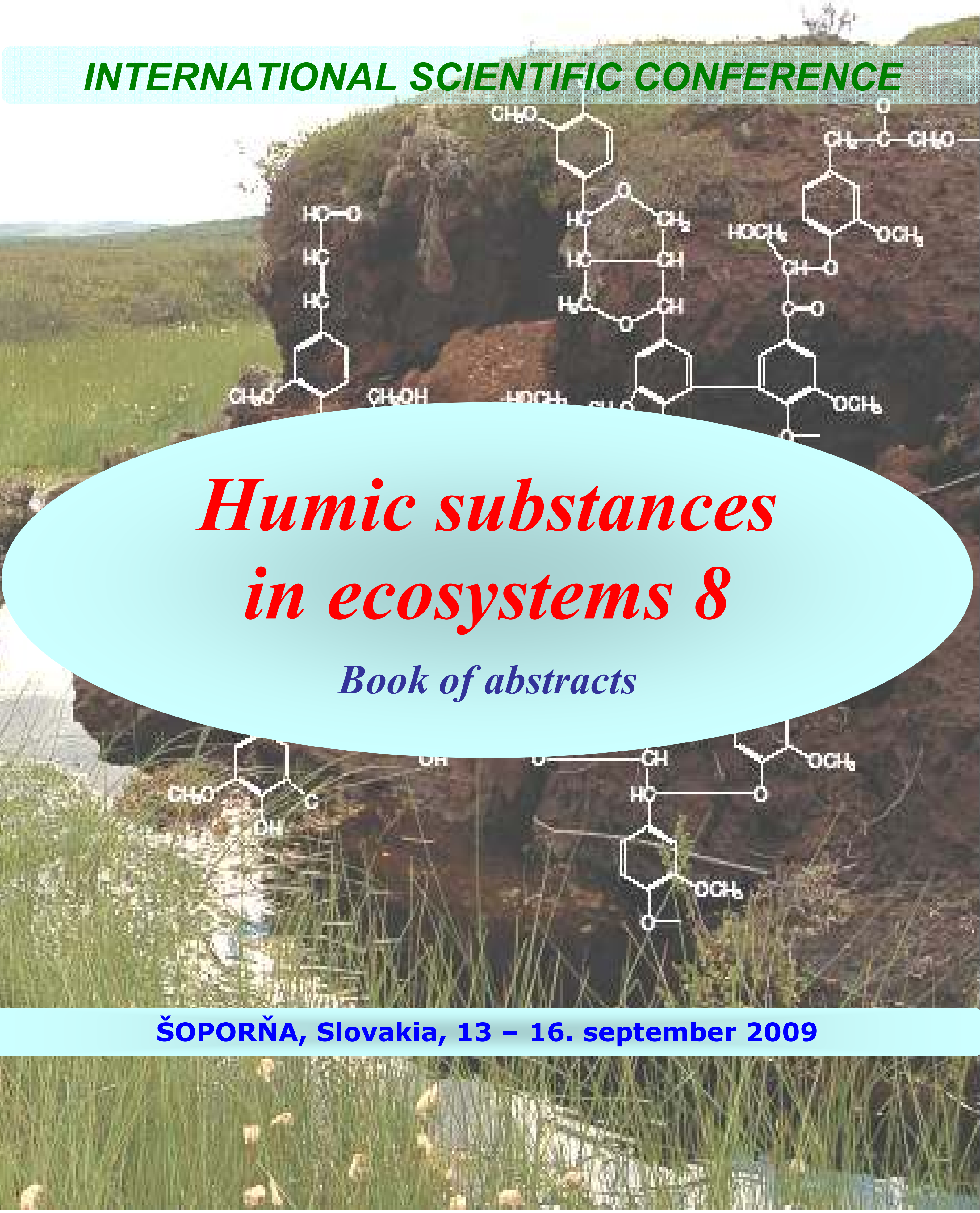

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Humic substances in ecosystems 8

Book of abstracts

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Contents

THE INFLUENCE OF ANTHROPOGENIC POLLUTION ON THE PROPERTIES OF HUMIC ACIDS OF LIGHT SOIL MANURED WITH ORGANIC FERTILIZERS

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Sudden development of technology contributed to a phenomenon of mounting number of technological processes in which for many years so called environment friendly production was not planned. Environmental pollution, local as well as global, appeared as its consequence. The research aimed at the assessment of the influence of anthropogenic acidification, salinification and alkalisation on the chosen parameters of humic acids, which to a large extent are responsible for the state of soils. Complex structure of humic substances and their changeability suggest research on new research methods, which would result in the greatest possible amount of information on their structure and transformation. High-performance liquid chromatography (HPLC) is one of the analytical methods, which may contribute to broadening the knowledge of humic substances transformation processes taking place in the soils. Incubation experiment was conducted in plastic vases of the capacity of 1l. To the ventilation of the incubated material plastic tubes (3 tubes/each vase) were used. The incubation was conducted through one year (from October to September) in the conditions of stable humidity (on the level of 50% of field capacity), in the variable temperature of the region. The initial material used for incubation consisted of light soil with/or without the addition of organic fertilisers (straw, vermicompost, cattle manure) In all the cases, a significant difference in the parameters controlling the level of pollution (pH- variant of acidification and alkalisation, proper conductivity- salinisation) was obtained. After the incubation, the samples from the vases were air dried, strained through a sieve with meshes diameter of 1mm, and humic acids (HA) were extracted. Basic physical and chemical parameters of the obtained HA preparations were determined. Moreover, the susceptibility to chemical oxidation was assessed and fractionation with the use of HPLC method was performed. After taking the measures, the ratio of percentage content of hydrophilic fraction to hydrophobic fraction (HIL/HOB) was calculated. On the basis of the tests conducted on the samples of humic acids the following conclusions may be drawn:

1. The short-term action of the polluting factors did not influence significantly the properties and transformations of humic substances described with the use of standard parameters (elementary composition), spectroscopic properties, susceptibility to chemical degradation).
2. However, the use of high-performance liquid chromatography (HPLC) proved the significant diversity of the examined humic acids considering their fractional composition. The analysis of the obtained results showed obvious influence of both: the polluting substance and the kind of organic fertilizer (the addition of vermicompost to the soil material caused the greatest difference in the examined humic acids).

KEYWORDS: humic substances, HPLC, anthropogenic pollution

PROPOSAL OF EVALUATION OF SOIL ORGANIC MATTER SORPTION CAPACITY

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Adsorption reactions are defined as reversible and equilibrium reactions. In soil compartment exists two main matrices where adsorption reactions can be realised. A whole a lot is known about the concept of adsorption by inorganic constituents or clay minerals. The theory of adsorption in soils is more concerned with the type of concentrating material at the solid-liquid interfaces of clay minerals and not much data are available on adsorption by humic substances (HS).

However, it is well known that sorption capacity of humic substances (HS) is much higher in comparison to clay minerals. HS can react with bases and acids, hence carry both positive and negative charges. All these charges are developed by the ionization or dissociation of various functional groups. The negative charges are attributed to dissociation of protons from the functional groups in the humic molecule. The two most important functional groups in this respect are the carboxyl and phenolic-OH groups. In general, these two functional groups control the electrochemical behaviour of humic matter and they are the main reason for adsorption, cation exchange, complex and chelation reactions. Carboxyl groups are the most important in the formation of negative charges. Since fulvic acids (FA) exhibit higher total acidity values than humic acids (HA), results of study on chelation and complexation analyses indicate that metal chelatation by humic acids appears more effective than by fulvic acids. The substantially larger molecules and the more complex structures of humic acids are accepted to be the reason for more binding sites and higher binding capacity in contrast to fulvic acids, which are smaller and less complex. Humic acids are higher in aromatic structures than fulvic acids and dispose higher chelatation capacity. Aromatic structures of HA play very important role in interaction/incorporation of HA with organic xenobiotics.

For this reason proposal of evaluation of soil organic matter sorption capacity use basic quantitative and qualitative humus parameters – content of soil organic carbon (SOC), ratio of carbon of humic and fulvic acids (Cha/Cfa) and optical parameter (Q^4_6) but also such selected parameters of HA chemical structure, which the most effect sorption capacity of humic acids – content of carboxylic groups and aromatization degree (α), which take into account humification degree of HA.

High sorption humus capacity is characterized for arable soil locality with soil organic carbon content higher or equal as 2, with ratio of Cha/Cfa > 1 and value of optical parameter $Q^4_6 < 4.5$. Locality with high sorption humus capacity have to dispose with high carboxylic groups (COOH>4) and degree of aromatization ($\alpha>50$). In Slovak agriculture soils there are mainly some localities of Fluvisols, Chernozems and Andosols. Low value of humus sorption capacity is characterized for arable soils of Planosols, Rendzinas and some of Cambisols.

Table 1. Proposal of evaluation of humus sorption capacity for agriculture soils

category	*SOC (%)*	*Cha/Cfa*	Q^4_6	*COOH (meq/1g HK)*	*α (%)*
I.	>= 2	> 1	< 4.5	> 4	>50
II.	1.5 - 2	0.8 - 1	4.5 - 5	3 - 4	40 - 50
III.	< 1.5	< 0.8	> 5	< 3	< 40

I. – high humus sorption capacity
II. – medium humus sorption capacity
III. – low humus sorption capacity

KEYWORD: soil organic matter, sorption capacity, humic acids

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NMR STUDIES OF HUMIC SUBSTANCES EXTRACTED FROM BOTTOM SEDIMENT AND WATER

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NMR spectroscopy has been used for characterization of humic substances extracted from bottom sediment and water. The samples for studies were collected in spring and in autumn season from eight places of the Goczałkowice Reservoir.

Fulvic acids were extracted both from bottom sediment and water whereas humic acids were present only in bottom sediment.

The ^{1}H NMR and ^{13}C NMR analysis of humic substances facilitates the identification of individual functional groups. It was also used to estimate the relative contents of aromatic and aliphatic protons in humic substances. The H_{Ar}/H_{Ali} ratio makes possible to determine at which stage of the humification process the water or the sediment occurs.

Solution 31P NMR spectroscopy has been used for determination the contribution of different classes of organic and inorganic phosphorus compounds in each sample.

KEYWORD: humic acids, fulvic acids, bottom sediment, ^{1}H NMR, ^{13}C NMR, ^{31} P NMR

DYNAMICS OF CHANGES THE SELENIUM CONTENT AND DEHYDROGENASES ACTIVITY IN SOIL DEVELOPED BY ORGANIC FERTILIZATION

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The concentration of selenium in plants and animals is strongly correlated with its concentration in soils. Plants and products derived from plants transfer the selenium taken up from the soils to humans. Selenium is one of the trace elements strongly affected by microbiologically mediated redox processes influencing its solubility and consequently its mobility, bioavailability and uptake in soil-plant system. Studies of enzyme activities in soil are important as they indicate the potential of the soil to support biochemical processes which are essential for the maintenance of soil fertility. Soil samples were taken from the long-term experiment established at the Experimental Station Grabow of the IUNG Pulawy on the soil classified as Albic Luvisols. The experiment was conducted with crop rotation system: potato - winter wheat - spring barley and red clover. The soil was affected of organic fertilization in a form of manure under potato in doses of 0, 20, 40, 60 and 80 t/ha. Total selenium content was determined by the method of Watkinson with 2,3-diaminonaphtalene (DAN) using a Hitachi F-2000 spectrofluorometer. Dehydrogenases activity was assayed colorimetrically using TTC as a substrate. The application of manure resulted in the highest amounts of organic carbon in soil. The selenium content from control plots ranged from 0.090 to 0.115 mg/kg. Statistical analyses confirmed that application of manure resulted in the highest amounts of total selenium content in soil, with increasing doses of manure. We observed the increase of total selenium content about 40% in soil manured with the highest dose of FYM in comparison with soil from control plots. Mean value of dehydrogenases activity in soil from control plots was 0.012 mg $TPF \cdot g^{-1} \cdot 24h^{-1}$. We observed the increase of enzymatic activity with increasing doses of manure. The dehydrogenases activity in soil from plots manured with the highest dose was about 3 times higher than from control. We found a very significant correlation between total selenium content and dehydrogenases activity, and between this parameters and organic carbon in soil under study.

INFLUENCE OF LONG- TERM FERTILIZATION AND CROP ROTATION ON THE QUANTITY AND SELECTED PROPERTIES INDEXES OF QUALITY SOIL HUMIN SUBSTANCES.

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In researches examined and compared composition of soil organic matter fraction and spectrofotometric properties of humic acids (HA) from soil samples in dependence on agricultural treatments.

The research was performed on the basis of a multi-year long fertilization experiment carried out by SGGW since 1923 in Skierniewice Research Station. The research involved the use of soil samples from the stands under the monoculture and crop rotation of rye and potato, considering selected fertilization combinations.

It was found that humus in the stand after rye in monoculture was characterized by higher contribution of carbon of humic acids, higher value of humic acids carbon to fulvic acids carbon proportion (C_{KH}:C_{KF}) and by lower participation of humins.

In the 5-fields rotation system comparable relations as in monoculture were found in humus under potato. The highest values of C_{KH}:C_{KF} were obtained in both cultivation systems with complete mineral-organic fertilization, lower values were noted in soil fertilized only by NPK. Taking into consideration two fractions of humic acids – labile (FI) and strongly bound with mineral part of soil (FIII), higher values of absorbance ratios ($A_{2/4}$, $A_{2/6}$, $A_{4/6}$) were recorded for HAs of FI fraction extracted from soil fertilized with participation of manure under rye in monoculture and rotation. Absorbance ratios of HA from labile fraction were higher in soil in rotation system than in monoculture.

KEYWORD: fraction composition, UV-VIS, monoculture, crop rotation

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CARBON AND NITROGEN IN THE BOTTOM SEDIMENTS OF THE „ŻURSKIE" LOWLAND BARRAGE LAKE

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Publication presents results of analyses of carbon and nitrogen content as well as roasting losses from bottom sediments of barrage lake "Jezioro Żurskie".

The samples of sediments with consideration of 3 cm layers were taken from the core of sediments extracted by Instorf probe from central part of the lake. Obtained results indicate two layers of sediments. In the layer of thickness 62-41 cm (the oldest sediments) there was no significant vertical differentiation of analyzed parameters. Starting from the layer 38 cm characterized by the lowest values of examined parameters to the layer of present sediments there is noted systematical increase of carbon and nitrogen content as well as roasting losses. Carbon content in dry mass of sediments reached values from 10,86 to 15,95% and nitrogen 0,59 to 1,46%.

KEYWORDS: barrage lake, bottom sediment, carbon, nitrogen

EFECT OF THE EXTRACTION TIME ON PROPERTIES OF HUMIC SUBSTANCES ALKALINE EXTRACTS

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The aim of the present paper was to determine the effect of the extraction time on the alkaline properties of humic substances extracts from organic and mineral lake bottom sediments. The extraction was performed with the use of 0.5 M NaOH. Both for organic and mineral sediments, the ratio during extraction were 1:10 and 1:50 (w/v). In both variants the extraction time was, respectively, 1, 5, 12, 24 and 48 hours. In the mixtures of humic and fulvic acids obtained, the following were determined: the content of carbon and nitrogen and the spectrometric properties for the UV-VIS range. Based on the present results, the values of TOC/Nt, absorbance ratios, extraction efficiency and specific UV absorbance (SUVA) at the wavelength of 280 nm were calculated.

