



BOOK OF ABSTRACTS

— INTERNATIONAL CONFERENCE —

„NATURAL ORGANIC MATTER (NOM) GEOCHEMICAL FLOWS AND PROPERTIES:
FROM THEORY TO PRACTICE”

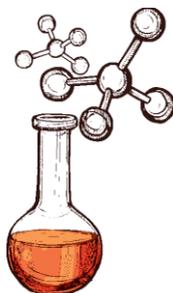
HUMIC



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5-8 JUNE 2019

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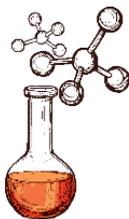
International Conference

**NATURAL ORGANIC MATTER FLOWS AND PROPERTIES:
FROM THE THEORY TO APPLICATION**

5 – 8 June 2019
Riga, Latvia

Book of Abstracts

University of Latvia
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The International conference of IHSS Nordic-Baltic Chapter is organised by University of Latvia and International Humic Substances Society (IHSS).

The aim of the conference is to exchange the results of recent studies and provide a place for creative discussions for those, who are interested in NOM and humic substances. We hope that the topics of the conference will be addressed by researchers not only from Northern Europe, but from other countries as well. We are inviting you to contribute to the success of the conference, enjoy warm and friendly atmosphere of Riga and meet old and new members of the NOM and humus research community.



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Dear friends of the humic research field!

Despite the very long history of studies of humic substances, key questions related to humification, structure, properties and functions of humic matter in the environment remains open. From the perspective of science, they are one of key elements in carbon biogeochemical cycle and their studies from perspective of science are just as important as biosynthesis and transformations of biomolecules in living organisms. Significant driver of humus research includes their functions in carbon capture and stability of humic matter in conditions of climatic change as well as relations between the whole pool of natural organic matter and its refractory part – humic substances. However, nowadays studies of humic substances have left laboratories of scientists as they are produced in amount of thousands of tons, at first for agricultural applications. It is a major challenge of humic matter research – studies of application efficiency, benefits

and possible problems of their use. Anyway: humic substances was, are and will be one of the most exciting and mysterious topics of the studies!

Organizers of the conference “Humic 2019” are really looking forward on exciting exchange of ideas, development of new contacts and cooperation as well as possibilities to meet new and old friends!

Chairman of the Organizing committee of the conference “Humic 2019”

Professor Maris Klavins



HUMIC 2019 Conference venue: UL Academic Centre House of Nature

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Plenary Lectures

POTENTIAL OF DISSOLVED ORGANIC MATTER (DOM) TO ASSIST REMEDIATION OF HEAVY METAL POLLUTED SOILS

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Keywords: Phytoextraction, soil washing, fulvic acid, low-molecular-weight-organic-acids, EDTA.

Abstract: Pollution of soils with heavy metals (HMs), can threaten human health and ecosystem functioning. Therefore, polluted soils must be remediated. Soil washing and phytoextraction seem currently the most attractive remediation methods. Both methods depend on HM solubility (extractability), which can be increased by addition of ligands such as EDTA, NTA and other aminopolycarboxylic acids. As an alternative to these synthetic and environmentally questionable chemicals, the possibility of using naturally occurring dissolved organic matter (DOM) to extract HMs from anthropogenic polluted soils is evaluated in this review based on mainly recently published laboratory studies. DOM isolated or extracted from soils consists of fulvic acid (FA) with some low-molecular-weight-organic-acids (LMWOAs), e.g. citric, oxalic and salicylic acids. In addition to soil DOM, results with other soluble humic substances and LMWOAs will be included.

