0.03	2.11	0.039	5.80	0.26	0.021	<.05
Rush (Reed-Sedge) Peat - W9c	0.25	1.22	0.01	0.75	0.034	6.12	0.19	0.020	<0.05

Content of trace metals (mg/kg)					
	Cr	Cu	Cd	Zn	Pb
Alder Peat Humus - W1	3.37	11.08	0.60	4.39	11.8
Brushwood Peat Humus - W9b	3.11	10.23	0.93	5.12	11.0
Rush (Reed-Sedge) Peat - W9c	3.06	5.58	0.51	4.61	11.6

Table 3. Ion exchange capacity and exchangeable ions structure in selected peat matter of different botanical origin and decomposition rate (Peat Humus W1, W9b, Rush Peat W9c and Hypnum Moss Peat W8).

Peat	pH	CEC_{pH7}	$CEC_{pH8.2}$	Exchangeable ions (cmol(+)/kg, (%)								Base saturation %
				Ca	Mg	K	Na	Fe	Mn	Al	H	
Alder Peat Humus - W1	6.45	121.3	125	112.56 (42.0)	8.10 (67.5)	<0.005	0.32 (34.4)	0.08 (0.12)	0.24 (16.4)	0.13 (0.10)	3.7	97.0
Brushwood Peat Humus - W9b	6.32	119.5	130	110.2 (53.2)	8.50 (65.1)	<0.005	0.37 (54.4)	0.16 (0.14)	0.27 (18.0)	0.26 (0.29)	10.5	91.9
Rush (Reed-Sedge) Peat - W9c	6.21	110.5	123	102.2 (46.7)	7.60 (80.2)	<0.005	0.36 (53.0)	0.09 (0.05)	0.25 (19.0)	0.19 (0.26)	12.5	89.8
Hypnum Moss Peat -W8	5.76	49.5	78	44.6	4.20	0.17	0.35	0.05	0.13	0.19	28.5	63.5

- is observed. Also, sorption of Cr^{3+} (in equivalent units), 2.5 - 3 times higher than CEC, reflects the marginal role of ion exchange in Cr^{3+} binding.

Sequential fractionation of Cu^{2+}, Cd^{2+} and Zn^{2+} sorbed onto studied peats confirms the diversity of the main fractions showing different binding strength for different ions.

Mainly, Cr^{3+} was stably bound in immobile forms (fraction F5, 52.54-69.5%) and in mobilizable forms (F3+F4, 12.13-28.31%), probably as chelating complexes between two carboxyl groups or carboxyl and hydroxyl phenolic groups. Mobile forms (fractions F0+F1+F2) played a marginal role.

Cu^{2+} has been bound in mobile forms (fraction F0+F1+F2, 40.85 - 44.77%). A lower amount of Cu^{2+} is in mobilizable forms (F3+F4, 22.66-40.77%). Also, its percentage in stable forms (fraction F5, 10.26 - 34.38%) was significant, especially for peats W9b and W9c.

As far as the Cd^{2+} and Zn^{2+} binding forms in peats are concerned, these metals are similarly bound in the labile forms (fractions F0-F2, 78.9 - 86.91% and 70.21 - 80.80%, respectively) and should therefore be more susceptible to remobilisation due to changes in the chemical environment. Other fractions are poor in Cd, but the percentage of Zn in the fraction F3+F4 is significant (11.6-25.7%). Enrichment of mobile fractions F1 and F2 in Cd^{2+} and Zn^{2+} suggests that the sorption of these metals is mainly due to Ca ion exchange [13].

Conclusions

1. Studied peats appeared to be very good sorbents of Zn, Cu, Cd and Cr for the wide range of metal concentrations in solutions. Sorption capacities depend on the physico-chemical properties of peats themselves (decomposition rate, pH defined by Ca-buffering capacity, and CEC) and properties of studied metals. Sorption capacities of peats are similar to sorption capacities of other natural sorbents - clay minerals and zeolites - but strongly depend on pH of the solution.