The results demonstrate, most of all, that the extraction time has a significant effect on the properties of extracts. It was observed that the extracts after a longer extraction time, in general, showed a higher content of carbon and nitrogen as well as higher SUVA values. The present research revealed that in the case of sediments, the extraction performed in the ratio of 1:50 (w/v) is more efficient as compared with the extraction in the ratio of 1:10 (w/v).

KEYWORD: lake, humic substances, extraction

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CHROMATOGRAPHIC CHARACTERISTICS OF HUMIC ACIDS OF SOIL FERTILIZED WITH VARIOUS ORGANIC FERTILIZERS

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The aim of the present paper was to determine the effect of the kind of organic fertilisers applied and the soil grain fraction the organic matter accumulates in on the hydrophilic-hydrophobic properties and the polydispersity of humic acids.

In the model incubation experiment organic fertilisers (cattle manure, vermicompost and wheat straw) were mixed with soil material (sandy texture). The soil was sampled for testing after one year and a three-year period of incubation. Each sample was separated, according to graining, into two fractions: grain diameter >0.1 mm (sand fraction) and <0.1 mm (silt and clay fraction) and then humic acids were isolated. For the humic acids isolated hydrophilic-hydrophobic properties were defined using the RP-HPLC, and the division was made into low- and high-molecular-weight fractions (HPSEC).

It was demonstrated that introducing organic fertilizers to soil resulted in a decrease in the share of the fraction of hydrophilic properties and an increase in the high-molecular fractions in HAs molecules. However, there was shown no clear-cut effect of the kind of organic fertilizers on the hydrophilic-hydrophobic properties and the polydispersity of humic acids. Humic acids of fine-grained fraction ($\phi < 0.1$ mm) demonstrated a higher share of hydrophilic fractions and, as a result, higher values of the HIL/HOB ratio as compared with HAs sand fraction. The relationships recorded show that the organic matter accumulated in finer grain fractions of soil is more humified than the organic matter of coarser grain fractions.

KEYWORDS: organic fertilizers, humic acids, polydispersity, hydrophilic and hydrophobic fraction

ROLE OF POST-HARVEST RESIDUE IN DEVELOPING THERMAL PROPERTIES OF HUMIC ACIDS IN THE SOILS OF DIFFERENT TYPES

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The aim of the present paper was to determine parameters of thermal decomposition of humic acids of the soils of different types with no additives and when mixed with post-harvest residue before and after 360 days of incubation.

The research was based on a model incubation experiment carried out at the Department of Pedology and Geology of the Slovak Agricultural University in Nitra. Plant residues (mixtures of aerial parts and roots) of corn, oilseed rape, sunflower, potato and rye were mixed in the ratio 10:1 with the following soil samples: luvisol, chernozem, arenosols and gleic phaeosems and the mixtures were incubated at 25°C and 60% of field water capacity. The plant-soil mixtures were analysed prior the experiment and after 360 days of incubation. Humic acids were separated from the control soil (without plant residue), and plant-soil mixtures before and after incubation with the standard Schnitzer method. Thermal properties were determined with the use of the Derivatograph C (MOM, Hungary). Samples of 40 mg humic acids were mixed with Al_2O_3 (1:9) and heated in the air at the rate of 3.3 $°C \cdot min^{-1}$.

The results of thermal analysis showed that parameters of thermal decomposition of humic acids were determined both by the soil type and by the properties of post-harvest residue introduced into soil. The process of decomposition of post-harvest residue was connected with, e.g. a decreased value of the parameter corresponding to the burning heat of humic acids. Low values of parameter 'Z' were due to the presence of non-decomposed lignin and cellulose structures in the molecules of humic acids

KEYWORDS: *post-harvest residue, humic acids, TG, DTG, DTA*

DYNAMICS OF SOIL ORGANIC CARBON: AN APPROACH OF COMBINED FRACTIONATION TOOLS FOR ISOLATING ECOLOGICALLY RELEVANT FRACTIONS

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Up to now the most commonly used parameter for soil quality is the total organic carbon (TOC) content in soil. Changes of TOC as well as its distribution in differently stabilized soil organic matter (SOM) pools are very slowly running processes.

SOM research is connected with questions of SOM extractability, structure, turnover, stability and function. However, actually no applicable methods and practical solutions for managing carbon content in soil could be developed.

Studying SOM dynamics we have to consider at least two pools: a stable / stabilized (relative “inert”) pool and a decomposable pool of SOM. The “inert” fraction has almost no considerable share in carbon transformation processes having residence times of some hundred years. Only the decomposable pool will be transformed in relevant time intervals and may be influenced by human activities. This part is strongly correlated with transformation processes of organic substances in soil (transformation of nutrients as well as pollutants).

Recently a wide range of methods are used to isolate and characterize SOM pools for estimating both their amount and suitability as indicators for soil quality.

Depending on the scientific question several methods and techniques can be used for discrimination of different SOM pools:

- Hot water extraction (HWC)
- Cold water extraction (WEOM)
- Potassium permanganate oxidization (labile C)
- Clay associated organic matter (stable carbon)
- Specific light organic matter (different stability of organic matter).

Our approach for assessing of SOM quality is a combination of physical and chemical separation techniques, including size-density fractionation and isolation of a readily decomposable organic carbon pool by hot-water extraction. C content in hot water extractable fraction is a simple determinable parameter for estimating decomposable SOM supply and nutrient release. However, management (fertilization) also contributes to C pool associated to clay minerals of soil matrix.

The objectives of here presented research are: (1) to give a short overview of selected methods of SOM pool discrimination, (2) to show relations between selected pools, (3) to demonstrate the suitability of hot water extractable C for estimating and calculating decomposable SOM pool.

Results from long-term field experiments support hypotheses that impact of management practices on SOM could be discriminated with the hot water extractable SOM fraction while organic matter in size-density fractions represent more stabilized OM with special importance for sustainability and C accumulation.

KEYWORD: hot water extraction, particle size and density fractionation, stability of SOM

SPECTROSCOPIC CHARACTERISTICS OF HUMATES ISOLATED FROM DIFFERENT SOIL TYPES

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The aim of our work was to compare spectroscopic properties of soil humates isolated from different soil matrices (Haplic Cambisol, Leptic Cambisol, Eutric Cambisol, Luvi-Haplic Chernozem). The optical methods (VIS and SFS) on this project have been used. Synchronous fluorescence spectra (SFS) were measured by Spectrofluorimeter Aminco Bowman Series 2, Thermospectronics. Bandpass of both monochromators was set to 4 nm, temperature was 20°C and constant difference between excitation and emission monochromators was ($\Delta\lambda = (\lambda_{em.} - \lambda_{ex.}) = 55$ nm). VIS spectra were measured by spectrometer Varian Cary 50 Probe within the range 300 - 700 nm.

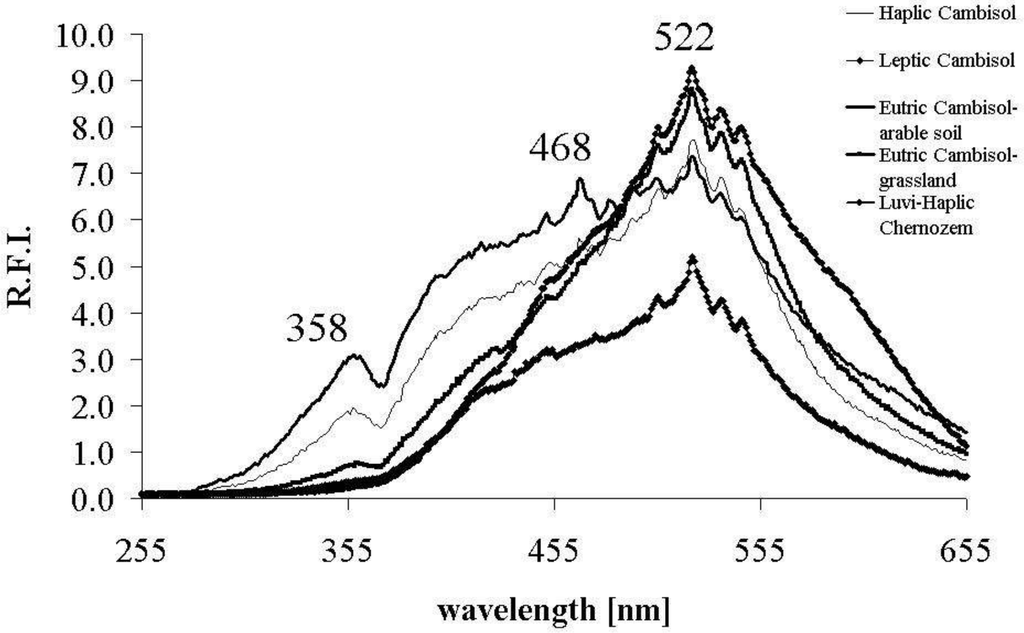
Isolation of HA preparation was made according to the IHSS method. Elemental analysis of isolated HA was kindly made in Engineering Test Institute Brno. We followed total carbon content, fractional composition, and humification degree.

The highest humic acids content had Eutric Cambisol and the lowest in Leptic Cambisol. The highest humification degree had sample Luvi-Haplic Chernozem and the lowest Leptic Cambisol. This result is equal to humic substances maturity in different soil types.

The highest content of organic carbon and humus was in Eutric Cambisol (grassland), the lowest values was in Haplic Cambisol. The highest humic acids content was in Eutric Cambisol.

SFS spectra (Figure 1) measured in range from 200 to 600 nm (at $\Delta\lambda$=55 nm) contained 5 or 6 peaks at $\lambda_{ex.}/\lambda_{em.}$=413/468, 450/505, 467/522, 482/537, 492/547 (303/358). Last one was observed in two Eutric Cambisols samples and in Haplic Cambisols. The maximum relative fluorescence intensity at 522 nm gave Haplic Chernozem. The lowest relative fluorescence intensity gave Leptic Cambisol at the same wavelength. Higher value of relative fluorescence intensity gave the sample of Eutric Cambisol isolated from grassland to compare with the sample isolated from arable soil. We have founded out that SFS spectra gave to main fluoprophores with respect of changing of $\Delta\lambda$ difference between both monochromators at about: 450/480, 467/500-530 nm. The relative fluorescence indexes were calculated from SFS spectra (as the ratio I_{468}/I_{522}). Colour indexes ($Q_{4/6}$) were calculated as ratio A_{465}/A_{665} from VIS spectra. The highest fluorescence index (F) was obtained in Eutric Cambisol (arable soil) and the lowest in Eutric Cambisol (grassland). The highest Q4/6 index had Leptic Cambisol and the lowest had Luvi-Haplic Chernozem. Linear correlation between organic carbon content and fluorescence indexes was found (R^2=0.92).

Fig.1. SFS spectra of soil humates at Δλ=55 nm



KEYWORD: soil humic substances, Synchronous fluorescence spectroscopy

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UV-VIS SPECTROSCOPIC PROPERTIES OF HOT WATER-EXTRACTABLE ORGANIC CARBON IN SOIL

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Surface organic soil layers are the main source of allochthonous organic matter for water reservoirs. This kind of soil formations after dewatering undergoes the processes of rapid transformation of humic substances, which are transformed and mineralised. This leads to the modification of organic compounds composition. Their water repellency and lability in soil solution changes. The study comprises three groups of soil formations – with an ongoing process of organic matter accumulation, dewatered organic formations containing more than 12% of OC, and dewatered soil formations containing less than 12% of OC which are considered degraded.

UV-VIS spectroscopic properties of soil organic matter soluble in hot water were studied. Soil samples were extracted in a closed system for 18 hours and then filtered through 0.45 µm filters. The spectra were taken out in the range of 200-700 nm in 1 cm quartz cuvette using double beam scanning spectrophotometer Shimadzu 1601PC. Quantitative measurements of dissolved organic carbon using analyser Shimadzu TOC5000 were made as well. The results enabled us to compare the dynamics of absorbance A_λ and $SUVA_\lambda$ as well as the ratio for various values of λ. It was estimated that the organic compounds of the analysed soil formations had different sizes, degree of condensation (humification), lability and solublity in water. The degraded soil formations (<12% of OC) contain more hydrophobic condensed aromatic cores, which was proved by the highest values of $SUVA_{280}$.

KEYWORD: organic soil, hot water solubility, UV-Vis spectra, HWC, DOC

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SPATIAL VARIABILITY OF SOIL ORGANIC CARBON CONTENT (SOC): COMPARISON BASED ON DIFFERENT DATA SOURCES

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Common crop management is based on the assumption according which any field being a basic spatial unit of agricultural production is considered to be homogenous for its natural conditions. Uniform agricultural technologies such as soil agrotechnology, fertilization, and plant protection are applied over the whole area of individual fields. Moreover, any field is considered to be a basic spatial and statistical unit for specifying the relevant soil and landscape properties. On the other hand, there is a significant spatial variability in soil organic carbon content which does not respect artificial land parcels. Organic carbon represents a key soil component with significant impact on soil physical, chemical and biological properties of soil (including the soil production potential).

The aim of this paper is: i) to demonstrate the existence of spatial within-field variability in relation to the content of soil organic carbon (SOC) and map this variability; ii) to delineate homogenous areas based on SOC content classification and to quantify their spatial extent; iii) to compare historical and the most recently measured data on SOC content at the same areas, and iv) to demonstrate vertical variability of SOC content at selected soil profiles which are to characterize some of the identified homogenous areas.

The experiment was carried out on pilot area consisting of 7 different plots of arable land with the total area of 720 ha. Model area is located at Podunajská nížina lowland which is characterized as both the warmest and very dry climate region in Slovakia (with average yearly temperature 10 °C and average yearly rainfall about 550 mm). The soil sampling oriented to determine SOC content was performed by auger sampling in regular triangular network (with a side of 131,5 m) and with a density of approximately 1 sampling point per 1,446 ha. Totally, 521 soil samples were taken from depth of 0-0,2m and analyzed for SOC content (Cox) by standard laboratory methods. Position (longitude, latitude) of all sampling points was recorded by GPS.

The results of experiment confirm the existence of within-field spatial variability related to the SOC content, as well as significant differences in SOC content has been proven among the studied plots (the SOC content difference is from very low to very high depending on the SOC content classification used). Relatively homogenous zones delimited on the basis of applied SOC content classification have a potential to explain the SOC balance in soil within the individual plots. The comparison of historical and our measured data have shown an increase in SOC content from 8 to 104%. Moreover, the delimited zones homogenous as for its SOC content after they are further characterized by additional soil and landscape data can provide the spatial units for the crop production modeling in detailed scales.

KEYWORD: spatial variability, soil organic carbon

ACKNOWLEDGEMENT:

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THE STRUCTURE OF HUMIC ACIDS OF MECHANOACTIVATED PEAT AND THEIR INFLUENCE ON DYNAMICS OF NUMBER AND DESTRUCTIVE ACTIVITY OF HYDROCARBON-OXIDIZING MICROORGANISMS

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Due to development of nature-protecting biotechnologies the interest to the study of processes with participation of aerobic hydrocarbon-oxidizing microorganisms (HOM) has increased. First of all it is concerned with the pollution of soil, surface and underground waters by oil and oil products. The intensity and character of decomposition of oil hydrocarbons in soil basically is defined by a functional activity of HOM, capable to assimilate of oil as a unique source of carbon [1]. Processes of soil self-cleaning under conditions of environment proceed extremely slowly and require stimulation. As hydrocarbon-oxidizing microorganisms are constant components of soil biocoenosis, there was an aspiration to use them catabolic activity for restoration of petropolluted soils by the addition of preparations on a basis of humic acids (HA) of peat into polluted soil [2].