The review clearly shows potential of DOM as HM extractant. Through its carboxylate and/or phenolate functional groups, DOM can form soluble complexes with cationic HMs, e.g. Cd^{2+} and Cu^{2+} , while extraction of anionic HMs, e.g. arsenate depends on dissolution of the sorbents, mainly Al and Fe oxides. In addition to the soil HM extraction potential, use of DOM will probably extract organic pollutants, stimulate microbial activity and improve soil structure. However, the efficiency of DOM as extractant depends of numerous variables/factors, e.g. composition of the DOM and polluted soil, and of external conditions such as pH, solution: soil ratio and extraction time. The influence of these variables will be indicated by examples of DOM extraction of HMs from various polluted soils. Furthermore, the difference between use of soil DOM and LMWOA DOM will be outlined.

HUMIC SUBSTANCES FROM A POINT OF BIOLOGICAL EVOLUTION AND PLANT PHYSIOLOGY: UNLIKELY, POSSIBLY, POTENTIALLY

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Keywords: adaptogenic activity, biological evolution, plant growth-affecting activity, plant physiological adaptations

Abstract: In spite of growing awareness on potential beneficial effects of humic substances on plants within the last decade, many existing controversies together with significant lack of general scientific evidence still restrict the wide use of the respective products in agricultural practice. The aim of the present talk will be to analyse putative effects of humic substances on plants on the basis of both evolution of plant adaptations to the environment as well as on plant functions, especially, at the level of nutrition and environmental constraints. Emphasis will be given on sorting out these effects and possible mechanisms of action according in respect to their probability to generate practical benefits of use in agricultural practice. It is evident that plant growth cannot be analysed separately from soil processes, where microbiological activity is a main provider of mineral nutrients for plant needs. In this respect, humic substances, acting through stimulation of certain aspects of soil microbiology, will benefit plants indirectly. Plant hormone-like activity of humic substances is another possibility for consideration, but growth stimulation through exogenous hormones will benefit plant only in the case of optimum mineral nutrient supply. Last but not least, humic substances can increase plant adaptogenic potential, acting as inducers of certain defence responses. However, concept of induced defence implies that some significant part of internal plant resources need to be converted from supporting growth to defence, benefiting plant only in conditions of severe environmental problems.

