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THE KOMPLEXATION OF MERCURY BY HUMIC ACIDS

KOMPLEXACE RTUTI HUMINOVÝMI KYSELINAMI

Abstract

The samples of soil P and of the river sediment S were divided into five fractions by means of the sieve analysis (> 10; 2 – 10; 0.63 – 2; 0.2 – 0.63; < 0.2 mm) and the concentration of mercury was determined. The results show that the highest contents of mercury were in the finest fractions of the samples of soil and sediment too. Also, the dependence of the mercury content on the loss by ignition (organic matter) was observed. The mercury content was higher with a higher value of the loss by ignition at the sediment but not at the samples of soil. The humic acids were extracted in compliance with the Czech national standard ČSN norm. With regard to the low concentration of mercury in the observed samples and to the low concentrations of humic acids, no relation was found between the mercury concentration and the humic acids concentration. By means of the second method (Wallschläger), no humic acids were extracted. Sulphur and carbon were determined in the samples. The samples of the soils with higher sulphur concentration had higher mercury concentration too. The relation was not found at the samples of sediment. No relation was found between mercury content and carbon content at both the types of samples.

The correlation is very good in the cases of the dependencies of mercury content on the sulphur content of the soil, on the particle size of the sediment, and on loss by ignition of the sediment. (Correlation coefficient 0.7). As for the other dependencies, the correlation was very low and the correlation coefficient had, in fact, null value.

Abstrakt

Vzorky půdy P a říčního sedimentu S byly rozděleny sítovou analýzou do pěti zrnitostních tříd (> 10; 2 – 10; 0,63 – 2; 0,2 – 0,63; < 0,2 mm) a v jednotlivých třídách byla stanovena celková koncentrace rtuti. Výsledky ukazují, že nejvyšší koncentrace rtuti byla v nejjemnější frakci půdy i sedimentu. Dále byla sledována závislost obsahu rtuti na ztrátě žíháním (obsah organické hmoty). S vyšší hodnotou ztráty žíháním byl nalezen vyšší obsah rtuti v sedimentu, u půdy nebyla nalezena podobná závislost. Podle ČSN byly extrahovány huminové kyseliny. Vzhledem k nízkým koncentracím rtuti ve sledovaných vzorcích a nízkým koncentracím huminových kyselin nebyly nalezeny žádné korelace. Metodou podle Wallschlägra nebyly vyextrahovány žádné huminové kyseliny. Ve vzorcích byla stanovena síra a uhlík. Vzorky půdy s vyšším obsahem síry obsahovaly také vyšší koncentrace rtuti, u sedimentu nebyla nalezena odpovídající závislost. Nebyla nalezena žádná závislost mezi obsahem uhlíku a obsahem rtuti ve sledovaných vzorcích.

Velmi dobrá korelace byla nalezena v případě závislosti koncentrace rtuti na obsahu síry v půdě, na velikosti částic v sedimentu a na ztrátě žíháním v sedimentu (korelační koeficient 0,7). Pro ostatní závislosti byla korelace velmi nízká a korelační koeficient má prakticky nulovou hodnotu.

Keywords: Contaminated Soils, River Sediment, Content of the Carbon, Sulphur, Humic Acids, Grain Size of Materials, Determination of Mercury, AMA 254.

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Introduction

The presence of the mercury in the highly contaminated soils in the surroundings of large industries was caused by the deposition of cookery plant and metal industry. The presence of metal mercury, mercury chloride and mercury sulphide non-specifically chemically bounded on the matrix is expected.

For the investigation of the pollution of the environment by the trace elements**,** especially the late impact of the waste products on the ground water, the knowledge of the mobility of the heavy metals in the soils is very important.

As the mercury in the soils occurs in very low concentrations and the determination of the rest of mercury in the extracts is difficult, no quantitative research of the solubility of mercury from the waste materials and soil by various leaching agents has been done so far. No literature studies about the mechanisms which observe the concentration of mercury in contact with solid matrix are available [1].

The most toxic forms of mercury are "methylmercury" and "ethylmercury." As it was verified, the micro organisms are able to transform all compounds of mercury (HgS, $Hg(OH)_2$, $HgCl_2$ etc.) into the toxic form. Therefore, there is no more or less toxic compound [2, 3]. About 95 % of the methylmercury is absorbed by the alimentary tract of the living organism; the biological half-life in organism is about 70 days [4].

Mercury forms stable complexes with the organic substances of the soils. Therefore, the "fouling" mercury in the neutral, humic soils is quickly bound into the complexes and the availability of the mercury to the plants is low [5]. The average contents of mercury in different types of the soils are in range of the concentrations 0.01 – 0.3 $\mu g.g^{-1}$ [6, 7]. In general, the soils with higher content of humus have a higher content of the mercury too [8].