The purpose of this investigation is to study the influence of mechanoactivation (MA) of peat on changes of structure of HA and to investigate the influence of HA on dynamics of number and destructive activity of HOM of petropolluted soil.

A high-moor moss peat of «Temnoe» field of the Tomsk Oblast (Russia) with a low degree of decomposition of 5 % was the subject of the present study.

MA was carried out in the AGO–2 planetary mill-activator without additives (HA2) and in the presence of solid alkali 3 % NaOH (HA3). HA1 from initial nonmechanoactivated peat served as the control.

MA of peat results in the changes in yields and quantitative characteristics of main organic components [3]. The efficiency of HA extraction after MA raises – their yield has increased in 7 times. The increase of the HA yield may be explained by the destruction of the hard-to-hydrolyse substances. Moreover, results obtained with use of gel-permeation chromatography and ^{13}C NMR– spectroscopy testify about the decrease in molecular weight and a structural reconstruction of macromolecules of HA. The presence of aromatic skeleton in HA provides their ability to binding organic compounds that are result of hydrophobic interactions. Therefore, the affinity of HA with hydrophobic organic compounds increases due to increase of contribution of aromatic skeleton in their structure. The greatest degree of aromaticity and the least degree of oxidability have observed for HA after mechanoactivation of peat with alkali.

It is known, that the first stage of oil degradation begins its physicochemical and microbiological destruction [4]. In this period a relative content of alkanes decreases and a quantity of resinous substances increases in residual oil. This stage of recultivation corresponds to the most toxic geochemical situation, a maximum inhibition of biocoenosises and on this stage it is expediently to carry out actions for the intensification of microbiological processes and photochemical and physical processes of decomposition of oil.

The analysis of a chemical composition of petropolluted soil in 30 days after introduction of HA has shown that the quantity of extracted bitumen-like compounds decreases in 40 %. In structure of bitumen-like compounds the share of paraffin-naphthene fractions has decreased, in particular, n-alkanes and the quantity of resins has increased. It testifies about a destructive oxidizing activity of microorganisms stimulated by HA.

It is known, that the oil pollution increases of activity of HOM which play the important role in the decomposition of oil and detoxication of soils [5]. The growth of bacteria and actinomicetes – basic destructors of oil, has noted in the end of experiment (in 30 days of growth). The additions of HA in pure soil were intensifying the growth of both groups, and in great degree of bacteria. The greatest stimulating effect of studied groups of microorganisms has been observed after the addition into soil of HA3 solutions. The essential increase in number of actinomicetes and bacteria was noted for petropolluted soil after the addition these HA. Obtained data can be explained that a soil microflora uses peripheral parts of HA molecules in an initial period of growth.

The change of fermentative activity of soil microflora is one of indicators of oil biodestruction. The growth of microorganisms' number was accompanied by the increase their fermentative activity which provides processes of oil hydrocarbon destruction.

A stimulating action of HA3 on a destructive activity of soil microflora has confirmed by the method of IR-spectroscopy. Spectral coefficients, calculated according to optical density of absorption bands in a certain area of spectrum and which characterize biodegradation processes, testified about the decomposition of paraffin hydrocarbons, increase in degree of branching and, as a whole, about a deeper processes of oil biodegradation with the use of HA3.

Thus, results of researches have shown that the addition of HA (0.005 mass % from soil weight) isolated from mechanoactivated peat (in the presence of solid alkali 3 % NaOH), in petropolluted soil increases the number of heterotrophic bacteria in 8 times, actinomicetes in 5 times and fermentative activity of microorganisms in 3 times. The content of extracted bitumen-like compounds decreases to 40 %. A biochemical essence of stimulating effect of HA was caused by the activation of cell fermentative activity which depends on a growth rate and biomass accumulation and mechanochemical activation of peat allows to improve the efficiency of HA extraction and can cause the increase in availability of their separate components and parts of molecules, including micro-and macroelements which are used as sources of nutrition and energy by a microbic cell.

Obtained data will make it possible to extend our knowledge about the influence of HA on the development of hydrocarbon-oxidizing soil microflora and can represent a practical interest for the development of technology of new humic preparations production from peat which can be used for biological recultivation of petropolluted soils.

KEYWORD: peat, mechanochemical activation, humic acids, petropolluted soil, hydrocarbon-oxidizing microorganisms

LEAF LITTER FALL DECOMPOSITION IN AGE-DIFFERENTIATED POPLAR STANDS OF HYBRID 275

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Plant litter fall decomposition is a critical stage in nutrients turnover in ecosystems. Habitat conditions such as temperature, humidity and the biological activity of the soil, as well as the chemical composition of the initial material, are decisive factors determining the intensity of this process. The contents of such substances like lignin, waxes, tannins and resins greatly influence the rate of decomposition. These substances resist decomposition and make organic remains less attractive to microorganisms. Chemical composition, and in particular the presence of diverse substances resistant to decomposition, is a feature of each plant species and each fraction of the litter fall. This feature changes over time. As plants age the chemical composition of their organs might change, each to a different extent, which is then reflected in the chemical properties of the litter fall. Considering this, it might be expected that the decomposition rate of fractions of the litter fall would be connected with the age of the contributing plants. The aim of this study is to compare the decomposition of leaves, the main component of the plant litter fall, among plantations of Black Poplar (*Populus nigra* L.) clones Hybrid 275 of different ages.

The study was conducted in 2000-2002 at three plantations of Hybrid 275 Black Poplar of different ages. These plantations are in northern Poland in Wierzbiczany (17 years old), Gronowo (28 years old) and Ostromecko (54 years old) forest districts. All these plantations have similar total precipitation, temperature ranges and soil nutrients abundance. Studies of the decomposition were conducted using 30 cm x 30 cm litter bags made of 1 mm mesh nylon netting. Each bag was filled with 15 g of dry leaves collected in the autumn of 2000 when litter fall was at its maximum. Ten bags were located at each of 5 points in each study plot. Every two months one bag was collected from each point and analyzed (content of C, N, P, K, Mg, Ca). The content of lignin in the initial material was measured by weight after extraction with 72% H_2SO_4.

The process of decomposition occurred at a different rate at each plantation. It was fastest in the 54-year-old stand (54Y), slightly slower in the 28-year-old stand (28Y) and slowest in the 17-year-old stand (17Y). After 12 months in the 54Y stand almost 80% of the initial mass was decomposed, in the youngest stand it was slightly more than 40%. The coefficients of decomposition, based on Olson's model, were 1.49 for 54-year-old plantation, 0.97 for 28-year-old plantation and 0.61 for 17-year-old plantation. Poplar leaves decomposed quickly in comparison with other broadleaved trees. The index of decomposition was closely related to the age of the trees, with a correlation coefficient of 0.99. Because the temperature and humidity conditions were similar at all locations, the different rate of decomposition can be attributed to the different chemical composition of the initial material. The content of phosphorus, calcium and magnesium varied greatly in the initial material, and the content of the nitrogen, lignin and the ratio C/N varied less. However, only the lignin content was correlated with the age of poplars, with their proportion decreasing with the age of the trees. A high correlation coefficient between the content of lignin and the intensity of decomposition of leaves (-0.97) was obtained. The important role these compounds play in shaping the rate of decomposition of plant remains has been pointed out by many authors. Other important factors that affect the rate of decomposition are the content of nitrogen and the ratio C/N in the initial material. These are limiting factors in the development of the soil microorganisms responsible for the decomposition. The content of nitrogen, both in the initial material and in the humic horizon of soils (0.082 – 0.087 $g \cdot kg^{-1}$), was similar at all stands. So this was not the differentiating factor. The ratio C/N in the initial material was high and similar at all the plantations. During decomposition at all the locations the ratio C/N narrowed to values of about 25:1, which was linked to the immobilisation of the nitrogen. Nitrogen concentration had a constantly increasing trend. On the one hand this was an effect of slower rate nitrogen was released compared with other elements, and on the other hand it reflected the absolute accumulation of nitrogen, due to its influx with rainwater, the binding of atmospheric nitrogen by microorganisms, and also the result of mycelium filaments penetrating the litter bags. After the first 10 months of the experiment the store of nitrogen in the decomposed material increased, despite the loss of leaf mass. Immobilization of nitrogen occurs with a high ratio of C/N. A strong deficit of nitrogen in the relation to carbon takes place when microorganisms decompose material with a high C/N ratio and all the nitrogen released in this process is used by the microorganisms to build their own proteins. An actual release of nitrogen at all the poplar stands was observed only in the second year. Potassium was leached out quickly during decomposition. At all the plantations most of the potassium store had already been released during first two months. This tendency has often been observed by other researchers. Potassium occurs in organic remains as ions, which are easily leached out by rainwater. The concentration of phosphorus and magnesium remained relatively constant during decomposition, which differed at each plantation. The stores of these elements decreased with the loss of leaf mass. The concentration of calcium tended to rise at all the plantations, but its supply decreased gradually.

Despite the differences in the chemical composition of the initial material at the poplar plantations analysed, the dynamics of the concentrations of each nutrient and of their supplies showed similar trends.

The study showed a high intensity of leaves decomposition at plantations of poplar clone Hybrid 275 in comparison with other species of broadleaved trees. A high correlation coefficient between the age of poplars and the rate of decomposition was found. Leaves of old trees decomposed quicker than those of younger trees. The observed differences most probably result from different chemical composition of the initial material. Distinct differences were noted between the plantations in the content of phosphorus, potassium and magnesium. Only for lignin were high negative correlations obtained between their concentration and the age of the poplars from which the leaves originated, and the index of decomposition. Only small differences were observed in the nitrogen content and the C/N ratio, which excludes these as differentiating factors.

KEYWORDS: poplar, Hybrid 275, leaf litter fall, decomposition, nutrient turnover

SOIL ORGANIC MATTER AND PHYSICAL CHARACTERISTICS

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The paper deals with soil organic matter and its influence on physical soil parameters on the permanent grassland. In 2005 – 2007 the effect of these attributes were observed in conditions of the Hrubý Jeseník Mountains. The experiment is situated in 400 m above sea level. The soil is sandy-loam of the cambisol type. We used organic fertilisation with three graduated systems of load. The soil bulk density, total porosity, maximum capillary water capacity from physical properties and organic soil carbon were determined. Soil samples for determination of physical and chemical properties were taken from depth 0.02 – 0.15 m and 0.15 – 0.30 m in spring. The aim of this work was to show relationship between organic soil carbon and selected physical characteristics in these conditions. Statistically significant relationship was found between organic soil carbon and soil bulk density. No statistically significant impact was found between organic soil carbon and porosity and maximum capillary water capacity. Obtained data were tested by GLM statistics.

KEYWORDS: soil organic matter, bulk density, porosity, maximum capillary water capacity

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EFFECTS OF AGROTECHNICAL TREATMENTS ON SPECTROPHOTOMETRIC PROPERTIES OF HUMIC ACIDS OF BROWN PODZOLIC SOILS

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Characteristics of humic substances is usually done by investigations of the properties of soil extracts isolated with the use if selective solvents and by the analysis of some groups of selected compounds, such as humic and fulvic acids. One of the criterions used in the characteristics of a complex nature of humic substances are the values of absorbance of their solutions in the range of ultraviolet and visible light (UV and VIS). Also infrared spectroscopy (IR) is an important method of such studies of humic substances. The objective of the investigations was to evaluate effects of agrotechnical treatments on physicochemical properties of humic acids of brown podzolic soils. The investigations were carried out as a part of a long-term static experiment of the Puławy ITFSS. There were three experimental factors: 1 – crop rotation (A-potato, wheat, spring barley, corn; B-potato, winter wheat + charlock as aftercrop for ploughing, barley with companion crop, mixture of clover with grasses), 2 – fertilization with manure, 3 – fertilization with mineral nitrogen. Humic caids separated by according to Schnitzer were analysed for optical properties in the UV-VIS range and their IR spectra in the range 400-4000 cm^{-1} were recorded. Crop rotation appeared to be the basic factor affecting the optical density properties of humic acids. Rotation of crops enriching the soil in organic matter caused higher absorbance values of humic acids solutions than in the one depleting the soil. Higher values of the $A_{2/4}$ and $\Delta\log K$ parameters in the crop rotation B indicated that humic acids isolated from the soil suplemented with organic matter had a higher content of humus in the starting point of decomposition than humic acids of the variant depleting the soil. The kind of crop rotation modified spectroscopic parameters of humic acids. Humic acids of the soil under rotation of crops introducing less organic matter had a higher percentage of lignin structures than those of other one crop rotation. As compared with mineral fertilization manuring generated the development of humic acids of a smaller molecular weight. A clear presence of absorption bands in the range 1460-1000 cm^{-1} in the IR spectra of humic acids separated from the combination enriching the soil in organic matter showed their "chemical youth".

KEYWORDS: humic acids, fertilization, crop rotation, IR, UV-VIS

THE EFFECT OF THE ECOLOGICAL AND INTEGRATED SYSTEM ON THE SOIL PHOSPHATASE ACTIVITY

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The aim of the present paper was to determine the effect of organic and integrated farming with varied fertilization on the phosphatase activity of soil and how it affects the content of phosphorus available for plants. In the organic system there was used only organic fertilization in a form of cattle manure, while in the integrated system – organic fertilization combined with mineral fertilization (NPK). The soil was sampled twice during the vegetation period of crops: in spring – in April and in autumn – in September . It was found that both the organic system and the integrated system affect the changes in the parameters researched. There was demonstrated an increase in the content of available phosphorus in the soil sampled in autumn. There was observed a significant effect of the farming system on the activity of alkaline and acid phosphatases.

KEYWORD: available phosphorus, activity alkaline and acid phosphatase, soil

UPTAKE OF HUMIC SUBSTANCES BY WHEAT PLANTS: PREFERENTIAL ACCUMULATION IN LIPID FRACTION

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Humic substances (HS) have been the subject of numerous scientific studies due to their beneficial effects of HS on living organisms. The principal effects exhibited by HS onto living organisms include an increase in biomass accumulation, nutrient uptake, biosynthesis, antiviral activity, and others [1]. In spite of numerous studies on the biological effects of HS, the mechanism of their action remains unclear. The main reason seems to be the stochastic nature of HS. In contrast to common biological macromolecules, which are synthesized by a living organism according to the information encoded in DNA (nuclear acids, proteins, enzymes, antibodies etc.), HS are the products of stochastic synthesis. They are characterized as polydisperse materials having elemental compositions that are non-stoichiometric, and structures, which are irregular and heterogeneous. The above features hamper a use of common biological approaches to study biological activity of HS.

Several studies on the uptake of HS by higher plants have been performed. Earlier work relied on the color changes in the plant organs as an indication of HS uptake. The more recent study used ^{14}C-labeled humic-like substances or ^{3}H-labeled HS [2, 3]. Those studies also established that both humic-like substances and HS and were taken by the plants. Therefore, next goal in going deeper inside understanding mode of action of HS is a study distribution of HS in plant tissues. This study was aimed to find out uptake and distribution of HS in wheat seedlings.

For this study humic acids (HA) derived from leonardite and IHSS standard fulvic acids (FA) were used. To synthesize isotope-labeled HA, an approach developed in [4] for the preparation of tritium-labeled HS was used. The obtained ^{3}H-HA sample was dissolved in a phosphate buffer (0.028 M, pH 6.8) and purified by dialysis during a month at 4ºC. It allowed eliminating exchangeable tritium of OH^-, $COOH^-$, and NH_n groups of HS. Seeds of wheat *Triticum aestivum* L. were germinated at 24°C in the dark for 72 h followed by transferring seedlings into the 0.5 l tanks containing Knopp nutrition solution. After another 72 h plants were transferred into the vials containing HS at concentration 50 mg l^{-1} with specific radioactivity 0.1-0.2 Curie l^{-1}. Then lipid fraction was extracted according to [5] followed by radioactivity measurements.