VARIABILITY OF HUMIC ACID PROPERTIES DEPENDING ON THEIR PRECURSOR MATERIAL: A STUDY OF PEAT PROFILES

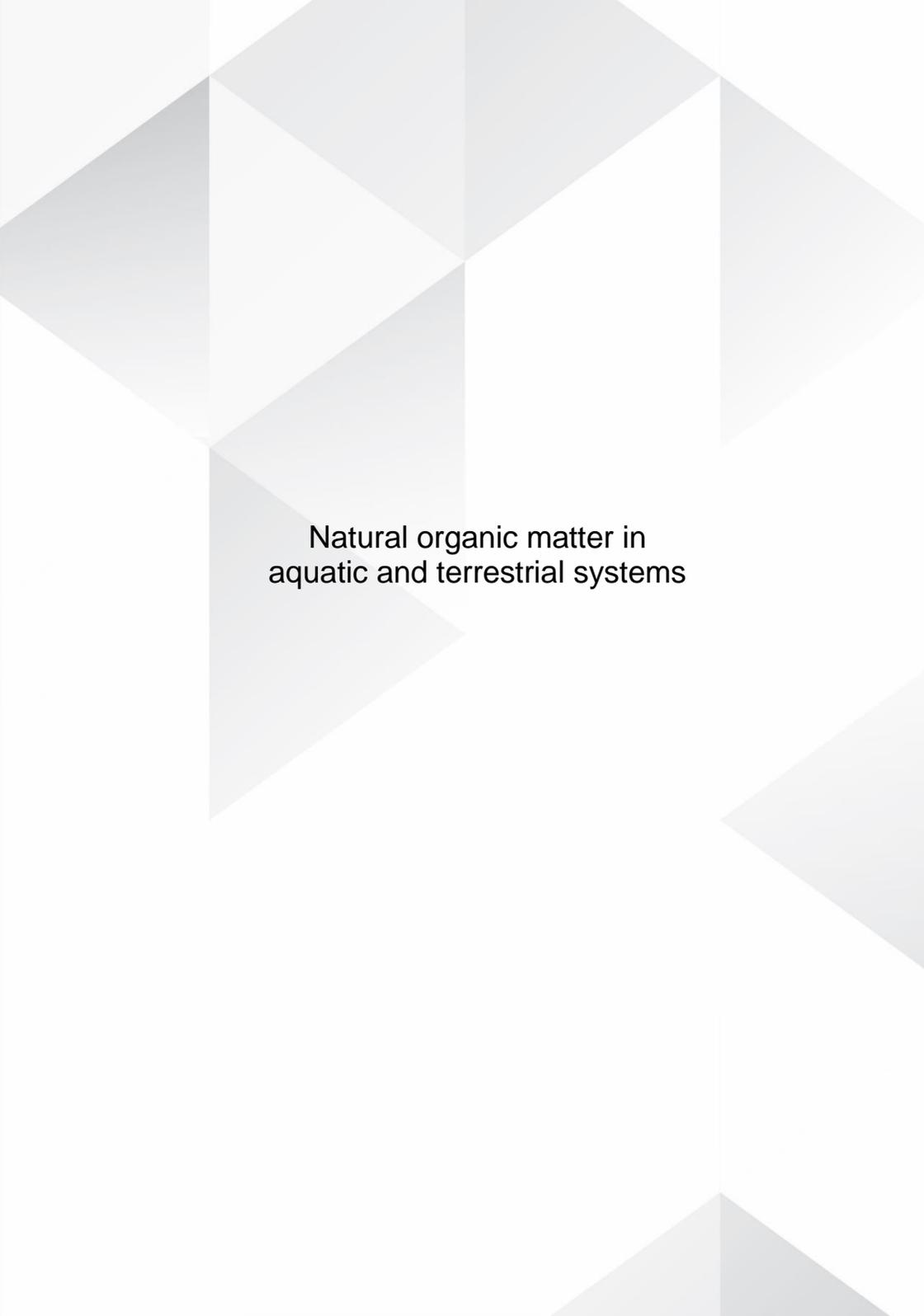
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Keywords: peat, multiproxy analysis, humic acids, humification

Abstract: Analysis of peat composition variation, presence of trace elements in the peat and HSs within peat profiles can provide information on the character of transformation of organic matter, important for C biogeochemical cycling, but also about impacts of climate change and human activities. In peat the transformation and decay process of living organic matter (humification) is retarded by the acidic and anaerobic environment, but at the same time the peat can provide information on environmental and paleo-environmental conditions of the past. The aim of the present study is to analyse the elemental and functional composition, spectral characteristics of humic acids isolated from a well characterized raised bog peat profiles to evaluate the impact of the character of humification processes on the peat HA properties. A comparative and complex characterization of humic acids (HAs) isolated from peat profiles of different origin in Latvia was carried out. Elemental and functional analysis of the isolated HAs was done, their acidity and molecular weights estimated. Spectral characterization included UV–Vis, IR, and electron spin resonance and fluorescence spectra. Structural characterization of HAs was by both ^1H and ^{13}C nuclear magnetic resonance spectra. Comparison of position of studied humic acids in the Van Krevelen graph was done, thus locating them in the biogeochemical transformation processes of organic matter. Properties of HAs isolated from the Latvian peat were compared with HA from other sources (soil, water, coal and synthetic humic substances). Major properties of peat HAs depended on their origin, indicating the importance of humification processes. HAs isolated from peat of more recent origin were more similar to soil HAs, but from older sources there was a greater degree of humification. Changes of surface tension of solutions of humic acids stress the differences in aggregation character – ability to form supramacromolecular complexes of humic substances and impact of environmental conditions on the surfactant properties of humic matter. Amongst the main objectives of the study was the identification of the dependence of the humic acid properties on the composition of original living matter in the peat, especially considering high variability of peat composition in the studied bogs. Despite some correlation between peat botanical composition and properties exist, in general the similarities are much more expressed, thus indicating the significance of microbial decay processes on the properties of humic material.