To find new information about properties of the contaminated samples was the aim of this work. The first aim was to verify the relation between the mercury concentration in the soil and river sediment and the loss by ignition because the value of the loss by ignition can demonstrate the content of organic matter in the contaminated samples. The detailed information about the mercury binding in the samples can be given by the indication about the content of humic acids, sulphur and carbon content.

The mercury presence in the soil and sediment is caused by the anthropogenic activity and therefore we can expect that the mercury is fixed predominantly on the surface of the matrix.

The last aim of this work was to verify the influence of the grain size of the particles of soils and sediment on the content of mercury.

The mercury compounds with humic substances

The humic acids have complex properties. The reason of these properties is the presence of carboxyl and phenol-hydroxyl groups. The solubility of the complexes with cations depends on the mass ratio of both the components. The higher is the concentration of cation, the lower is the solubility of the complex. The formation of the complexes is one of the reasons of the extraction of the metals from soils and sediment by means of humic substances and a cause of the higher concentration of iron and manganese in peat waters [9, 10].

The basic fraction of the natural organic matter in waters and soils is formed by the humic substances (HS) (about 50 %). The rest consists of different classes, groups, like peptides, polysaccharides, lipids and pigments. In some specific parts of ecosystem, i.e. water algae, flowers or bio-films, the living organic matter can contribute to the total content of organic matter. Humic substances are further distributed according to the solubility. According to the definition: fulvo acides (FA) are soluble in the whole range of the pH scale, humic acids (HA) are soluble only in the alkaline conditions and humats are not soluble without destruction. This order of the decreasing solubility correlates with increasing molecular weight [11].

Concentrations of Hg and organic carbon (OC) in waters, soils and sediments are generally closely correlated but only few studies have investigated the mechanism and implications of this association beyond the mere correlation.

If Hg was really bound to humic substances by S-containing ligands, the Hg-S-HS bond could be considered chemically inert under environmental conditions, and the availability of Hg from these complexes could be very low. However, it is not known whether the biotic processes can either break down the Hg-S bond in those complexes or even metabolise the whole HS in those compounds. Both these processes would ultimately liberate Hg, therefore it cannot be assumed a priori that Hg-HS is in environmentally safe binding form [12].

The mercury compounds are accumulated in the environment mainly in the marine sediment. The distribution of the mercury in the Baltic Sea and the factors which affect it remain unknown. The total mercury content was measured in the sediments of the Gdansk Basin along the Vistula mouth, transect in order to assess the spatial distribution of the toxic element. The mercury measurements consisted of the acid digestion of the sample followed by CV-AAS determination of the mercury concentration.

The sequential extraction procedure was employed in order to investigate the mercury speciation (mercury species water soluble, bound to the humic substances and insoluble).

On the basis of the speciation results the potential stability and remobilization were assessed. The second aim was to demonstrate that mercury gradients exist in vertical profiles of the investigated sediments cores. The total mercury content varied from 28 to 844 ng.g^{-1}. Mercury associated with organic matter and sulphides were the dominant species of this element. The results indicate that the contaminated river is the source of mercury in the area [13].

The binding of the Hg^{2+} cation with organic matter of soils and waters controls the transport and transformation of this element in terrestrial and aquatic ecosystems. The competitive complexation method using the strong complexation of the Hg^{2+} cation by Br^- anions was developed for the determination of the mercury strongly bound in organic soils at natural and decreased mercury concentrations [14].

For the assessment of mercury speciation in soils and sediments, a new mercury-specific sequential extraction procedure was developed and tested. The method was applied to determine mercury speciation in the floodplain topsoil and surface sediments along the mercury contaminated part of the river Elbe. At the same time, some information about the remobilization potentials for Hg from these matrices was derived. The distinct differences between mercury speciation in the floodplain and in the sediments were also discovered. Mercury deposited in the floodplain soils shows speciation patterns that indicate stronger fixation compared with Hg in the sediments. This difference is attributed to the association of the mercury with larger quantities of organic matter, which presumably also has higher molecular weight. By comparison, Hg in the sediments was distributed among weaker binding forms, which are more likely to liberate Hg. Particularly; sediments showed a total lack of sulphides binding forms for Hg. Distinctive geographical trends were detected in the mercury speciation along the river transect, with a general downstream shift from weaker to stronger binding forms, probably due to increased association with organic matter. These studies indicate that mercury speciation in riverine ecosystems is dynamic and reflects the chemical mechanisms underlying biogeochemical processes like distribution and transport [15].