Obtained results are presented in the Table 1.

Table 1. Contents of HS in lipid fraction of wheat plant

HS	Contents of HS in lipid fractions, % of taken up		
	Roots	Shoots	Total
Coal HA	82±6	16±2	98±8
Aquatic FA	49±10	16±8	64±5

As it can be seen from the Table, almost entire amount of HA that were taken up by plants were found in lipid fraction (98%); for FA that value decreased to 64%. Taking into account that contents of lipid fraction in plants were about 3-5%, one could conclude on preferential accumulation of HS in lipid fraction. Accumulation coefficient which was calculated as ratio of HS concentration in plant to concentration in lipids was as 43±2 and 25±2 for HA and FA respectively. On the other hand, lipid contents in HS usually vary in the range 3-8%. Therefore, preferential HS accumulation in lipid fraction was evident for preliminary transformation of HS on the root surface or nearby it before HS entrance into the plants. That finding could be also confirmed by equal amounts of HA and FA in lipid fraction of shoots (16%). The latter indicated that only specific fragments of HS, probably hydrophobic, were able to enter plants vascular system.

So, our experiments demonstrated that HS taken up by plants were preferentially accumulated in lipid fraction. Before entrance HS were seemingly to be partly transformed and mainly their hydrophobic fragments were adsorbed by plants. However, lipid fraction in plants is well known to be a wide group of natural compounds distinguishing greatly in both structure and functions. They are presented by several different compounds including pigments, fats, fatty acids, waxes, steroids, cutin, suberin and others. Therefore, further study of distribution of HS in lipid fraction of plants is required.

KEYWORDS: wheat, uptake, lipid, tritium, label

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THE STRUCTURE AND PROPERTIES OF HUMIC SUBSTANCES FROM BROWN COAL 11 YEARS AFTER ADDITION INTO SOIL

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Transformations (mineralization and humification) of soil organic substances lead to formation of humic substances (HS), the most spread in nature group of organic compounds. Diversity of organic matter and the environment create varying structures and compositions, and thus differences in properties of HS. Soils in many areas of Poland are characterized by low contents of organic matter, which greatly contributes to their limited fertility and productivity, and higher vulnerability to contamination and degradation. Soil degradation in some areas causes a dramatic need to improve the structure and contents of organic matter.

The requirements of EU legislation are key factors controlling soil protection. Although the EU has no soil directive yet, 2 documents have an impact on the requirements for national legislation and policy on soil protection. In the Communication “Towards a Thematic Strategy for Soil Protection” (COM 2002, 179), depletion of soil organic matter is mentioned as one of 8 main hazards for soils. According to the Directive establishing a framework for the protection of soil (COM 2006, 232, final), soil can be considered a non-renewable resource as degradation processes are usually faster that soil formation and remediation processes.

Recently, the use of organic amendments other than traditional manure showed to be efficient for the improvement and/or restoration of soil organic matter. One of the potential sources of organic matter in soil is an organic-mineral preparation obtained from brown coal, the so-called Rekulter (Kwiatkowska et al 2005). Organic matter from brown coal added to soil may be transformed into HS in (micro)biological and abiotic ways.

The objective of this study was the qualitative evaluation of structure and physical-chemical properties of HS in soil 11 years after application of brown coal in the form of Rekulter (a dose of 40 t ha^{-1}) as a source of organic matter. Structural analyses were carried out for humic acids (HAs) extracted from the Haplic Luvisol, and they include: solide-state ^{13}C NMR spectroscopy, electron paramagnetic resonance (EPR), infrared and UV-VIS spectra, share of hydrophilic and hydrophobic fractions by High Performance Liquid Chromatography (HPLC), as well as elemental composition and parameters of thermal decomposition by differential scanning calorimetry (DSC) measurement.

Application of organic matter from brown coal resulted after 11 years in an increases of the carbon contents of HAs extracted from soil, and consequently decreased values of the H:C ratio. HAs of amended soil showed higher absorbance values in the UV-VIS region, higher contents of oxygen functional groups, and were more resistant to thermal decomposition compared with non-amended ones (control). HAs molecules were also richer in aromatic structures and resistant to decomposition with a high potential of sorption properties. For FT-IR spectra of HAs an increase of the relative intensity of peaks at 1720 cm^{-1} with respect to that at 1670 cm^{-1} was observed, thus providing spectroscopic evidence of higher contents of carboxylic groups in aromatic rings, as compared to HAs extracted from non-amended soils.

Organic matter from brown coal introduced to soil in the form of Rekulter relatively slowly undergoes transformation and causes permanent soil enrichment with HS of properties similar to these originating from traditional sources. It also demonstrates long-term positive effects on physical-chemical parameters, composition and structure of SH and soil.

Table 1. Elemental composition (in atomic percentage), atomic ratios and degree of internal oxidation (ω) of HA extracted from soil

Object	C	H	N	O	H:C	O:C	O:H	N:C	ω
„0" - control	36,1	43,4	2,7	17,8	1,20	0,49	0,41	0,074	0,002
Rekulter (40 t · ha^{-1})	36,6	45,0	2,6	15,8	1,23	0,43	0,35	0,072	0,150

notation: ω - internal of oxidation degreee

Fig. 1. FTIR spectra of HAs extracted from soil

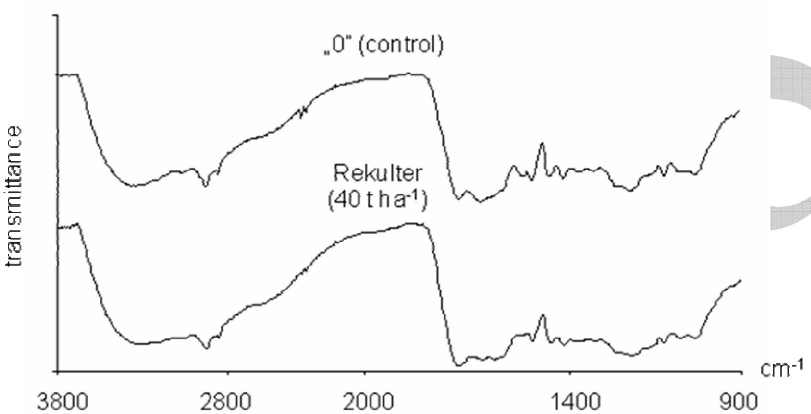

Table 2. Spectral properties of HAs extracted from soil

Object	A_{280}	A_{465}	A_{600}	A_{665}	$A_{2/4}$	$A_{2/6}$	$A_{4/6}$	ΔlogK
„0" control	5,2	0,99	0,362	0,201	5,20	25,7	4,95	0,680
Rekulter (40 t · ha^{-1})	6,9	1,13	0,403	0,226	6,09	30,3	4,98	0,690

Table 3. Percentages of some carbon links in HAs molecules calculated from 13C NMR spectra

Object	C_{al}	C_{ar}	C_{lig}	C-COOH	P	C_{al}/C_{ar}
„0" - control	54,5	30,4	5,3	9,7	14,9	1,79
Rekulter (40 t · ha^{-1})	49,5	32,9	7,0	10,6	17,5	1,50

notation: C_{al}, C_{ar}, C_{lig} – C in aliphatic, aromatic and lignite structures

KEYWORD: structure, properties, soil, humic substances, brown coal

Humic Substances in Ecosystems 8, 2009

THE INFLUENCE OF BROWN COAL ON PHYSICO-CHEMICAL PROPERTIES OF SANDY SOILS

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Soil organic matter plays an important role in stability and fluxes of trace greenhouse gases between land surface and atmosphere. A steady decline of organic matter in soils in Poland is observed, therefore the pending problem and new challenge for soil and environmental scientists is to increase its level, particularly in sandy soils. A growing interest was observed in last decades in different sources of organic matter, for example from brown coal, its derivatives and composts that are considered as an important source of enriching the soil with organic matter (Dębska *et al.* 2002; Kwiatkowska *et al.* 2005).

The long-term experiment was carried out in a test field in Klon on rusty soil originated from light sands. The Rekulter – a brown coal fertilizer was introduced 20 cm deep into the soil in autumn 1987 at 2 doses of 80 and 160 tons/ha. After 1 (1988) and 20 (2008) years soil samples were taken at the depth of 20 cm, and the following parameters were determined: pH_{H20} and pH_{KCl}, hydrolitic acidity (Hh) and total exchange basic (TEB) cations by the Kappen's method, the total organic carbon (TOC)–by the Tiurin method, and the total nitrogen (Nt) content–by the Kjeldahl method. Additionally, cations exchange capacity (CEC) and base saturation (BS) were calculated.

Applying the Rekulter resulted in changes of physicochemical properties of the soil (Table 1). One year after application, the highest increase in soil reaction pH (pH_{H2O}=7.5; pH_{KCl}=7.4) was found in the case of higher dose of Rekulter, and the same behavior (pH_{H2O}=7.2; pH_{KCl}=6.4) was observed 20 years after its application. In objects with higher dose of the Rekulter, the TOC decreased from about 20 $g\cdot kg^{-1}$ after 1 year to 15 $g\cdot kg^{-1}$ after 20 years of its application. The highest growth of the Nt content of 1.1 $g\cdot kg^{-1}$ (1988) and 0.9 $g\cdot kg^{-1}$ (2008) occurred at higher dose of the Rekulter. The highest value of TOC to Nt ratio of 20 obtained for soil sample with higher dose of the Rekulter was due to the highest carbon content in this object. In other experiments with the Rekulter and brown coal amendments similar results were obtained (Maciejewska et al. 2001).

Table 1. The effect of the Rekulter on basic properties of soil samples

Sample	Year	Dose ($t\ ha^{-1}$)	pH in H_2O	pH in KCl ($g\cdot kg^{-1}$)	TOC ($g\cdot kg^{-1}$)	Nt	TOC:N
"0" (control)	1988	0	5.6	4.7	7.6	0.6	12.7
	2008	0	5.9	4.7	6.3	0.4	14.6
Rekulter	1998	80	7.0	6.8	14.5	0.9	16.1
	2008	80	7.1	6.3	11.5	0.7	16.2
Rekulter	1988	160	7.5	7.4	22.1	1.1	20.1
	2008	160	7.2	6.4	15.5	0.9	19.5
LSD = 0.05			0.2	0.4	0.7	0.08	-

Selected physical-chemical properties of soil after application of the Rekulter are presented in Table 2. A decrease of Hh was observed in the case of both doses applied, with the lowest value of 0.7 cmol (+) ·kg found in the case of higher dose of the Rekulter. The high sorption capacity of the Rekulter significantly influenced TEB, CEC and BS of amended soil.

The Rekulter applied to soil demonstrates long-term positive effects on basic properties and physical-chemical parameters of the sandy soil.

Table 2. The effect of the Rekulter on hydrolitic acidity (Hh), total exchange basic (TEB) cations, cation exchange capacity (CEC) and base saturation (BS) of soil

Sample	Year	Dose of amendment ($t\ ha^{-1}$)	Hh	TEB	CEC	BS
			cmol(+) $.kg^{-1}$			%
"0" (control)	1988	0	4.1	2.6	6.7	39.3
	2008	0	3.8	3.6	7.4	48.6
Rekulter	1988	80	0.9	13.9	14.7	93.9
	2008	80	1.9	19.7	21.6	91.2
Rekulter	1988	160	0.4	32.0	32.4	98.9
	2008	160	0.7	36.6	37.3	98.1
LSD = 0.05			0.1	2.1	3.3	4.2

KEYWORD: organic matter, physico-chemical properties, soil, brown coal, Rekulter

RELATIONS OF ENZYME ACTIVITIES WITH DIFFERENT FRACTIONS OF SOIL ORGANIC MATTER

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Important ecological function of humic substances is their capability of stabilization of extracellular enzyme activities that are the primary means by which soil microorganisms decompose complex organic compounds into assimilable subunits. Humus–enzyme complexes have a functional capacity under unfavorable conditions; they are resistant to proteolysis as well as to chemical or physical stresses. Stable humus pool and humus–enzyme complexes play an essential role in the functioning of soil systems.

The objective was to establish the relations of enzyme activities with the contents of stable and active SOM fractions. Cellulase and invertase were chosen for their critical role in the C cycle in soil. Urease was studied because of its role in releasing inorganic nitrogen in the N cycle.

Long-term organic amendments (8 and 16 t ha^{-1} of FYM in rotation) positively affected the contents of stable and active SOM fractions in Luvisol loamy sand soil. Close correlations were found between stable humus pool and hydrolase's activities in soil (R^2; $P < 0.05$): for cellulase – 0.71 – 0.91; for invertase – 0.88 – 0.92; for urease – 0.73 – 0.76. Regression analysis revealed reliable but not so close relationships of hydrolase's activities with decomposable fractions of SOM (R^2; $P < 0.05$): for cellulase – 0.63 – 0.68; for invertase – 0.57 – 0.69; for urease – 0.66 – 0.71.

KEYWORD: SOM stable and active fractions, cellulase, invertase, urease

BIOLOGICAL ACTIVITY OF HUMIC SUBSTANCES AND THEIR FE-ENRICHED DERIVATIVES TOWARDS CUCUMBER PLANTS UNDER FE-DEFICIENCY CONDITION

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Humic substances (HS) are generally considered to increase availability of micronutrients such as Fe, Zn, Mg, Mn, Ca and others, low levels of which cause leaf yellowing called chlorosis. So, some HS preparation enriched with micronutrients are available in the agricultural market. The observed beneficial effect of HS is generally attributed to the chelating activity of HS that provides plants with micronutrients in easily assimilated form. However, HS are known to be universal bio-activators providing plant adaptation to stress of various nature. Therefore HS could be expected to mitigate negative effects of chlorosis due to their own biological activity. This study was aimed to compare influence of HS, their Fe-enriched derivative and commercially available iron supplier on cucumber plant growth under Fe-deficiency conditions.

Following preparation were used: potassium humate derived from coal (Solntsevskoe deposit, Sakhalin Island, Russia) assigned as K-Sh, its Fe-enriched derivative assigned as Fe-HS, and commercially available agricultural iron additive ferrous chelate of ethylenediaminedi(o-hydroxyphenylacetic) acid (Fe-EDDHA). The content of iron was measured using o-phenantroline method after oxidative digestion and was as 1%, 9%, and 6% in K-HS, Fe-HS and Fe-EDDHA respectively.

To estimate biological activity of HS under iron deficiency conditions we applied bioassay technique. Plants of cucumbers *Cucumis sativus* L. were used as a target object. Cucumber seeds were grown in distilled water for 120 hours at 25°C in the dark followed by transferring seedlings into 0.05 mM solution of $CaSO_4$ for 24 hours. Then seedlings were transferred to plastic pots containing 0.1 l of Hoagland's nutrition solution supplied with 25 μmol/l of iron and 15 mg/l of HS. Values of pH of all the solutions were adjusted to 8. The cucumber plants were grown with 12-hours light day. Hoagland's nutrition solution without Fe was used as blank.

After 32 days of growing plant photosynthesis efficiency were estimated in terms of the maximum activity of PSII (Fv/Fm) using pulse amplitude modulation (PAM) fluorometer (PAM-2000, Walz, Germany). Then cucumber plants were harvested and subjected to measuring shoots and roots length and weight and chlorophyll content. The content of iron in plant tissue was measured using o-phenantroline method after oxidative digestion.