Acknowledgements: This work has been supported by the Latvian Council of Science, Fundamental and applied research project Nr. lzp-2018/1-0009 “Properties and structure of peat humic substances and possibilities of their modification”



Natural organic matter in
aquatic and terrestrial systems

ISOLATION, CHARACTERIZATION AND QUANTITATIVE ANALYSIS OF HUMIC ACIDS OF TURKISH PEATLANDS

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Keywords: Peatland, Humification, Humic Acid, FTIR, UV-vis spectroscopy.

Abstract: Humic acids (HAs) are versatile natural products which are alkali soluble part of humic substances (HA, FA and Humas). HAs are used in many applications such as agriculture, animals health and feeding, pharmaceutical, foods, cosmetics and biomedical applications. In our present study, extraction and purification of HA were carried out from 45 samples, which were collected on different depth from eighteen points of Danamandira Çatalca lake, Istanbul, Turkey. Purified HAs were characterised through spectroscopic analysis and, identified the more humic concentrate region of the lake. Humic acids were isolated by the classical method. Percentage yield of HAs of different peat samples was calculated using electric balance. HAs obtained from Turkish peat samples were characterized by the use of spectroscopic analysis. Powder forms of HAs were used for FTIR analysis but in case of UV-vis and fluorescence spectroscopy, 10 mg isolated HA dissolved in 10 ml of 0.05 N sodium hydroxide solution and required amount of solution used for analysis. In Quantitative analysis, maximum and minimum yield of isolated HAs were 43% and 0.517% . In FTIR analysis, absorbance peaks at 3350 cm⁻¹, 3210 cm⁻¹, 2950 cm⁻¹, 1700 cm⁻¹, 1608 cm⁻¹, 1423 cm⁻¹ and 1223 cm⁻¹ attributed to the stretch of (-OH), (-COOH), (-C-H), (C=O), (C=C of aromatic ring) and (C-H of aliphatic groups) respectively, were observed. UV-vis spectroscopy analysis showed maximum absorbance peak at 215 nm which was same for all isolated HAs. In Fluorescence Spectroscopic analysis, all purified HAs were showed the same emission peak at 460 nm (excitation wavelength 370 nm). Isolated HAs were considered as pure and HA content of Danamandira Çatalca lake's peatland was satisfactory.

CHANGES IN ORGANIC MATTER AND NUTRIENTS IN HUMAN AFFECTED SOIL SYSTEM FROM POLAND

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Keywords: forms of organic matter; nitrogen; phosphorus; soil; peat

Abstract: The aim of the present study was to investigate the organic carbon, nitrogen and phosphorus compounds in mineral soils and peats depending on their age and plant composition. Different plant covered structures, like shelterbelts (SB) around the agricultural fields and peats can control organic and nutrients cycles in soils. In addition, they show substantial ability to decrease distribution of chemicals among the ecosystems. Nowadays, it is important to limit pollutants concentration and spreading into surrounding watershed in order to maintain water quality.

The study involved the soil samples from two SBs of different age and composition of plants on hapludalfs soils, and a transect of 4.5 km long peatland, located in the General Dezydery Chłapowski Landscape Park in Turew, Poland. Total organic carbon (TOC), hot water extractable organic carbon (CHWE) and dissolved organic carbon (DOC) were determined by high-temperature combustion and high-performance size exclusion chromatography (HPLC-SEC). The compositional changes of DOC were evaluated spectrophotometrically using absorbance ratios at several wavelengths. Moreover, nutrients nitrogen (total, nitrate, ammonium, organic) and phosphorus (total, inorganic, organic) were determined by HPLC and spectrophotometry.