Several criteria, including persistence (P), bioacumulation (B), their related factor bioavailibility, toxicity (T), and potential for long range transport (LRT) are currently applied when assessing the environmental hazard and risk associated with the use of chemicals of commerce. Whereas information about B and T criteria may be obtained by experimental measurement using standard tests or by the use of mass balance models, in the case of P and LRT no such standard tests exist, except for certain degradation rates in single media. Nor can these properties be measured in the environment at large. Here we focus on the criterion of persistence and its evaluation using steady-state multimedia mass balance models. It has been proved that it is possible to determine the persistence of all chemical matters, including the organic, inorganic and metal matters, using a common methodology in which mass balance models are applied to describe the substance's behaviour in a specific environment or „unit world“. This avoids inconsistent evaluation and excessive regulatory fragmentation, which is likely if assessment procedures are specific to classes of chemicals. It is essential and persistence be recognised as only one of several factors influencing hazard and risk. Regulatory actions must also thus reflect other attributes such as toxicity, bioaccumulation, quantities used, and the societal value of the substances [16].

Sorption by soil colloids largely determines the bioavailibility of heavy metals and their movement in soil and aquatic environments. Due to soil constituents' interaction, the sorption behaviour of natural soil colloids may not correspond to the simple sum of their individual constituents. In this work, sorption of Pb (II) and Hg (II) ions by binary and ternary model particles containing Wyoming montmorilonite (SW), poorly crystallised ferrihydrite (Ferrih), and soil humic acid (HA) was investigated and the obtained results were compared with the sorption behaviour of the individual constituents. The results of this study confirmed that the sorptive behaviour of colloidal particles and heavy metals is not a simple sum of the contributions of individual components, indicating the usefulness of considering polyphasic model sorbents to achieve a more realistic interpretation of the sorption process in soil [17].

A combination of a computer controlled titration device with a cold vapour atomic absorption spectrometer was set up to examine the kinetics of the reaction between humic substances and Hg (II.) Subsequent injections of Hg (II.) into an excess of humic acid produce data about long term changes in the reaction velocity of humic substances. This experimental design is suitable for the examination of the effects of pH, reaction time, different HS concentrations, and the acquired data agree with data from the literature. By the accumulation of the produced elemental mercury on gold net it is possible to enhance the sensitivity of the method. This enables examinations at environmental concentrations [18].

Ordinary drinking water from the Mourne Mountains in Northern Ireland is treated by the traditional process of coagulation and filtration. Semiconductor photocatalysis was investigated as an alternative. Aldrich humic acid solutions (100 mg.dm^{-3}, filtered through 0.22 μm Millipore filters) were photolysed in a 0.1 % suspension of Degussa P 25 titanium oxide using a mercury lamp. Degradation of humic acid was observed over time by measuring colour in Hasen units, 254/400 nm absorbency, fluorescence (excitation 237 nm, emission 400 nm) and size exclusion by high performance chromatography. The extent of complete oxidation was determined by measuring dissolved organic carbon, chemical oxygen demand and carbon dioxide release. It took approximately 12 min to reduce the humic acid concentration by half; however 50 % of complete mineralization took 60 min. Some of the intermediates of reaction were highly fluorescent. In the absence of oxygen, light or titanium dioxide no significant degradation occurred [19].

The influence of humic acid (HA) on the transport and transformation of mercury in soil was studied. No available Hg could be detected (less than 2.5 μg.kg-^{1}) in alluvial soil when the content of HA-carbon (HA-C) was higher than 0.2 g.kg^{-1}, although a large amount of Hg (8 μg.kg^{-1}) was applied to the soil. The available Hg decreases with the increase of HA in purple soil (r = 0.735). There are significant correlations between HA concentration and organic Hg in tested soils (r = 0.979 for the purple and r = 0.979 for the alluvial soil). The growth of HA create decrease of Hg adsorbed by plant from the soil. A loss of Hg from soil caused by microbes was observed [20].

In [21] the authors observed the binding of the mercury to the humin substances in water. Conditional distribution coefficients for the Hg (II.) binding to seven dissolved organic matter isolates were measured at environmentally relevant ratios of Hg (II.) to dissolved organic matter. The results show that conditional distribution coefficients prime values for different types of samples (humic acids, fulvic acids, hydrophobic acids) isolated from diverse aquatic environments were all within 1 order of magnitude, suggesting similar Hg (II.) binding environments, presumably involving thiol groups, for the different isolates. Conditional distribution coefficients/organic matter prime values decreased at low pHs (4) compared to values at pH 7, indicating proton competition for the strong Hg (II.) binding sites. Chemical modelling of Hg (II.) - dissolved organic matter binding at different pH values was consistent with bidentate binding of Hg (II.) by one thiol group and one other group in the dissolved organic matter, which is in agreement with recent results on the structure of Hg (II.). Dissolved organic matter bonds were obtained by extended X-ray absorption fine structure spectroscopy (EXAFS).