The obtained data showed that in the lack of iron in the nutrition media poor cucumber growth was observed. Plants demonstrated sings of chlorosis such as yellow or yellow-white leaves, poor photosynthesis efficiency (Fv/Fm = 0.45), and low chlorophyll a/b ratio (1.8). When iron was added in the form Fe-Sh or Fe-EDDHA no chlorosis symptoms was observed, and values of Fv/Fm and chlorophyll a/b ratio increased to 0.77-0.78 and 2.4-2.6. As a consequence, the biometric parameters of the treated plants – length and weight – were substantially increased as well (Figure 1).

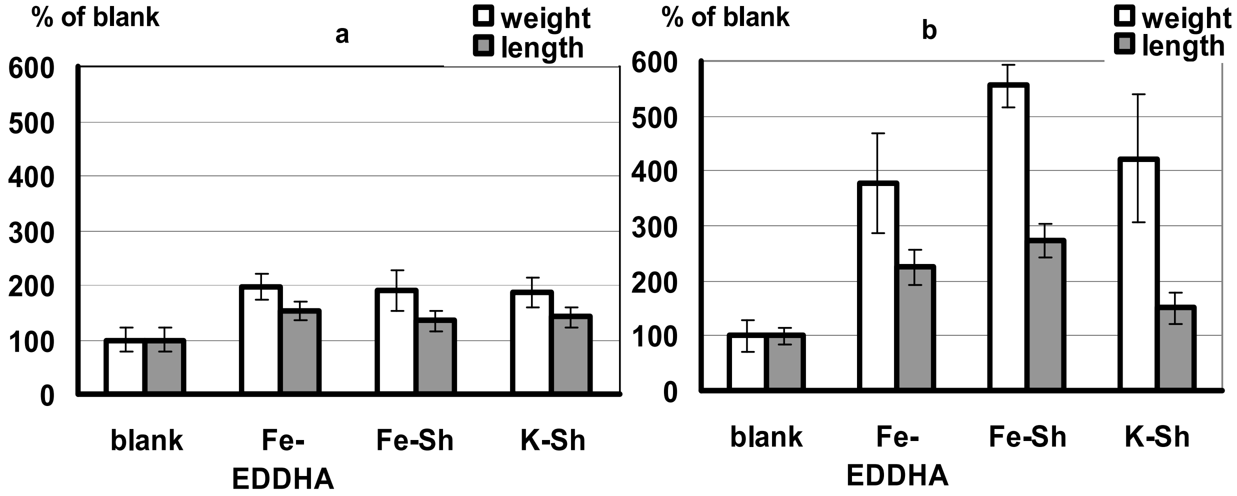

Figure 1. The influence of commercial iron chelate Fe-EDDHA, parent humic material K-Sh and its Fe-enriched derivative Fe-Sh on cucumber shoots'(a) and roots' (b) weight and length increase.

As it can be seen from the Figure 1, plants treated with Fe-EDDHA or Fe-Sh possessed higher weight and length of both shoots and roots as compared to blank. However, efficiency of studied iron suppliers did not differ one form another if shoots parameters were used as a target function, whereas substantial differences were observed for both length and weight of roots.

Of interest was that addition of K-Sh solely also led to a partial recovery of the Fe-deficient plants. In particular, the photosynthesis efficiency ($Fv/Fm = 0.77$) and chlorophyll a/b ratio (2.4) were significantly increased in humus-treated plants. At that, length and weight of cucumbers' shoots and roots were similar to those of plants treated with Fe suppliers.

Fe content in the leaves of treated plants were estimated as 508, 158, and 93 mg/kg of dry weight for Fe-EDDHA, Fe-Sh, and K-Sh respectively. The highest iron content was found in Fe-EDDHA treated plants whereas humics treated plants possessed much lower iron. The latter was evident for the fact that both Fe availability in the nutrition media and beneficial effect of HS were responsible for plants' recovery from Fe-deficiency chlorosis. So, mitigating activity of humic-based Fe additives under Fe-deficiency conditions resulted not only from the fact that plants could use Fe, but from protective activity of HS in relation to photosystem II either.

PROPERTIES OF HUMIC SUBSTANCES EXTRACTED FROM BOTTOM SEDIMENT AT GOCZAŁKOWICE DAM RESERVOIR

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Studies of humification processes of bottom sediments collected from various points of the Goczałkowice dam were conducted. The humic and fulvic acids were extracted from the collected sediment. For study of physico-chemical properties of humic and fulvic acids EPR and IR spectroscopy was used. For extracted humic and fulvic acids, concentration of free radicals and the g factor were determined with EPR. The presence of characteristic functional groups was confirmed with IR spectroscopy.

It was found that humic and fulvic acids extracted from bottom sediment at 8 places of the Goczałkowice Reservoir are characterized by similar physico-chemical properties, which points to a similar composition of bottom sediment in the whole reservoir. Humic acids are relatively high aromatised, have a low free radicals content and a low value of the g factor. They have condensed aromatic rings with side-aliphatic chains. However, the extracted fulvic acids are less aromatised than humic acids. They have a weakly formed aromatic core with the dominance of side- aliphatic chains.

The influence of the depth of the lake on the content of oxygen functional groups in the extracted humic and fulvic acids was also observed.

KEYWORD: humic acids, fulvic acids, bottom sediment, EPR, IR

CHARACTERIZATION OF SOIL ORGANIC CARBON AND ITS FRACTION LABILE CARBON IN ECOSYSTEMS

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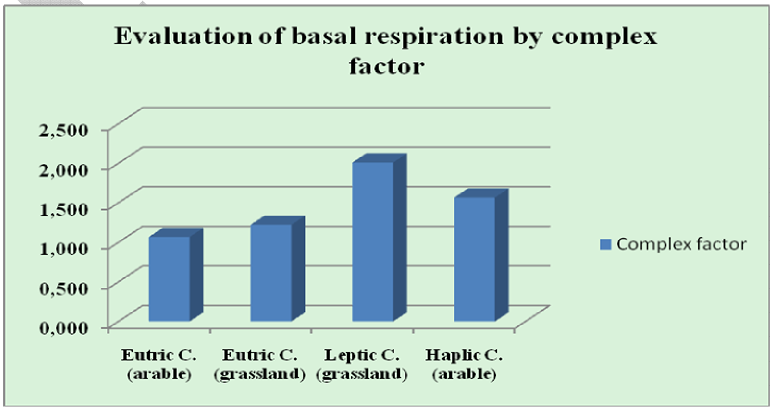
Parameters evaluating humus content and quality were determined in soils under different management systems. Our work represents a part of long - term field experiments that are carried out in the Czech Moravian Upland. Soil samples were selected from the topsoil of the following soil types: Leptic Cambisol (Ocmanice, grassy soil), Haplic Cambisol (Náměšť n/Oslavou, arable soil), Eutric Cambisol (Vatín, grassy soil), Eutric Cambisol (Vatín, arable soil). Among the all parameters labile soil carbon and basal respiration activity were measured. Oxidimetric titration for total organic carbon content determination was used. Humic substances (HS) sum, humic acids (HA) sum and fulvic acids (FA) sum were determined by short fractionation method. Basal respiration was determined under laboratory conditions using Vaisala GMT 222 apparatus. Hot water extraction for labile organic carbon determination was used. UV-VIS spectra were measured in the mixture of 0.1 M sodium pyrophosphate and 0.1 M NaOH.

Results showed that total carbon content varied from 1.3 – 1.8 %. Higher content was determined in grassy soils. Labile carbon content was higher in grassy soils to compare with arable soils (varied from 540 – 620 mg/kg). HS sum was the lowest in grassy soil (locality Ocmanice) about 6.5 mg/kg. Quality of humus was low and HA/FA ratio was less than 1 for all samples. UV-VIS spectral characteristics showed low absorbance and high color indexes $Q_{4/6}$ for all samples. Humification degree was low (less than 20%). Basal respiration was higher in arable soils to compare with grassy soils. Production of CO_2 varied from 0.31 – 3.8mg CO2/100g/h. Complex factor (Fig.1) is connected with C and N microbial utilization after both elements application to the soil samples. Results showed higher average values in grassland. We can conclude that total carbon content, labile carbon content, basal respiration and humic substances quality were mainly affected by land use.

KEYWORD: *labile soil carbon, basal respiration activity, humus fractionation, UV-VIS spectroscopy*

This study was supported by the Research plan No. MSM6215648905 “Biological and Technological Aspects of Sustainability of Controlled Ecosystems and their Adaptability to Climate Change“, which is financed by the Ministry of Education, Youth and Sports of the Czech Republic and by the project NAZVA QH 81200.



Humic Substances in Ecosystems 8, 2009

SOIL ORGANIC CARBON AND PARTICLE SIZE DISTRIBUTION OF ARABLE SOILS IN WINTER WHEAT CROPPING

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In order to investigate effects of cropping systems on content of soil organic carbon (SOC) and distribution of particle size fractions of soil, different cropping systems of winter wheat were analyzed. Soil samples were collected from the long-term experiments carried out at the Rimski Sancevi experimental station, Novi Sad. The following treatments were analysed:

1. Three–year crop rotation (maize-soybean-wheat), mineral fertilizer 100 kg N ha^{-1} + crop residues
2. Two–year crop rotation (maize-wheat), mineral fertilizer 100 kg N ha^{-1} + crop residues
3. Monoculture (wheat-wheat), mineral fertilizer 100 kg N ha^{-1} + crop residues
4. Two–year rotation (maize-wheat), without fertilizers + crop residues
5. Three–year rotation (maize-soybean-wheat), without fertilizers + crop residues
6. Four–year crop rotation (sugar beet-spring barley-maize-wheat), 40 t ha^{-1} manure without mineral fertilizers
7. Four–year crop rotation (sugar beet-spring barley-maize-wheat), 40 t ha^{-1} manure + mineral fertilizer 100 kg N ha^{-1}
8. Four–year crop rotation (sugar beet-spring barley-maize-wheat), mineral fertilizer 200 kg N ha^{-1}without crop residue
9. Four–year crop rotation (sugar beet-spring barley-maize-wheat), mineral fertilizer 200 kg N ha^{-1} + crop residues
10. Control, native vegetation with short grasses (the adjacent land which has never been cultivated)

Three soil depths were analyzed (0-20, 20-40 and 40-60 cm). Organic carbon content was determined by CHNS analyzer. Particle size fractions (>2000 µm, 2000-250 µm, 250-53µm and <53µm) were obtained by dispersion in water with series of sieves.

The use of organic and mineral fertilizers influenced SOC content and particle size fractions. Obtained results showed deterioration of soil structure in arable soil compared with control as a result of applied management practice. Significantly higher content of macroaggregates in 0-20 cm soil layer was found in soil samples from control plots compared with wheat cropping systems. Addition of manure without crop residue incorporation was not sufficient for soil structure preservation. In arable soil higher content of microaggregates (<250 µm) was found in 0-20 and 20-40 cm soil layers, whereas 40-60 cm depth had equal proportion of macro- and microaggregates as clay fraction predominates.

SOC content decreased with the depth and differences in SOC among depths were associated with the below-ground biomass of crops in rotation. Higher content of SOC in 0-20 cm and 20-40 cm depths of different size fractions was observed with addition of mineral fertilizer (200 kg N ha^{-1}) and incorporation of crop residues. An increase of SOC content with increased particle size was observed. Accordingly, macroaggregates turnover was crucial in the processes of soil organic matter stabilization.

KEYWORD: soil organic carbon, particle size fractions, cropping systems

THE ROLE ORGANIC MATTER AS SOLID SUPPORT OF HEAVY METALS IN THE WATER ENVIRONMENT

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Metals are perceived as pollution but they are also natural substances in environment. Metals get into the water environment from atmosphere as a result heavy rainfall or snowfall. They are often leaches from rocks or soils. Contents of heavy metals are very often exceeded because of emission from industrial land (Stögbauer *et al*., 2008). Among pollution the most durable are heavy metals. Their contents in water environment components is very divers, but the biggest of heavy metals contents are in suspension (about 80%), while the littlest are in water (Adamiec and Helios-Rybicka, 2002; Aleksander - Kwaterczak and Helios - Rybicka, 2004; Helios - Rybicka *et al*., 2005; Luck *et al*., 2008). The surface water environment is under the influence of continuous industrial pressure.

Pollution of surface water environment which find to the water ecosystem direct or indirect occur various forms. They are solution as well as suspension. Suspense Particular Matter (SPM) is very essential component of surface water. SPM plays essential role in metals pollution transport (Blo et al., 2003; Cenci, Martin, 2004). Solid phase of SPM consists of mainly from inorganic compounds but they are also organic compounds. Most trace elements, especially of heavy metals don't stay a long time in dissolve form. Heavy metals as few from inorganic compounds have strong adsorptive properties. They are stopped on phase line among other suspension and other solid body occurred in water. Heavy metals consist in surface water components decrease in rows: suspension > deposit > water (Luck *et al*., 2008).Heavy metals ratio in industrials components are very divers because of outside factor and biogeochemical processes.

The aim of researches was determined of heavy metals contents in the water in form dissolve and suspension. The samples of water were taken from Bobrza River, from source of a river to Sitkówka - Nowiny. Chosen length a river encompasses different lands about various degrees degradation of the environment. They are: source-naturals, Białgon - sour, Sitkówka – Nowiny - alkaline. In the samples of water was determining: pH, conduction, suspension and concentration of heavy metals in the water in the form dissolve and suspension.

KEYWORD: heavy metals, organic matter, solution, suspension

QUALITY OF SOIL ORGANIC MATTER IN DIFFERENT ECOSYSTEMS

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This study deals about quality of soil organic matter in natural ecosystems and arable land. Sampling places were located in Nitra, Komjatice, Močenok and Šaľa on soil types Eutric Fluvisols and Haplic Chernozems. There were four different ecosystems- agri-ecosystem (arable land), forest ecosystem, meadow ecosystem and anthropic soil included. The highest quality of soil organic matter, evaluated according to extracted carbon of humic acids, was in agri-ecosystem 19 %, next it was in forest ecosystem 18 %, meadow ecosystem 16 % and with the lowest value 13 % it was in anthropic soil. The highest soil organic matter quality in agri-ecosystem on Haplic Chernozems was in variant CM-03, with share of cereals 72 % (maize 42 %), root crops 14 % and oil crops 14 %. Just in this variant the highest carbon and nitrogen contents were determined. In Eutric Fluvisols the highest soil organic matter quality was in variant FM-04, with share of cereals 72 % (maize 14 %), root crops 14 % and with the highest share of oil crops 14 % just in this crop rotation. In this variant also in one year spring cereal and maize for grain were growing. In other variants maize was growing for silage.

KEYWORD: ecosystem, crop rotation, humic acids, soil organic matter

COMPARISON THE PROPERTIES OF HUMIC ACIDS FRACTIONATED FROM AGRICULTURAL RICE AND FOREST SOILS

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This study aimed to evaluate the properties of humic acids (HA) fractionated by conventional humic acids extraction methods. The humic acids from agricultural rice and forest soils were fractionated by the International Humic acids Society (IHSS) methods subjected to elemental, infrared and E4/E6 ratio analyses, and compared for their differences of physical and chemical properties, the characteristics and structures of humic acids. The degree of humification of the Chi-Shan (CS) agricultural rice soils was lower than that of the Ta-Ta-Chia (TTC) forest soils. It was caused by the tillage or fertilization in the agricultural rice soils and showed the lower degree of humification. Under the different climate and vegetative conditions, the forest soils are more favor to the degree of humification than that of agricultural rice soils.