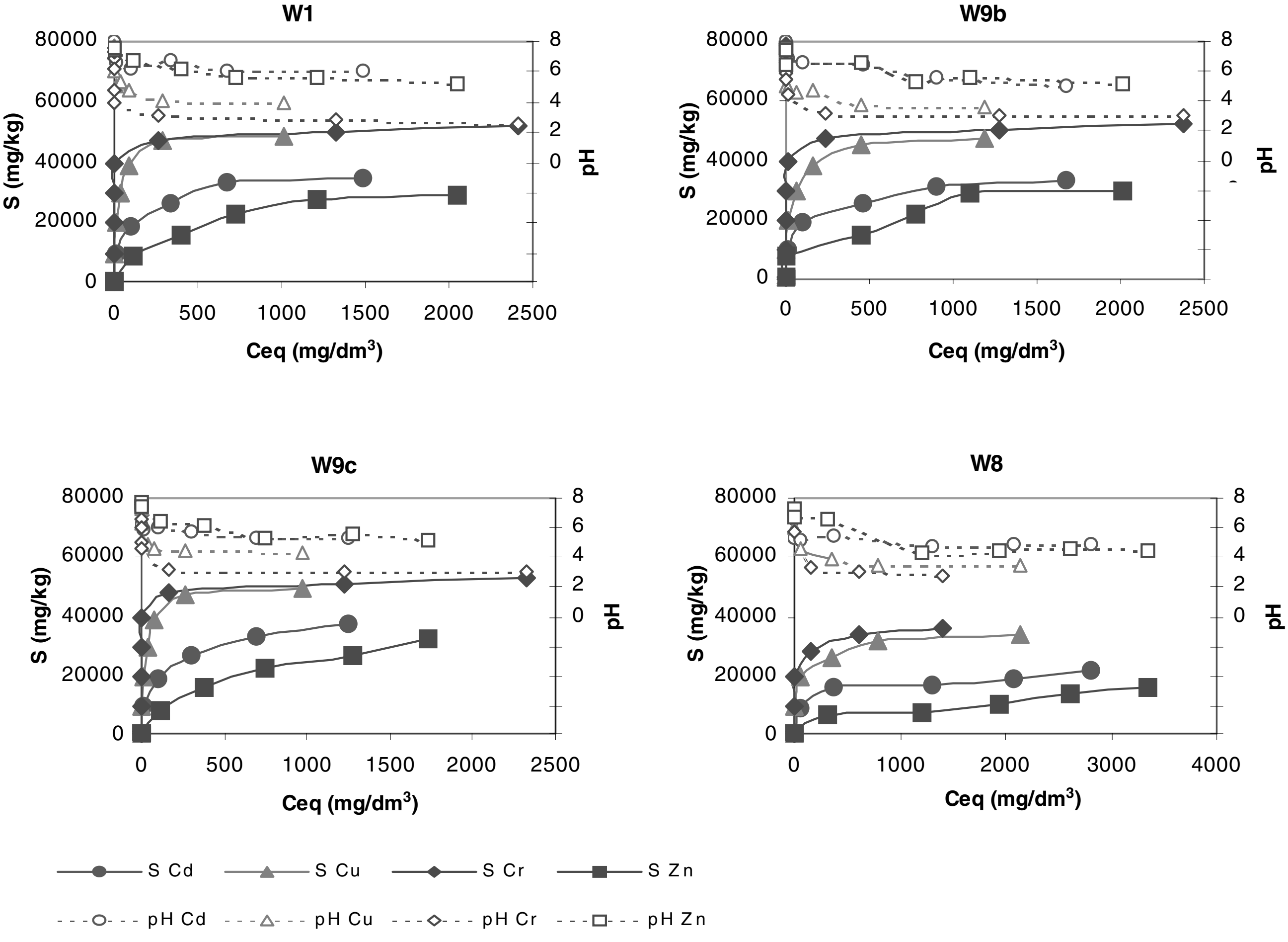

Fig.2. Equilibrium mass isotherms for Cr^{3+}, Cu^{2+}, Cd^{2+} and Zn^{2+} on selected peats W1 - Alder Peat Humus, W9b - Brushwood Peat Humus, W9c - Rush (Reed-Sedge) Peat, W8 – Hypnum Moss Peat.