Mercury accumulation in the food chain, as a consequence of gold mining in Brazil, has been an issue of concern. Reactions of Hg in the environment are quite complex, and can involve various Hg chemical species. Laboratory experiments were carried out on solubility, Hg complexation and sorption on river sediment from a gold mining region in Brazil. The reactivity and the mobility of the Hg species were considered. Results indicate that methyl mercury is more mobile than ionic mercury, and that the presence of humic acid enhances drastically the solubility of Hg^{0}. The formed soluble complex has a relatively lower interaction at the sediment/water interface and is more prone to spread through the aquatic environment [22].

In seawater and lake water the complexation of several heavy metals, present in the dissolved state at relevant trace levels, with humic substances isolated from marine and estuarine sediments has been studied by differential pulse anodic stripping voltammetry at a hanging mercury drop electrode. In seawater humic acids originating from different sediments have very similar complexing properties for Zn (II.). In both types of natural waters, the sedimentary fulvic acid is less efficient in complexing Zn (II.) than the respective humic acid from the same site. In general, the complexing efficiency decreases in the order EDTA > HA > FA. The finding provide further direct evidence for the conclusion previously drawn for existing complexation data that because of the rather low levels of dissolved humics in large parts of the oceans, the complexation efficiency of humics for Cd, Pb, and Zn is too low to affect the speciation pattern of these three heavy metals [23].

Methods and results

Characteristics of the samples

For the observation of the common properties, a sample of contaminated soil (P) from the Ostrava region and a sample of the river sediment (S) from the bottom of Černý potok from Ostrava-Přívoz were taken. The sample of soil consisted of small and bigger stones and had a tar smell. The sample of river sediment consisted of small and bigger stones, the rests of grass and had a putrefactive smell. The chemical analysis of these samples demonstrated no differences between the compositions of individual samples.

The contents of majority oxides SiO_2, CaO, SO_3, K_2O and Al_2O_3 are higher in the soils than in the sediment (66.6 – 1.7 %). The contents of the rest of minority oxides (MgO, Fe_2O_3, TiO_2, MnO, P_2O_5 and Na_2O) are lower in the soil than in the sediment (1.4 – 0.07 %). For the chemical analyses of both the samples was used the spectrometer SPECTRO X-LAB, SPECTRO Al (Germany).

Pre-treatment of the samples

The samples of soil and sediment were homogenised and aliquots were taken for determinations of the grain size according to the ČSN 015030 [24] and of the loss by ignition, samples were also subjected to granulometric measurements (divided into 5 fractions of different grain), as the tables 1 and 2 show.

The determination of total mercury content in the individual fractions was carried out by means of the instrument AMA-254, (AAS-CV), average of too results. The values are given in the tables 1 and 2. The results of the loss by ignition of individual fraction are in the tables 1 and 2 too.

Table 1: The individual fractions and mercury contents in the soil

Fraction	Grain size [mm]	Weight [g]	Mercury content [$mg.kg^{-1}$]	Loss by ignition [%]
P1	< 0.2	254	1.588	9.90
P2	0.2 – 0.63	614	0.793	7.00
P3	0.63 - 2	644	0.668	10.82
P4	2-10	750	0.755	8.29

Table 2: The individual fractions and mercury content in the sediment

Fraction	Grain size [mm]	Weight [g]	Mercury content [$mg.kg^{-1}$]	Loss by ignition [%]
S1	< 0.2	317	0.993	12.90
S2	0.2 – 0.63	238	0.565	10.15
S3	0.63 – 2	282	0.489	11.63
S4	2-10	354	0.212	10.21

The dependence of mercury content on the loss by ignition

We can expect that in some cases the higher value of loss by ignition (LI) could probably mean the higher content of organic mass that the mercury complexes made. Therefore, along with the increasing value of loss by ignition the content of mercury could increase as well. The results in the table 1 do not indicate the dependence between mercury content in soil and the loss by ignition (correlation coefficient 0.06).

The results from the observed fraction of the sample of river sediment are given in the table 2, fig. 1. We can expect that mercury content correlates with the loss by ignition (correlation coefficient 0.7).