KEY WORDS: C/N ratio. E4/E6,humic substance, humification, infrared analysis

STRUCTURE AND PROPERTIES OF COMMERCIAL HUMATES FROM COALIFIED MATERIALS, PEAT AND SAPROPEL

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Since the beneficial role of humic substances (HS) in the environment is well known, today many companies all over the world produce commercial humates (HUM) from organic raw materials and promote them as soil conditioners, plant growth stimulators, for remediation of degraded soils, and sorbtion of toxicants. Industrial companies manufacture HUM using a big variety of raw source materials and different industrial processes, and therefore the products have highly variable properties and there are not enough data about their structure and actions. Since the mechanism of HS-action is apparently correlated with their certain chemical parameters, the effect of HS will be different depending on their origin. In this study a possible connection between the origin of organic matter, and the ability of HUM to stimulate plant growth was investigated. A number of HUM produced from coalified materials (brown coal BC, leonardite Le, lignite Li and humalite Hu) and plant-originated resources peat (Pe), sapropel (Sa) and organic waste material (OW) were examined in respect to their chemical composition and structure, content of HS and auxin-like activity.

Chemically HUM are mostly Na or K humates with different additives – microelements, silica, or nutrients. A detailed chemical analysis was conducted for HUM-products. Content of C total varies between 30-45%, being higher for products from Pe, BC and Le and lower for ones from Sa, Hu, Li and OW (Fig.1). HUM from coalified materials contain minor amount of N, whereas products from Pe and Sa are significantly higher in N most probably due to presence of proteins in raw materials (Fig.2). Some individual samples contain up to 4-7% of S.

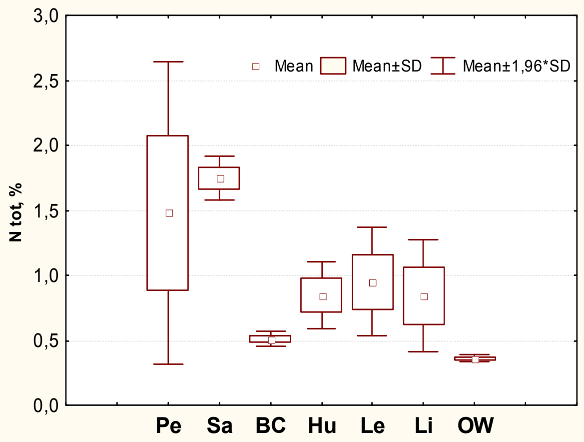

Fig.2. Box plot of N tot

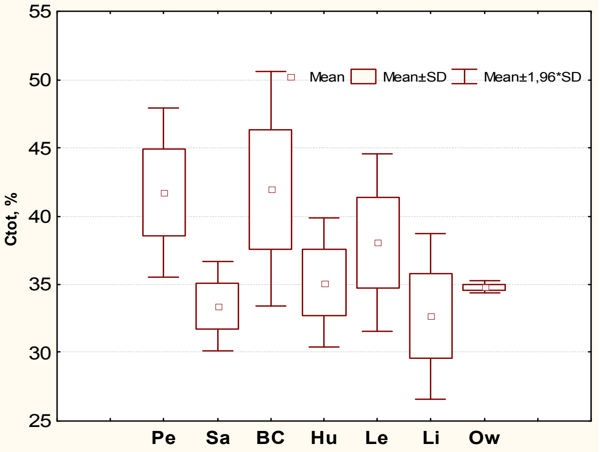

Fig.1. Box plot of C total

Active ingredients in HUM-products are considered to be HS: HA or probably FA. For all the samples total extractable C achieved 20-40%, which is approximately equal to 16-75% from TOC. The distribution pattern demonstrates that HUM from Sa, Hu and Li content the lowest amounts of extractable C most probably due to links with mineral impurities (Fig.3). Amount of HA and fulvic acid fraction in individual samples varies greatly, although ratio C_{HA}/C_{FA} shows uniform distribution except of BC-products rich in HA and poor in FA (Fig.4).

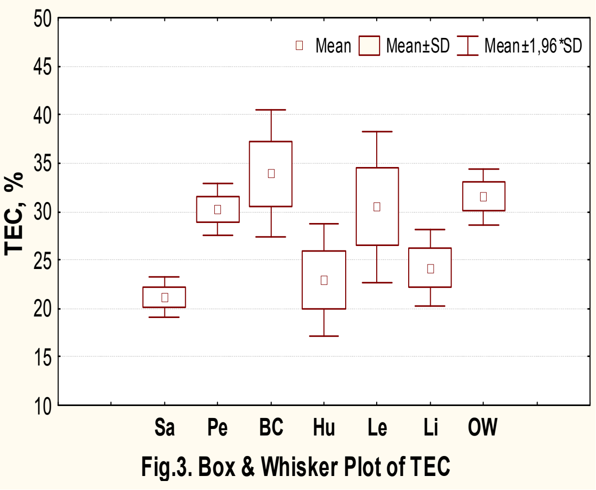

Fig.3. Box & Whisker Plot of TEC

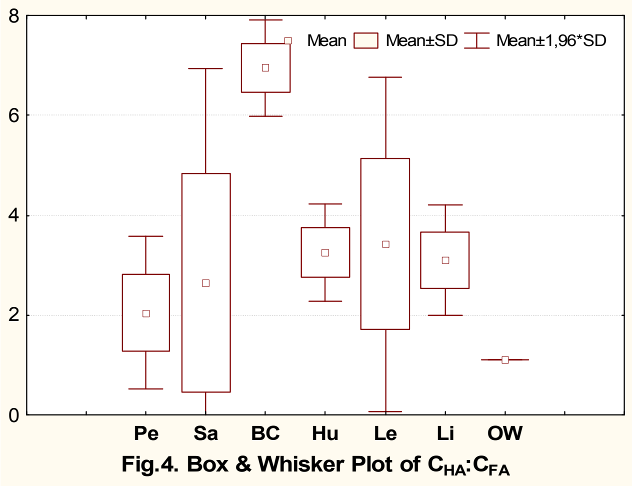

Fig.4. Box & Whisker Plot of C_{HA}:C_{FA}

Advanced investigations of molecular structure of HA extracted from selected HUM were performed; results are discussed in presentation. In brief, molecular structure HUM from plant originated material (Pe, Sa and OW) were enriched in O-containing functional groups, whereas HUM from coalified materials in aromatic moieties.

In vitro experiments were conducted with plants treated with and without HUM. Reddish seeds (*Raphanus sativis* L.) have been soaked in solutions of HUM at concentrations 625, 125 и 12,5 mg/L, and germinated at dark at 27 o C for 72 h. The physiological activity of HUM was estimated as a change in primary root length of seedlings. Not all of the HUM tested demonstrated auxin-like activity. The level of growth-stimulating activity varied greatly for different HUM-brands, depending on their chemical structure and organic matter origin. FA-fraction of HUM acted more actively then HA-fraction, whereas the highest effect was revealed for unfractionated HUM-products.

Statistical evaluation of possible correlations between structural parameters and auxin-like activity have been performed.

KEYWORD: humic substances, humic fertilizers, commercial humate,auxin-like activity

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Humic Substances in Ecosystems 8, 2009

THE EFFECT OF GAMMA IRRADIATION ON PROPERTIES OF SOIL HUMIC ACIDS

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Humic substances are naturally occurring, biogenic, heterogeneous organic substances that can generally be described as yellow to black in colour, of high molecular weight and refractory. Humic acids (HA) are the fraction of humic substances that is insoluble in water under acidic conditions (below pH=2), but is soluble at higher pH values. HAs play an important role in creation of many soil properties profitable for plant development but the processes of their formation have not been entirely discovered so far. The HAs are resistant to chemical and microbial decomposition, therefore their mean residence time in soil is evaluate on about 1000 years.

The aim of this work was to identify if humic acids are relatively resistant not only to chemical and microbiological factors but to gamma irradiation too.

HA samples were extracted from soil samples (LAS – from O-horizon of Albic Aresonol under pine forest; PUL – from Ap horizon of Haplic Luvisol used for agriculture; TOR – from 0-30 layer of Eutri-Fibric Histosol) and purified by the standard Schnitzer's methods. Samples of HA were divided into those that have been exposed to gamma radiation and for those that have not been exposed to radiation. In the experiment "cobalt bomb" was used with ^{60}Co as the source of gamma rays. Time of irradiation of samples was 1.5 months, the radiation dose was 160 kGy. Irradiated and not irradiated HA samples were analysed for: elemental composition, infrared, ^{13}C-NMR CP/MAS solid state and UV-VIS spectra.

Obtained results showed that humic acids are resistant to gamma irradiation at the dose of 160 kGy. Elemental composition (see table), UV-VIS, IR and NMR analysis of irradiated HA samples did not differ from comparable HA samples not irradiated. Studies have shown clearly the differentiation in structure and properties of HA depending on their source of origin (type of soil).

Table 1. Elemental analysis (in atomic percentage) of HA samples

Sample	Variant	atomic %				H:C	N:C	O:C	O:H	ω
		C	H	N	O					
LAS	0 kGy	35.4	40.7	2.0	21.9	1.15	0.06	0.62	0.54	0.257
	160 kGy	35.5	40.5	1.9	22.1	1.14	0.05	0.62	0.54	0.265
PUL	0 kGy	32.8	43.7	2.8	20.7	1.33	0.09	0.63	0.47	0.186
	160 kGy	32.9	43.4	2.8	20.8	1.32	0.09	0.63	0.47	0.201
TOR	0 kGy	35.0	42.3	1.8	20.9	1.21	0.05	0.59	0.49	0.140
	160 kGy	34.9	42.3	1.8	21.0	1.21	0.05	0.60	0.50	0.146

KEYWORDS: humic acids, gamma radiation

STATUS OF ORGANIC MATTER IN FOREST SOILS AFTER FIRE

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Samples were taken 13 years after the fire (2900 ha, surface fire) from the following sites: control (area not burned, 90-years old *Pinus sylvestris* L. stand) and burned (area after surface fire, stand as in control). Morphology of the soil profiles (Brunic Albic Arenosol, WRB 2006), soil properties and stocks of organic carbon were determined.

The organic horizon in control soil consists of two sub-horizons: Ol and Ofh. In soil on area after surface fire, the organic horizon consists of the sub-horizon Ol (“fresh build after fire) and the sub-horizon named Os (“old” litter, burned during the fire). Thickness of the Os varied from 0.3 to 2.5 cm. Os sub-horizon was characterized by black colour (N 2/0 when moist, 10YR 2/1 when dry), 8-22% of organic matter content and 10-13 of C:N ratio. Degree of aromaticity of the Os horizon organic matter was 1.5 (after 13-C NMR CPMAS spectra), higher than Ofh horizon – 0.7. Organic matter stocks in organic horizon of buried area (2.66 kg/m^2) were lower than in soil organic horizon of non-buried area (4.55 kg/m^2). Lower organic matter stocks in humus horizon were noted also, respectively.

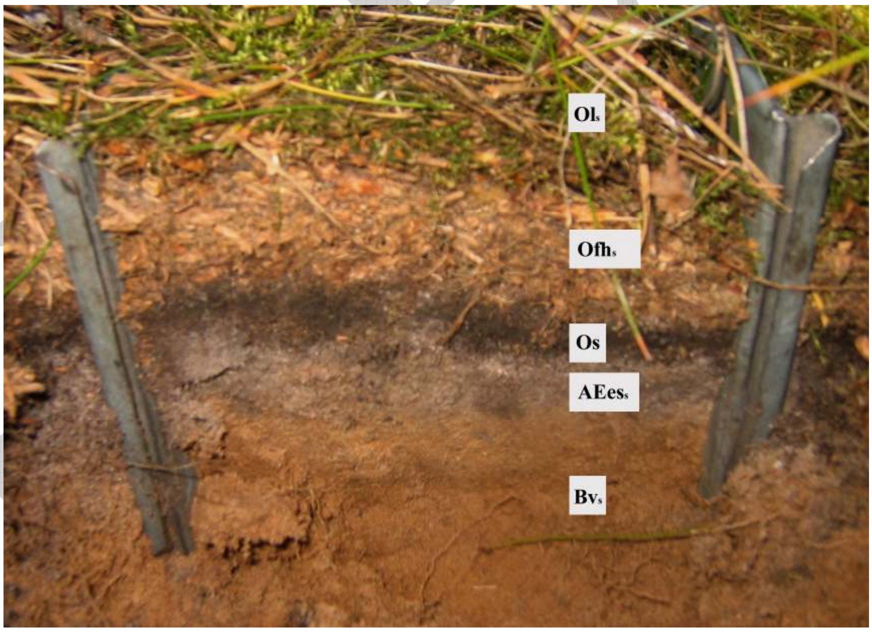

Fig. 1 Typical soil profile on burned area with characteristic Os sub-horizon

KEYWORDS: organic matter stock, forest soils, forest fire, humus

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HUMIC SUBSTANCES EFFECT ON POMEGRANATE NURSERY PRODUCTION

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In the Eastern Region of Afghanistan is well known about its large scale horticulture production. But it is also common knowledge, that climatic and soil conditions are very difficult. In this region, where the annual precipitation is very low, the heat is very high, the soil shows very weak development. The tested soil is a young soil in early stage of weathering. Its originated from sedimentary material, which was deposited in the area. The little difference between the horizons and the absence of E horizon also indicates the young age and poorly structured soil. The high content of clay size particles makes the soil compact and poorly ventilated. The water penetration is also limited into the soil.

The chemical property tests show, that the soil strongly alkaline and the nutrient content, except the Phosphorus and Potassium, is low. The nutrient availability for plant is difficult in the alkaline context. Iron deficiency is a common problem in the production. The clayey structure, high pH, the reducing environment and low nutrient content makes difficult to work with this soil. This land is the less suitable for high quality nursery production, which is a crucial factor for the production. Therefore, the use of biostimulants, such as humic substances, can improve the production radically.

The aim of the research had been to increase pomegranate cutting survival rate and the number of quality saplings in nursery production through humic and fulvic acid application during the growing period. The nursery production has been working since February 2007. The survey study in 2007 indicated, that approximately 44-45% of the saplings were acceptable for transplant. It is also established, that the climatic and soil conditions affected the growth of 55 % of the total cuttings.

One of the objectives of the experiment was to establish the effect of the humic substances on the quality of the saplings in term of length, diameter, root system development and vigor.

The research established the changes of the soil physical and chemical properties and nutrient availability in the soil comparing them with the results of the original soil test.

The experiment had been conducted in four repitions. Each plot contained 100 rows. Every 5th row functioned as control row. The production technology followed agro-ecological concepts. Controlled furrow irrigation had been used according to calculations. The plant nutrition method added animal manure to the DAP and Urea basal application. Humic acid had been applied twice as side application and fulvic acid once as foliar application.

After 9 months the trial showed the following results:

1. The height and diameter of the test plants increased with an average of 30-35% more than the diameter and height of the control plants.
2. While 90% of the test plants achieved the required development stage by the end of the production season, only 55% of the control plants could qualify under the same standard.
3. The root system analysis established that the root weight of the test plants were 2,62 times heavier than the root weight of the control plants. The number of roots with a diameter of 2-4 mm, 4-7 mm and over 8 mm were 4-5 times larger in case of the test plants.