Significant differences were observed in chemical and physical properties among studied soil samples. The soil character affected TOC value, being highest in soil under old (52.4 g kg⁻¹) and lowest under young (6.9 g kg⁻¹) SBs, and between 245 to 329 g kg⁻¹ in peat soils. Old SB DOC contained more aromatic condensed organic constituents than the other samples. Our results revealed that over 97% of the nitrogen in peat soils was in organic form. The content of phosphorus decreased in the order: peat, old SB, new SB.

Present study showed the usefulness of chromatographic and spectrophotometric methods in soil organic matter investigations. Our results can be used for better understanding the migration of carbon and nutrients in different ecosystems.

VOLTAMMETRIC DETECTION OF IRON-HUMIC COMPLEXES. A POWERFUL TOOL TO QUANTIFY THE ROLE OF HUMICS IN THE BIOGEOCHEMICAL CYCLE OF IRON IN SEAWATER

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Keywords: iron-humic complexes, catalytic cathodic voltammetry, iron ligands seawater

Abstract: One of the many analytical principles used to determine bulk concentrations of humic substances is their adsorption on the surface of the mercury electrode and detection by voltammetry. The preferred method in oceanography relies on the adsorption of iron-humic complexes with reduction of iron during a cathodic scan and catalytic enhancement of the signal by addition of the strong oxidant bromate. Since 2007, the method has been successfully used to determine the concentration of humics in seawater after calibration with IHSS standards. The excellent limit of detection has allowed the report of bulk HS concentrations not just in estuarine and coastal waters but also in remote and deep ocean waters. Here we present an upgrade of our catalytic voltammetric method designed to measure the concentration of iron-humic complexes at natural iron concentrations. This new method constitutes a change of the analytical paradigm in the study of metal organic speciation in seawater; in addition to the measurement of the total concentration of a metal and the bulk concentration of its ligands, we may determine the concentration of iron bound to a specific type of ligands. Since iron cycling is strongly dependent on its organic complexation, this development will improve our understanding about the solubility and reactivity of iron in the ocean. We also present here the application of the method to the analysis of surface Arctic samples collected in the Eurasian basin across the Transpolar Drift. Our results confirm previous indirect observations that humics control iron transport from the Siberian coast, across the Arctic into the Fram Strait.

FTIR SPECTROSCOPY AS A TOOL FOR CHARACTERIZATION OF SOIL ORGANIC MATTER DEPENDING ON SOIL TYPE AND TEXTURE

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Keywords: FTIR spectroscopy, soil organic matter composition, soil type, texture

Abstract: Soil organic matter (SOM) composition can be defined as the amount of functional groups (i.e. carboxyl (C=O), alkyl (C-H) and hydroxyl (O-H) groups). Differences in SOM composition can be analysed with Fourier Transform Infrared (FTIR) spectroscopy which is a powerful tool for identifying the chemical structures of SOM as soil samples are measured directly and provide the information of SOM structure without using solvents.

The objective of this study was to examine SOM composition of different soil type. The effects of soil texture and moisture regime on composition were also estimated. Soil samples were collected from humus horizons of 72 fields (66 arable land and 6 long-term grasslands) in Estonia. In total 13 different soil type were presented including 4 gleysols. The soil texture and soil organic carbon (SOC) content were measured. Spectral characterization of bulk soil samples was performed by Thermo-Nicolet iS10 FTIR (ThermoFisher Scientific) for bands representing organic functional groups, including phenolic O-H with amine and amide N-H (3365 cm^{-1}), aliphatic C-H (1417 cm^{-1}) and aromatic C=C (1633 cm^{-1}).

Significant differences occurred among some soil types in SOC content and absorbance of selected peaks. There are a strong positive relationships between SOC and absorbance of selected functional groups. The absorbance of aromatic C=C, aliphatic C-H and phenolic O-H were highest in gleysols which also had the highest SOC content. Soils with clay texture had highest SOC content and the highest aromatic C=C and phenolic O-H absorbance and these absorbance's are higher also in grassland soils compared to soils of arable land though the differences in SOC content depending on land use is missing.