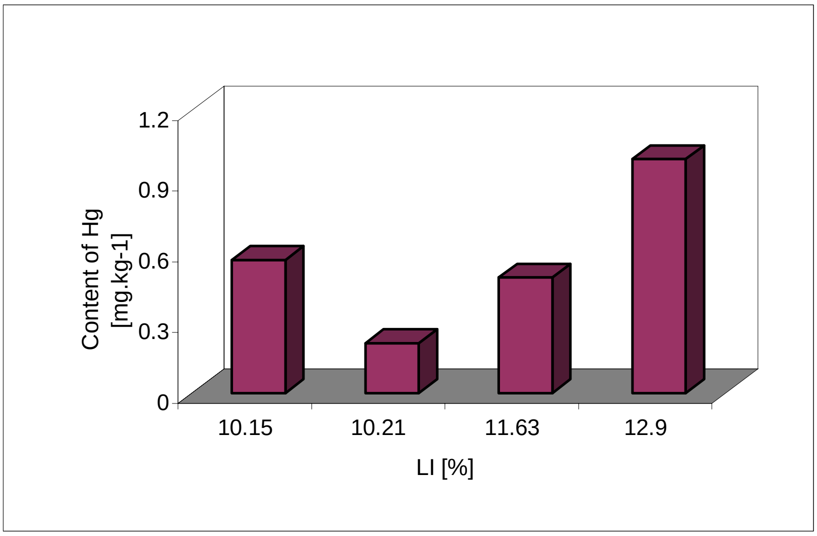

Fig. 1: Dependence of the mercury content on the loss by ignition at river sediment

Extraction of the humic acids according to the Czech standard ČSN [25]

Into each of 10.0 grams of the fraction sample of the soil and sediment (P1, P2, P3, P4, S1, S2, S3, S4) about 50.00 cm^3 solution of 1 % NaOH and 50.00 cm^3 of demineralised water was added. The suspension was boiled for 10 min., it was cooled and filtered. The humic acids were precipitated by adding solution HCl (1:1) until the acid reaction. The precipitate of humic acids was centrifuged and was dissolved again in the solution of NaOH (1:1). The insoluble part of clay was filtered and the humic acids were precipitated with a new portion of solution HCl (1:1). To the precipitate of humic acid was added 100 cm^3 of demineralised water with 2 cm^3 of HCl, the suspension was stirred and filtered. The humic acids were dried by the temperature of 60 °C and they were weighed.

The results in the table 3 show that the amount of humic acid extracted from the sample of the soil is small. Therefore the content of mercury in humic acid was not determined. The mercury from the soil was not extracted into supernatant, neither into humic acids. After the extraction by the solution of NaOH the mercury remained in the soil. The content of humic acids, they can the mercury strong in the complex bond, is in this soil samples very low.

Table 3: The content of humic acids and mercury concentrations after extraction from the soil

Fraction	Mercury content [$mg.kg^{-1}$]	Mercury content in the soil* [$mg.kg^{-1}$]	Humic acids content [%]	Mercury content in HA [$mg.kg^{-1}$]	Mercury content in filtrate** [$mg.l^{-1}$]
P1	1.588	1.250	0.06	no measured	0.001
P2	0.793	0.664	0.06	no measured	< 0.001
P3	0.668	0.799	0.06	no measured	< 0.001
P4	0.750	0.743	0.01	no measured	0.001

Legend: * The rest of mercury content in the solid sample after extraction HA
** The rest of mercury content in filtrate after separation of HA

In the table 4 are given the results from the extraction of HA from the individual fractions of river sediment. In comparison with the results from the soil, it is evident that the content of HA in sediment is higher. The mercury was determined in this HA but not all mercury was found in this HA. A large amount of mercury remained in strong bond with the matrix of the sediment. It was probably caused by the fact that the HA content in the sample was not high enough for all the mercury to be bound into the complexes with HA. The mercury content in the filtrate after the separation HA is by all fractions less than < 0.001 $mg.l^{-1}$.

Table 4: The content of humic acids and mercury concentrations after extraction from sediment

Fraction	Mercury content [mg.kg^{-1}]	Mercury content in the sediment* [mg.kg^{-1}]	Humic acids content [%]	Mercury content in HA [mg.kg^{-1}]	Mercury content in filtrate** [mg.l^{-1}]
S1	0.993	0.742	2.59	5.450	<0.001
S2	0.565	0.475	0.84	9.445	<0.001
S3	0.489	0.419	2.31	3.585	<0.001
S4	0.212	0.108	0.06	no measured	< 0.001

Legend: * The rest of mercury content in the solid sample after extraction HA
** The rest of mercury content in filtrate after separation of HA

According to the literary date, it was expected that with the increasing content of HA the mercury content in the sample would increase as well. From the results given in table 4 it is not obvious that the correlation in the observed samples really exists.

In spite of the fact that the separation method according to the Wallschläger method [15] was strictly followed, the results given in the tables 5 and 6 show that no HA were separated. The method is not applicable to the separation of HA from soil and sediment with low contents of HA.