4. The soil properties showed the following results:
    1. EC in 0-15 cm depth: Increased
    2. EC in 15-30 cm depth: Slightly decreased
    3. EC in 30-45 cm depth: Decresed
    4. pH in 0-15 cm depth: Decreased
    5. pH in 15-30 cm depth: Decreased
    6. pH in 30-45 cm depth: Increased
    7. Non-salinity in all depth
    8. Available NPK content: Radically increased
    9. Iron deficiency symptoms: Disappeared

The conclusion of the trial confirms that the main importance of humic substances in agricultural production lies in their capacity to:

- Improve the soil physical properties
- Stimulate plant growth
- Enhance the effect of fertilizer

Substantial fraction of the mass of the humic acids is in carboxylic acid functional groups, which endow these molecules with the ability to chelate positively charged multivalent ions (Mg^{2+}, Ca^{2+} Fe^{2+}, most other "trace elements" of value to plants. By chelating the ions, they facilitate the uptake of these ions.

The trial clearly showed that the usually present iron deficiency did not develop in the test plants. The mechanism how the insoluble iron oxide is absorbed by the plants requires further tests. However, since plants have been shown to absorb and translocate the complex organic molecules of systemic insecticides, we can no longer discredit the idea that plants may be able to absorb the soluble forms of humus; this may in fact be an essential process for the uptake of otherwise insoluble iron oxides.

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RELATIONS BETWEEN ORGANIC HORIZON PROPERTIES AND FOREST FLOOR VASCULAR PLANTS COMPOSITION IN SCOTS PINE (PINUS SYLVESTRIS L.) STANDS IN SOUTH WEST POLAND

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Properties of organic horizon are strongly related to the species composition of phytocoenosis. Relations between organic horizon properties and vegetation composition are double-sided. Plants influence on upper soil horizons properties, but also the properties determine forest floor plant compositions. The second relation results from different plant species soil requirements. Scots pine (*Pinus sylvestris* L.) is species that strongly influences soil properties mainly by acidification upper soil horizons [e.g. Augusto i in. 1998]. In forest floor of pine stands species that tolerate acid conditions mostly prevail. Such situation takes place even on sites of deciduous forests where pine was planted in silviculture what was common in south west Poland [Olaczek 1976]. The aim of the paper was to evaluate the relations between organic horizon properties and forest floor vascular plants composition of Scots pine stands in selected plots in south west Poland.

The researches were conducted in 100 plots located in Bolesławiec, Głogów and Oława forest division (Fig. 1). In each plot phytosociological relevé was taken and organic horizon of soil was sampled. In descriptions of phytocoenosis Braun-Blanquet method was used [Braun-Blanquet 1964]. Nomenclature of plants follows Rutkowski [1998]. Soil samples were taken and analyzed by methods according to the instruction of polish forest survey [Instrukcja 2003]. Relations between vegetation and organic horizon properties were examined using Canonical Correspondence Analysis (CCA) in CANOCO 4,5 package [ter Braak, Šmilauer 2002].

Fig. 1. Location of Bolesławiec, Głogów and Oława forest division

The pattern of species distribution shown in figure 2 suggests that the first axis of the diagram refer to soil fertility that increases from the left to the right part of the ordination diagram. In its left part oligotrophic species are dominant (e.g. *Vaccinium vitis-idaea, Ledum palustre, Calluna vulgaris*) while in the right part species of high soil trophy preferences prevail (e.g. *Alliaria petiolata, Brachypodium sylvaticum, Dactylis aschersoniana*). It is confirmed by analytical determinations of organic horizons. The gradient of characteristics positively correlated to soil fertility (base saturation - BS, pH_{KCl}, N_t and basic cations content) increase to the right while gradient of acid cations ($H^+ + Al^{3+}$) content and C:N ratio increases to the left side of the diagram. Results of CCA, forward selection and Monte Carlo permutation test identified BS, C:N ratio, pH_{KCl}, Mg^{2+}, Ca^{2+}, K^+ and acid cations content as statistically important ($p < 0,05$) in the pattern of species distribution.

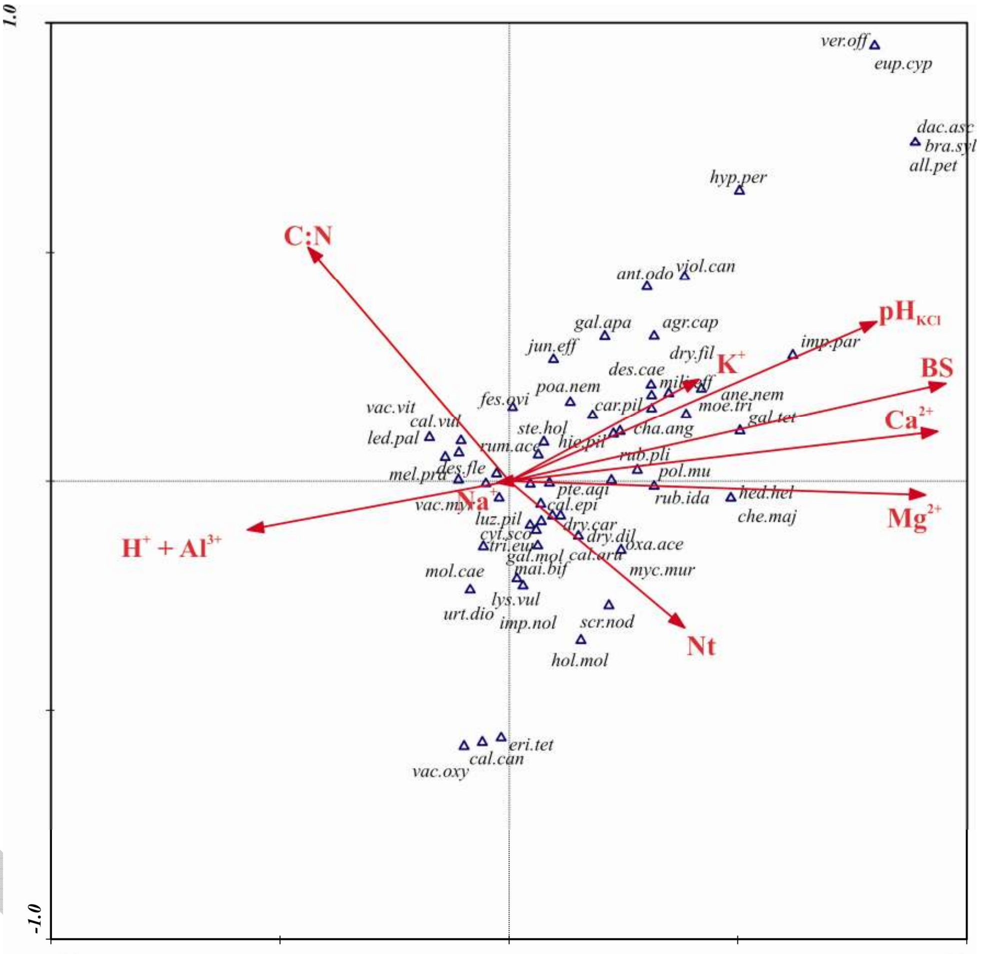

Fig. 2. CCA ordination diagram showing correlation between species composition and organic horizon properties

The species distribution shown in figure 2 suggests also that the second axis of the diagram refers to soil humidity. It is indicated by location of wet sites species mainly in a lower part of the diagram (e.g. *Calamagrostis canescens, Vaccinium oxycoccos, Erica tetralix*) and of fresh soils in middle and upper part of the diagram (Fig. 2). The occurance of species typical of deciduous forests (e.g. *Anamone nemorosa, Poa nemoralis*) indicate that some of investigated pine stands were planted on originally deciduous forests sites.

THE INFLUENCE OF ORGANIC MANURING ON THE CONTENT OF THE SOIL ORGANIC MATTER IN THE LONG - TERM MONOCULTURE

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Soil organic matter is the source of microorganism nutrition, it is very important in the tillage of soil, in the infiltration of air and water by promoting water retention and reducing erosion. The content and quality of soil organic matter positively affect physical, chemical and biological soil properties. The soil fertility depends on the humus content, which is the result of crop rotation and organic fertilization. Nowadays the market economy is the most important argument for the option of agricultural crops. This situation in many cases results in increasing the concentration of one crop and limited crop rotations. With regard to the threats brought about by continuous cropping the Research Institute of Plant Production Piešťany were carried out a field investigation in 1974 – 2009 concerning the questions: To what degree is it respectable to increase the share of cereals in crop rotations? What are the possibilities of the decreasing the negative impacts of the continuous cropping of cereals?

Stationary trial was established in 1974 in the experimental station Borovce. The field experiment is located on a medium heavy textured soil (Luvi-Haplic Chernozem on loess). The trial was situated in the area of continental climate. The trial had two parts. In the first part, the crop rotations were with 40 %, 60 % and 80 % share of the cereals. In the second part of our trial winter wheat and spring barley were grown in monoculture. In the first sequence there is growing winter wheat in "pure" monoculture. Three variants of fertilization were used. At the control variants are used only fertilizers. At the further variant straw of cereals was ploughed in the soil. At the third variant straw and organic manuring Veget were ploughed in the soil. In the second sequence there are rotated winter wheat and spring barley. In the third and fourth sequences: the introduction of compensating crops (maize on silage, grain maize, oat) were used. In the years 2007 – 2008 the effect of mineral and organic fertilization on the physical and chemical properties of winter wheat and spring barley in continuous cropping was investigated.

The winter wheat monoculture growing

During the period of 2007-2008 at the autumn sampling, the lower bulk density was determined at the variant with ploughed in straw (B: 1.34 Mg.m^{-3}) and at the variant with ploughed in straw and Veget (C: 1.35 Mg.m^{-3}) in comparison with the control variant with mineral fertilizers (A: 1.40 Mg.m^{-3}). At the same time the total porosity observed at the variants B (49.82 %) and C (48.15 %) was higher than at the variant A (45.16%).

The maximum water capillary capacity at the variants B (36.17%) and C (35.99%) with organic manuring were lower than the one at the control variant A (36.99). On the contrary, the non-capillary porosity was higher at the B (14.49 %) and C (11.90 %) variant than at the A variant (6.29 %). The variants B and C were characterized by higher average humus contents (B: 1.836 %; C: 1.737 %) than the control variant A (1.664 %) all the time (at the spring and autumn sampling in the years 2007 and 2008). The average phosphorus content was higher at the variants with organic manuring (B: 76 mg.kg^{-1}; C: 78 mg.kg^{-1}) than at the variant A (72 mg.kg^{-1}) in spring of the years 2007 and 2008. On the contrary, the average potassium content was lower at the variants B and C (B: 267 mg.kg^{-1}; C: 258 mg.kg^{-1}) than at the control variant (275 mg.kg^{-1}).

It can be supposed that the supplied organic matter in the form of ploughed in cereal straw or in the form of ploughed in cereal straw and organic Veget contributed to a higher total porosity, increasing of maximum water capillary capacity and increasing of content of humus. It is not possible to exclude that the differences can bring about the heterogeneity of soil, too.

The spring barley monoculture growing

In the spring of the years 2007 and 2008 the lower bulk density was recorded at the variant with ploughed in straw (E: 1.53 Mg.m^{-3}) and at the variant with ploughed in straw and Veget (F: 1.51 Mg.m^{-3}) than at the control variant with mineral fertilizers (D: 1.55 Mg.m^{-3}). mg.kg^{-1}) At the same time the higher total porosity was observed at the variants E and F (E: 42.24 %; F: 43.65 %) in comparison with the control variant D (41.34 %). The total porosity was slightly higher at the variant with ploughed in straw and Veget (E: 45.53 %) than at the control variant (D: 45.29 %) at the autumn sampling too. The maximum capillary water capacity was higher at the variant with ploughed in straw (E: 35.71 %) in comparison with the control variant (D: 34.87 %) at the spring sampling. In autumn the non-capillary porosity was lower at both variants with organic manuring (E: 9.28 %; F: 9.85 %) than at the control variant (D: 10.05 %). The variant with ploughed in straw and Veget was characterized by higher average humus content (F:1.655 %) than the control variant (D:1.622 %) all the time (at the spring and autumn sampling in the years 2007 and 2008). The soil reaction was at all the variants slightly acid (variant D: 6.49; E: 6.52; F: 6.57). At the variant with ploughed in straw and Veget (F: 76 mg.kg^{-1}) the content of phosphorus was higher than at the control variant (D: 68 mg.kg^{-1}). Average content of potassium was lower at the variants with organic manuring (variant E: 250 mg.kg^{-1} and variant F: 267 mg.kg^{-1}) than at the control variant (D: 275 mg.kg^{-1}). The introduced results suggested that the incorporation of straw by the continuous cropping is not sufficient for the maintenance of seasonable physical and chemical soil properties. The decomposition of straw in the soil lasts very long time and in the dry years the decomposition is especially decelerated. Therefore, the combination of straw ploughed in with the organic manuring Veget, which has a positive impact on the soil moisture maintenance, the air content in soil conditions, seems much more suitable.

By the continuous cropping of spring barley at the variant with ploughed in straw (variant E) the lowest content of organic carbon, the lowest content of potassium and phosphorus and the lowest total porosity was found in this variant. The present results are showing that the continuous growing of spring barley contributed to a stronger decline of soil physical and chemical properties than the continuous cropping of winter wheat. By the continuous cropping of winter wheat the average bulk density was lower by 7.14 % than by the continuous cropping of spring barley. The total porosity was higher by 7.16 %, the average maximum capillary capacity by 6.64 %, the average non-capillary porosity by 9.15 % and the humus content by 8.4 % by the continuous cropping of winter than by the continuous cropping of spring barley. These findings can be explains by the different root systems of winter wheat and spring barley. There is also another important factor: winter wheat, its radical system together the root system secretion influence the soil profile within almost 10 months, whereas spring barley only 3.5 – 5 months. This result in soil moisture retention, aeration of soil profile and it influences the soil structure.

KEYWORD: winter wheat, spring barley, long- term monoculture, organic manuring, physical and chemical soil properties, organic matter

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ORGANIC MATTER CONTENTS AND DISTRIBUTION IN CHERNOZEM-RELATED SOILS OF POLAND AND SLOVAKIA

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Soils containing relatively deep, black, humic horizons [A] of the mollic type in the top part of the profile, are situated among the most fertile and the most productive arable soils of the world. There are some types of such soils occurring on the territory of Poland and Slovakia in various geomorphological, lithological and hydrological conditions. Black color of these horizons is often marked in their names, according to local soil systematics, for example: černozem, čiernica, czarna ziemia, smolnica.

The aim of this study is to present basic properties of humic horizons of four exemplary profiles representing different soil types in that group of soils. Profiles are located in various landscapes, three in Poland: smolnica (Gniew, the Starogard Lakeland, terminoglacial lake deposits), czarna ziemia (Ostrówek, the Gniezno Lakeland, glacial till), czarnoziem (Witów, Poland, the Proszowice Plateau, loess) and one in Slovakia: černozem (L'udovitovà, the Nitra river valley, silt deposits). All the soils under study are in agricultural land use. They are developed in medium to heavy texture deposits (silt, loam or clay), containing 1 to 24% of calcium carbonate.

The humic horizons [A] are 40 to 70 cm deep and they are underlain by horizons transitional to parent material [AC], spread 70 - 110 cm down the profile. Organic matter contents vary from 1,7 to 3,7% (1.0-2.2% OC) in A horizons and from 0.7 to 1.7 (0.4-1.0% OC) in AC horizons. In general, they have narrow C:N ratio values (9-11) and neutral or alkaline reaction. Only one profile, czarnoziem from Southern Poland has wider C:N ratio (14) and acid reaction.