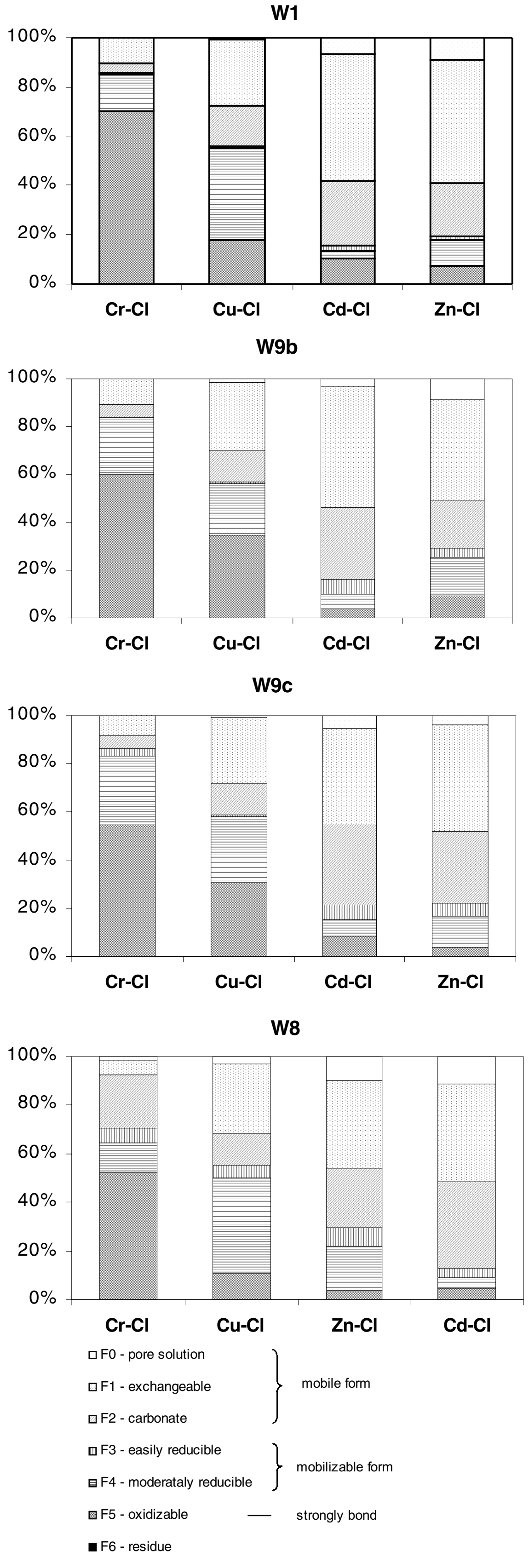

Fig.3. Sequential fractionation according to the increasing binding strength of Cr^{3+}, Cu^{2+}, Cd^{2+} and Zn^{2+} bound from Me-Cl solution under batch experiment onto selected peat W1 - Alder Peat Humus, W9b - Brushwood Peat Humus, W9c - Rush (Reed-Sedge) Peat, W8 – Hypnum Moss Peat.

2. Lowering of pH of equilibrium solution, accompanying the metal sorption and depending on examined metals, proves that besides Ca^{2+} and Mg^{2+} ions, H_3O^+ takes part in binding of metal ions, as well.
3. According to the applied sequential extraction, the prevailing part of Cr in peat is strongly bound, while Cu occurs mainly in the mobilizable and labile forms, and Cd as well as Zn are predominantly bound in the labile ones. It reflects the variability of susceptibility of sorbed metal ions being released.

References

1. ASTM D 2607-69. Standard classification on peat, mosses, humus and related products (approved April 25, 1966. 1989 Annual Book of ASTM Standards. Section 4. Construction, Vol.04.08, Soil and rock building stones. Geotextiles.
2. Polish Standart PN-85/G-02500. Peat. Genetic Division of Raw Material, **1985**.
3. FRANKIEWICZ J.K. Classification of peat. In: World's raw materials. Peat. Wydawnictwa Geologiczne, Warsaw, pp. 18-46, **1980**.
4. TESSIER A., CAMPBELL P.G.C., BISSON M. Trace metal speciation in Yamashe and St. Francois River (Quebec). Canadian Journal of Earth Sciences, **17**, **1980**.
5. KERSTEN M., FORSTNER U.: Assessment of metal mobility in dredged material and mine waste by pore water chemistry and solid speciation. In: Salomons W, Forstner U. (eds), Chemistry and biology of solid waste, dredged material and mine tailings. Springer-Verlag, Berlin Heidelberg, pp. 214-237, **1988**.
6. TWARDOWSKA I., KYZIOL J.: Binding and chemical fractionation of heavy metals in typical peat matter. Fresenius J.Anal.Chem **354**, 580, **1996**.
7. FRANCIOSO O., SANCHEZ-CORTES S., TUGNOLI V., CIAVATTA C., SITTI L., GESSA C. Infrared, Raman and nuclear magnetic resonance (^1H, ^{13}C and ^{31}P) spectroscopy in the study of fractions of peat humus acid. Applied Spectroscopy, **50** (9), 1165, **1996**.
8. TALIBUDEEN O.: Cation exchange in soil. In: Greenland D.J. Hayes M.H.B. (eds.) The chemistry of soil processes, John Wiley&Sons, New York, **1981**.
9. WIEDER R.K. Metal cation binding to Sphagnum Peat and sawdust: Relation to wetland treatment of metal polluted waters. Water, Air Soil Pollut. **53**, 391, **1990**.
10. COTTON F.A., WILKINSON G. Advanced inorganic chemistry; Wiley Interscience: New York, pp.45-47, **1988**.
11. KYZIOŁ J., TWARDOWSKA I. Effect of anions and contact mode of solution on the sorption capacity of low-moor peats for metal ions.7th Regional Meeting of the Central and East European Section of SECOTOX. Bratislava, Slovakia, 25-27 September 2000, Book of Abstracts, pp. 190-191, **2000**
12. BOURG A.C.M. Metals in aquatic and terrestrial systems: sorption, speciation and mobilization. W: Salomons W., U.Forstner (Eds.): Chemistry and biology of solid waste. Dredged material and mine tailings. Springer-Verlag, **1988**.
13. CRIST R.H., MARTIN R., CHONKO J., CRIST D. Uptake of metals on peat moss: an ion-exchange process. Environ.Sci.Technol. **30**, 2456, **1996**.