Table 5: The content of humic acids and mercury concentrations after extraction from soil according Wallschläger

Fraction	Mercury content [mg.kg^{-1}]	Mercury content in the soil* [mg.kg^{-1}]	Humic acids content [%]	Mercury content in filtrate with HA** [mg.l^{-1}]
P1	1.588	1.763	No precipitated	< 0.001
P2	0.793	0.994		0.001
P3	0.668	0.721		0.003
P4	0.750	0.692		0.002

Legend: * The rest of mercury content in the solid sample after extraction HA
** The rest of mercury content in filtrate after separation of HA

Determination of total carbon (TC) and total sulphur (TS)

Determination of total carbon and total sulphur in the soil samples (P1-P4) or sediment samples (S1-S4) was made by means of the Leco CS-244 at the department for analytical chemistry. The results are given in the tables 7 and 8.

Into the in-advance-burned-out crucible from bentonit was weighed 0.5 g ± 0.0001 g of soil sample (P1-P4) or sediment sample (S1-S4).

Table 6: The content of humic acids and mercury concentrations after extraction from sediment according Wallschläger

Fraction	Mercury content [mg.kg^{-1}]	Mercury content in the sediment* [mg.kg^{-1}]	Humic acids content [%]	Mercury content in filtrate with HA** [mg.l^{-1}]
S1	0.993	0.940	No precipitated	0.003
S2	0.565	0.666		0.005
S3	0.489	0.523		0.004
S4	0.212	0.253		0.001

Legend: * The rest of mercury content in the solid sample after extraction HA
** *The rest of mercury content in filtrate with HA after separation of the solid rest of sample*

Relation between mercury content and carbon content

The bond of mercury in the samples is affected by the content of organic matter, just as the literature date indicates [5]. According to the carbon content, the basic component of the organic matter, it would be possible to predict the mercury content. The carbon contents are given in the tables 7 and 8. The results of the carbon contents indicate that no correlation was found between mercury concentration (content) and carbon content in the soil and sediment samples. The results cannot be compared with the existing studies.

Table 7: Carbon and sulphur content in soil

Fraction	Mercury content [mg.kg^{-1}]	C [%]	S [%]
P1	1.59	2.64	0.31
P2	0.9	2.28	0.05
P3	0.67	3.19	0.07
P4	0.75	2.86	0.20

Table 8: Carbon and sulphur content in sediment

Fraction	Mercury content [mg.kg^{-1}]	C [%]	S [%]
S1	0.99	4.38	0.03
S2	0.57	4.36	0.08
S3	0.49	5.69	0.01
S4	0.21	4.94	0.02

Relation between mercury and sulphur content

According to the literary date, mercury is strictly bond on the HS (humic substances) through the functional groups with sulphur [12]. The results in the table 7 and Fig. 2 show that the mercury content increases with the increasing of sulphur content. The sample of soil with the highest sulphur content had the highest mercury content too (correlation coefficient 0.7). The same correlation was expected at the sediment samples as well. But there are visible differences between the speciation of mercury in the soil and the sediment. The sediments have deficit of sulphur groups for the bond with mercury [15]. The observed sediment had less sulphur groups than the observed soil. The table 8 shows no correlation between mercury and sulphur content.

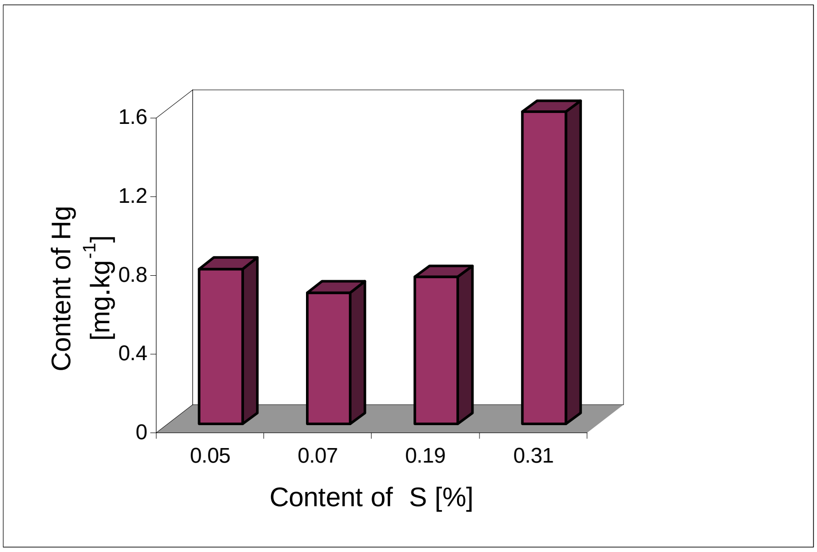

Fig. 2: Dependence of the mercury content on the sulphur content in the soil

Dependence of the mercury content on the grain size

It was expected that the finest fraction of soil (P1) would contain the highest content of mercury and the largest fraction the lowest mercury content. It is evident from the results in the table 1 and from the Fig. 1 that the smallest fraction contains the highest content of mercury and with the increasing size grain decreases the mercury content. The results from the table 1 are in good agreement with the literature date.