KEYWORD: Chernozems, mollic horizon, organic matter

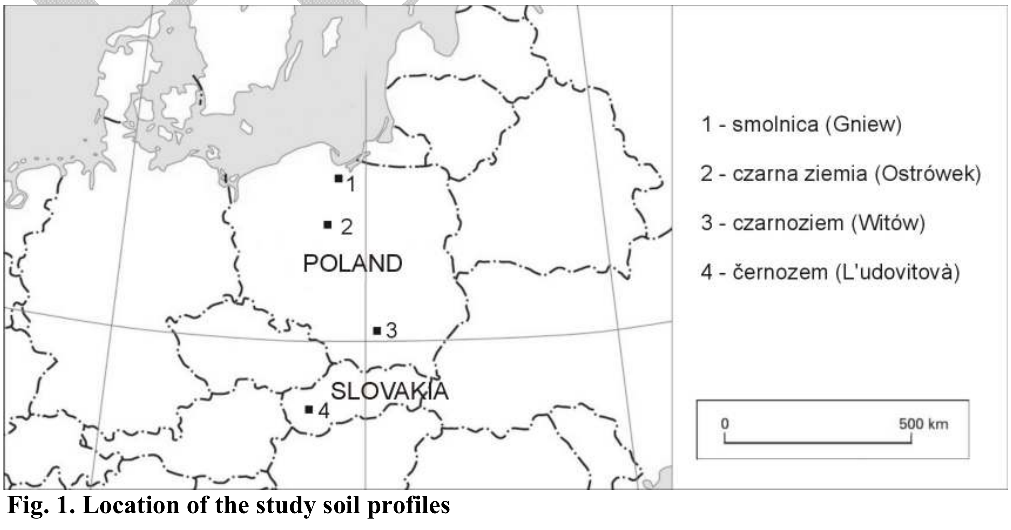

Fig. 1. Location of the study soil profiles

ANALYSIS AND CHARACTERIZATION OF HUMIC SUBSTANCES ISOLATED FROM PEAT AND SOIL USING OFF-LINE COMBINATION OF LIQUID CHROMATOGRAPHIC METHODS

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Humic Substances (HSs) belong to the most spread enviro-bio-polymers and they have direct influence to various processes playing significant role in an environment. Characteristic feature of this analytes group is created by diffuse non-distinct analytical signal that is produced by many detection principles. This fact is a consequence of their great complexity expressed also by their chemical, structural and physical poly-dispersity, which further translates itself in a great uncertainty of their analytical signal measured in almost all analytical methods, that are applied to investigation and measurement of HSs.

Liquid chromatography method arranged around RP HPLC using stepwise gradients of dimethylformamide (DMF) in buffered aqueous mobile phase and a wide-pore (30nm) octadecylsilica column had been applied to the analysis of soil and peat HSs, respectively, in order to demonstrate the usefullness of the approach for their characterization even at trace concentration levels.

Combination of acceptable DMF solvating and aggregation disturbing properties for HSs together with wide pore RP sorbent improves surface interactions of the analytes and suppresses influence of size exclusion effects in RP-HPLC. Thus it provides reproducibility of characterization profiles and robustness of the method. Very good reproducibility of retention times (± 0.5 % RSD) of peaks enforced by the step gradient shape supports well defined characterization and/or fractionation of HSs. This creates good conditions for its combination with the LC method based on totally different separation mechanism to create two-dimensional separation schema. Thus, individual fractions obtained by the described RP-HPLC method were off-line analyzed by size-exclusion chromatographic method (SEC) working on independent separation principle and also by the described RP-HPLC method.

In SEC we achieved relatively precise and accurate determination of relative molecular mass distribution under the assumption and condition that separation or fractionation is based entirely on separation according to size of molecule. Choice of a proper molecular mass calibration standards mimicking elution behavior of HSs in a given chromatographic system is very important with this respect and is discussed in more detail in poster presentation.

KEYWORDS: humic substances, RP-HPLC, step gradient, SEC, combination

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ON-LINE FLOW-THROUGH EXTRACTION–PRECONCENTRATION-LARGE VOLUME INJECTION REVERSED-PHASE LIQUID CHROMATOGRAPHY METHOD FOR TRACE DETERMINATION OF SELECTED PYRETHROIDS IN SLOVAK SOIL MICRO-SAMPLES

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Analytical chemistry is frequently confronted with the need to measure many substances present in a complex matrix either at low concentrations (multicomponent trace analysis) or in a small sample mass or volume (multicomponent micro-analysis). In some cases, as are e.g. forensic analysis or analysis of xenobiotics in the soil of rhizosphere of individual plant, we are faced with the problem of multicomponent trace or ultra-trace micro-analysis. In the last mentioned example the mass of available soil sample representing the problem is usually restrcted to several ten to hundred miligrams. However, this is contradicting our general sense for representativness of field soil sample, sampling plan and analytical or laboratory sample mass as is defined in numerous textbooks. We believe that the progress must be done also in the mentioned direction and so we decided to solve the problem of HPLC trace analysis of selected pesticides in soil micro-samples by proper design, selection, testing and study of quantitative manipulation with microsamples.

A rapid micro-analytical multiresidue method has been developed for the analysis of pyrethroids (kadethrin, cypermethrin and permethrin) in a micro-sample of soil (mass around 200 mg). The method is based on the on-line flow-through extraction of soil micro-samples (packed into a short glass column) with a methanol-aqueous citric acid buffer mixture, successive on-line solid-phase extraction preconcentration (SPE) of analytes from the extract and on-line RP-HPLC analysis with UV photometric detection.

The separation of pyrethroids was performed on a Purospher RP-18e column with methanol-water as mobile phase. Effects of sorbent placed at bottom of short column holding the soil sample and different kinds of on-line SPE columns were tested. Beside the influence of volume of the effluent on the pyrethroids recovery was also studied. Calibration curves were linear over the range assayed from 0.01 to 0.2 μg/mL with correlation coefficients of linear regression (least-squares method) in the range 0.998-0.999. Recovery studies were carried out at 0.25-1.00 μg/g dry soil fortification level and obtained recoveries were for kadethrin 81-84%, cypermethrin 56-59% and for permethrin 58-63%. Achieved detection limits of studied synthetic pyrethroids were for kadethrin 4.5 ng/g dry soil, 3.7 ng/g of cypermethrin and 3.6 ng/g of permethrin, respectively.

KEYWORDS: soil micro-sample, pyrethroids, on-line extraction, RP-HPLC

This work was supported by grant provided by Slovak Grant Agency VEGA 1/0870/09, VEGA 1/4474/07, grant APVV-0595-07, and VVCE-0070-07.

STUDY OF OFF-LINE COMBINATIONS OF HPLC AND CZE METHODS FOR ANALYSIS OF LOW MOLECULAR WEIGHT SUBSTANCES POTENTIALLY RELATED TO HUMIC SUBSTANCES DEGRADATION PRODUCTS

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Complexity of problem called humic substances invokes new way of thinking also in analytical chemistry and provokes to various activities leading to analytical systems of greater complexity just to get more general, or vice-versa more detailed information on their composition, concentration in the environment or adverse effects to chemical analyses of various substances in environmental compartments.

Design and development of novel systems for characterization of humic substances and/or their degradation products in solutions is still challenging.

Two-dimensional system devised in this work was created by off-line combination of gradient elution reversed-phase high performance liquid chromatography and capillary zone electrophoresis in an open system. Electrophoretic system was in our case used as a selective detector for collected liquid chromatographic fractions. We tested orthogonality of liquid chromatography and zone electrophoresis for group of 20 cationogenic and 28 anionogenic compounds under conditions of high compatibility of both separation systems (identical mobile phase and carrier electrolyte pH buffering components). The choice of the model substances was based on criteria of their potential presence in solutions of degradation products of humic substances (photolysis, hydrolysis, oxidation, oxidative photolysis, biodegradation etc.).

Migration and retention characteristics of analytes were evaluated both by Spearman rank correlation coefficients and Pearsons correlation coefficients.

We measured migration times in electrophoresis and retention times in chromatography, respectively, of 20 basic compounds by use of phosphate buffers of varying pH values. Similar experiments were done also with the set of 28 acidic compounds.

Combination of reversed - phase, or aqueous normal phase liquid chromatography, respectively, and capillary electrophoresis gives us results, that are interpreted as non-existence of proof of data sets correlations in studied combinations of CZE and HPLC systems. That practically means formulation of separation systems orthogonality. Similar combinations of orthogonal separation systems will be used also for the characterization of treated solutions of humic substances.

KEYWORDS: Liquid chromatography, RP-HPLC, capillary electrophoresis, CZE, combination, orthogonal, ionogenic substances

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UTILIZATION OF IMMOBILIZED ALUMINIUM(III) METAL ION AFFINITY CHROMATOGRAPHY FOR ANALYSIS OF HUMIC ACID

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Immobilized metal ion affinity chromatography (IMAC) method is based on the ability of macromolecules to form coordination complexes with metal ions, which have been chelated to a multidentate ligand immobilized onto a support material. In the present work, IMAC was developed for the fractionation of humic acid (HA).

In our case, Iontosorb Salicyl (Iontosorb, Czech Republic) was used as the chelating sorbent containing salicylic acid bound via azo group in side chains of modified bead-form cellulose. Sorption characteristics of Al(III) ions for this chelating sorbent were determined at different values of pH. Simple photometric detection at 590 nm was used for monitoring aluminium as SPADNS-Al(III) chelate in eluent during breakthrough experiments. Resulting sorption capacity is highest at pH 5.5 giving value 36 μmol of aluminium per 1 g of the sorbent.

Furher study was focused on the fractionation of the group of aromatic acids or HA by Al-loaded Salicyl IMAC technique. The aromatic acids were selected as potential constituents of the HA. The effect of various pH values (3.9, 6.7 and 8.9, resp.) on the retention of model sample of acids was investigated. The IMAC eluent fractions of acids were separated and determined by reverse-phase high performance liquid chromatography (RP-HPLC) with UV-VIS detection. Finally, IMAC technique was developed for the fractionation HA applying a buffer-based pH gradient (between pH 8.9 and 2.0) for their gradual elution. The HA fractions retained on the Al(III)-IMAC were eluted with eluent of decreasing pH value, and the fractions collected were characterized by UV–VIS detection. Based on the results obtained, IMAC appears to be a promising tool for chemical separation of HA. The results will help in the understanding of the nature of HA and their metal binding characterization, and in modeling natural environments.

KEYWORDS: Immobilized aluminum (III) affinity liquid chromatography, soil acids, humic substances

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THE CARBON AND THE FRACTIONS OF SULPHUR IN NATURE RESERVE ŽITAVSKÝ LUH IN SLECTED SOILS

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The aim of our work is to determine oxidizable carbon (C_{org}), selected fractions of sulphur in soil samples from Nature Reserve Žitavský luh. This area is located on the borders of the Žitava River, on foothill of hilly country of Hronska. The wetlands are interesting in not only from industrial point of view but they also play very important role in vegetation and composition of forest and plant communities by their position, climatic and soil conditions. We compared examined indicators in samples from different soil types, which were taken from the soils in Natural Reserve Žitavský luh in different depths, in years 2004 - 2006. From soil types there are Mollic Fluvisol and Eutric Fluvisol in the reserve. The environment protection and ecological measures oriented to decrease of discharged sulphur compounds caused the fall of the supply of sulphur. One of the limiting factors for vegetal production is the deficit of sulphur. Sulphur is one of the essential, irrecoverable nutrients in cultivating agricultural plants; it is a mobile element and in environment it is reliable to very important changes because of the variety of its chemical forms.

KEYWORDS: Nature Reserve, Žitavský luh, environment, soil type, fractions of sulphur, sulphur dynamics

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INFLUENCE OF FARMING SYSTEMS ON AREA HETEROGENEITY OF TOTAL ORGANIC CARBON CONTENT

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The aim of paper was study the influence of different farming systems on area heterogeneity of total organic carbon content. Soil samples were taken in spring 1997 and 2009 from top layer 0-0.2 m in long time field trial. The integrated and ecological farming systems were established at the Slovak Agricultural University Research Station Dolná Malanta on Haplic Luvisol clay-loamy soil in the fall of 1990. We measured total organic carbon content (Corg) in the fertilized and unfertilized variants of integrated and ecological farming systems.

In spring 2009 was on ecological farming system in the fertilized variant (with farmyard manure) average total organic carbon content 1.24% and in the unfertilized variant 1.09%. We note in comparing with the year 1997 higher content of total organic carbon by 0.06% in the fertilized variant and lower content by 0.31% in the unfertilized variant. In spring 2009 was on integrated farming system in the fertilized variant (with farmyard manure and NPK) average total organic carbon content 0.95% and in the unfertilized variant 0.82%. Compared with the year 1997 the total organic carbon content declined by 0.5% in the fertilized variant and in the unfertilized variant declined upon 0.82%. We can state, from results obtained in our study, that ecological farming systems is from long-term duration (12 years) more sustainable and stabile for total organic carbon content as integrated farming systems.

KEYWORDS: Soil organic carbon, arable systems, area heterogeneity

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HUMIC SUBSTANCES IN CRYOCONITE ON A SVALBARD GLACIERS

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Cryoconite is biogenic surface dust on the glacial surface, consists of mineral particles, organic matter and microbial communities (phototrophic microorganisms, cyanobacteria, hetrotrophic bacteria) and microalgae. Biogenic impurities and dark colored their products have been shown to affect the surface albedo of snow and ice. Cryoconite can thereby contribute to acceleration of melting the glacier surface leading to creation of cryoconite holes – small cylindrical depressions which occur on the surface ice of gleciers. Cryoconite holes are refugia for life in this extreme environment.

The high light absorbency of cryoconite is due to humic substances produced from microbial materials in cryoconite holes and/or to organic matter of soil origin. The aim of this work was to investigate the properties of humus material, especially humic acids, in cryoconites collected in a Svalbard glaciers.

Cryoconite samples from six glaciers (Aavatsmark, Waldemar, Irene, Blomli, Renard, Scott) in the Kaffiora and Bellsund Regions in the Svalbard were analysed. Organic carbon (Corg), total nitronen (Nt) and fractional composition of organic matter (fulvic acids, humic acids and humins fractions) in cryoconites were determined. Humic acids were extracted with 0.5M NaOH method and then analysed for: elemental composition, UV-VIS, IR and 13C-NMR CP/MAS spectra.

Corg content in cryoconte materials ranged from 1.77% to 3.87%, Nt content from 0.199% to 0.413%. The average value of Corg:Nt ratio was 9.1, what suggests the microbial origin of organic material. Fractional composition of cryconite organic matter was characterized by very low humic acids to fulvic acids ratio (average 0.07), not existing for soil organic matter. Participation of fulvic acids carbon in total Corg was 40%, humic acids carbon – 2.5%, humins – 58%. Extracted humic acids showed high aliphatic character. Atomic H:C ratio calculated from elemental composition was 1.50. Very high value of the N:C ratio of 0.11 indicate a relatively high content of nitrogen in humic acids structure. These results were confirmed by the infrared spectra. Integration of 13C-NMR CP/MAS spectra showed very high content of aliphatic carbons (41% in 0-45ppm chemical shift) and very low content of aromatic carbons (14% in 110-165ppm chemical shift). Calculated degree of humic acids aliphaticity was about 4.0 and 2-4 times higher than for soil humic acids.

KEYWORD: cryoconite, organic matter, humic acids