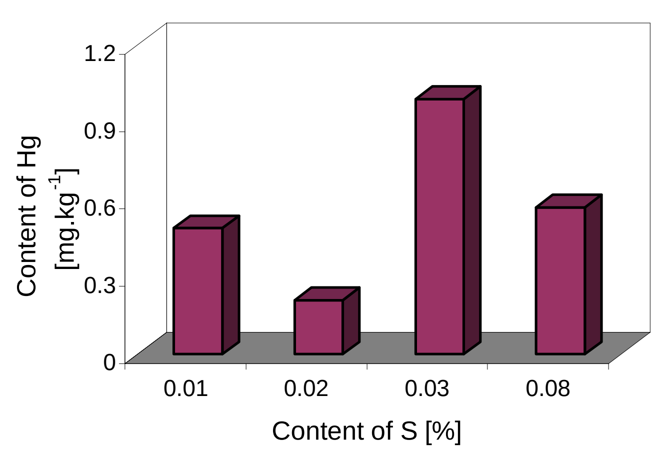

Fig. 3: Dependence of the mercury content on the sulphur content in the sediment

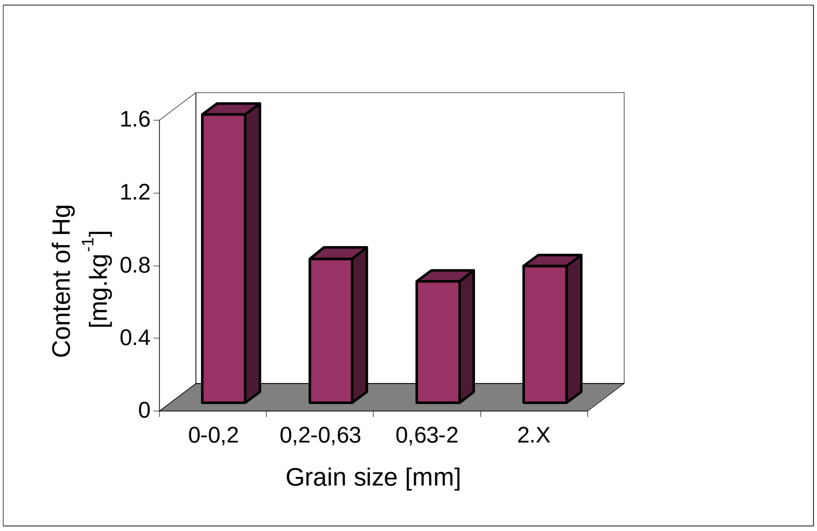

Fig. 4: Dependence of the mercury content on grain size in the soil

In the case of sediment, there was the same presumption as in the case of soil. In the table 2 and Fig. 5 we can observe, in comparison with the soil, a more marked dependence between the mercury content and grain size (correlation coefficient 0.7). The mercury content in the smallest fraction (S1) is the highest and in the biggest fraction (S4) the mercury content is the smallest (correlation coefficient 0.7).

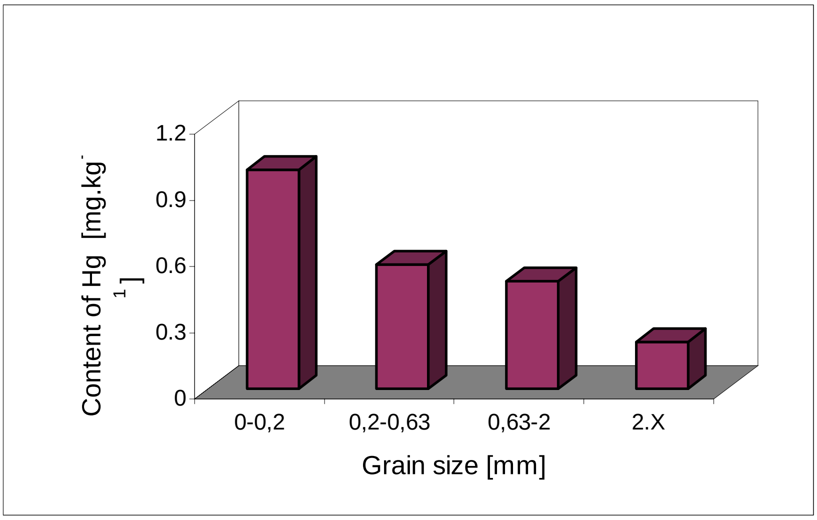

Fig. 5: Dependence of the mercury content on grain size in the sediment

Resume

The aim of this work was to verify whether the content of the humic acids (content of the organic matter), content of sulphur, carbon and loss by ignition in the observed samples of the contaminated soil and river sediment correlates with the mercury content in these samples.

The samples of the soil and the river sediment were divided into 5 fractions according to the size of the grain (> 10, 2 – 10, 0.63– 2, 0.2 – 0.63, < 0.2 mm). The mercury content was determined in the fractions of these samples by means of the advanced spectrometer AMA 254. In accordance with literary date the mercury content decreased with the increasing size of grain at the samples of soil and sediment.

The loss by ignition in the individual fractions of sediment and soil could theoretically represent the content of the organic matter in the samples. The mercury content in the fractions of the soils showed no dependence on the lost by ignition, at the river sediment there is probably a linear dependence between the mercury content and the lost by ignition (correlation coefficient 0.7).

From the soil and sediment fraction the humic acids (HA) were extracted by ČSN. With regard to the low concentrations of the HA in the samples of soil and sediment, no dependence was found between the mercury content and the humic acids content. The extraction by Wallschläger was not successful.

The content of the carbon was determined by LECO (there is a lower value in the soil than in the sediment). No dependence was found between the carbon content and the mercury content.

The content of the sulphur was determined by LECO. At the soil samples, an evident dependence between the sulphur content and the mercury content was found. At the sediment samples no dependence was demonstrated.

The correlation is very good in the cases of the dependence of the mercury content on the sulphur content, on the grain size and on the lost by ignition. In all of these cases the correlation coefficient is about 0.7. In the other cases, no dependence was found between the observed parameter and the mercury content. The number of samples mentioned in this work was not adequate. It is necessary to verify the results on a number of samples with a higher content of mercury and with higher content of humic acids.

Resume

Záměrem této práce bylo ověřit, zda obsah humicových kyselin (obsah organické hmoty), obsah síry, uhlíku a ztráta žíháním ve sledovaných vzorcích kontaminované půdy a říčního sedimentu korelují s obsahem rtuti v těchto vzorcích.

Vzorky půdy a říčního sedimentu byly sítovým rozborem rozděleny do pěti zrnitostních tříd (> 10; 2 – 10; 0,63– 2; 0,2 – 0,63; < 0,2 mm). Ve frakcích byla stanovena rtuť jednoúčelovým spektrometrem AMA 254. Ve shodě s literárními údaji se obsah rtuti zvyšoval se zmenšující se velikostí zrna.

Ztráta žíháním jednotlivých zrnitostních tříd teoreticky representuje obsah organické hmoty v těchto vzorcích. Obsah rtuti ve frakcích půdy nevykazuje žádnou závislost na hodnotě ztráty žíháním, u vzorku sedimentu pravděpodobně existuje lineární závislost mezi obsahem rtuti a ztrátou žíháním (korelační koeficient 0,7).

Ze vzorků půdy a sedimentu byly extrahovány huminové kyseliny podle ČSN. Vzhledem k nízkým koncentracím huminových kyselin a nízkým koncentracím rtuti ve vzorcích půdy i sedimentu nebyla nalezena žádná závislost mezi koncentrací rtuti a obsahem huminových kyselin. Extrakce huminových kyselin podle Wallschlägera nebyla úspěšná.

Obsah uhlíku byl stanoven přístrojem LECO. Vzorek půdy vykazuje nižší obsahy uhlíku než vzorek sedimentu. Mezi obsahem uhlíku a obsahem rtuti nebyla nalezena žádná závislost.

Také obsah síry byl stanoven přístrojem LECO. U vzorku půdy byla nalezena evidentní závislost koncentrace rtuti na obsahu síry ve vzorku. Nebyla nalezena žádná závislost u vzorku sedimentu.

Korelace je velmi dobrá v případě závislosti obsahu rtuti na obsahu síry v půdě, na velikosti zrna a na ztrátě žíháním sedimentu. Ve všech těchto případech je korelační koeficient 0,7. V ostatních případech nebyla nalezena žádná závislost mezi sledovanými parametry a obsahem rtuti ve vzorcích. Bohužel počet vzorků sledovaných v této práci je nedostatečný a také sledované koncentrace jsou velmi nízké. Proto by bylo žádoucí uvedené závislosti ověřit na větším počtu vzorků s vyššími koncentracemi sledovaných parametrů.

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