This study implicates that FTIR spectroscopy enables to describe composition of SOM depending on soil type, texture and moisture regime and generally different functional groups are related with SOC as main characteristic of soil quality.

INTEGRATIVE CHARACTERIZATION OF DISSOLVED NATURAL AND ANTHROPOGENIC ORGANIC MATTER USING HPSEC-UV-FLUORESCENCE

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Keywords: natural organic matter (NOM); anthropogenic organic matter; drinking water treatment; wastewater treatment; size-exclusion chromatography

Abstract: The climate change, accelerating industrial and agricultural activities, and other megatrends rapidly deteriorate quality of water resources through complex chemical contamination.

We report on application of a novel integrative analytical approach based on size-exclusion chromatography (HPSEC) for advanced characterization of dissolved natural and anthropogenic organic matter in aquatic environment and along urban water cycle. In HPSEC, molecules are separated according to their apparent molecular weight (MW) into fractions, which can be simultaneously characterized by several detectors (UV, fluorescence, etc.) to create unique fingerprints.

Several drinking and wastewater treatment plants, located in Finland, were systematically monitored using the one approach. Removal of high, intermediate, and low MW fractions of natural and anthropogenic humic-, fulvic-, and protein-like compounds was followed step-by-step (a) from raw water to tap water and (b) from untreated wastewater to treated wastewater effluent. Efficiencies of various treatment processes (pre-ozonation, coagulation, biological treatment, ceramic filtration, etc.) were evaluated. Recalcitrant low MW humic/fulvic-like fractions that passed through treatment systems were detected. Strong linear correlations were observed between BOD, COD, DOC, UVA254 and tyrosine-like, tryptophan-like fluorescence of wastewater organic matter.

The same HPSEC-based approach was also applied to trace wastewater effluent discharges in a receiving water body.

Small sample volume, minimal pre-treatment, speed of the analysis, possibility of automatic data processing is among practical advantages of the HPSEC approach, which can be used to monitor and optimize full scale water treatment processes and to screen quality of aquatic environment.

PROPERTIES OF SOIL ORGANIC MATTER IN HUMUS FORMS IN FORESTS FORMED ON DRY MINERAL SOILS IN LATVIA

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Keywords: forest soil, humus forms, carbon, humic substances

Abstract: Over the last decades more attention has been paid to carbon accumulation in soil, more recently, to soil humus forms, as they indicate environmental conditions and state of soil organic matter (SOM). There is insufficient information on soil and forest type impact on the chemical properties of soil, SOM and humus form. This knowledge about humus chemical properties is crucial for modelling C and N accumulation and storage in forest soils. Therefore, the aim of this study was to characterize soil humus forms, humus chemical properties and C stock in the forests formed on dry mineral soils, to clarify the relationships of spatial distribution of soil humus forms in the forests formed on dry mineral soils. We studied humus forms in 44 sampling sites in different types of forests. Soil samples were collected from genetic O and A (EA) horizons and analysed for organic carbon (C_{ORG}) and total nitrogen (N_{TOT}) content. Soil NaOH extracts were used to determine properties of SOM – alkali extractable carbon (C_{HS}), compositions and humification index (HIX) of soil humic substances (HS). Generalized linear model analysis showed that distribution of *psammomor*, *mor* humus forms are related to oligotrophic forest types, but glacial, glaciolimnic sediments are the main factors that determines the occurrence of *mull* humus form. *Psammomor* and *mor* humus have the lowest C_{ORG} stock in the topsoil, but more than 75% of the total C_{ORG} is accumulated in the O horizon. *Mull* humus form soils have the highest C_{ORG} stock in the mineral topsoil, it accumulates 80% of the total topsoil C_{ORG} stock. Ah horizons of the *mull* humus soils also have the significantly lower C_{HS} to C_{ORG} ratio. Humic acid (HA) to fulvic acid (FA) ratio varies from 0.51 in *mor* humus mineral topsoil to 0.86 in *moder*, to 1.13 in *mull* humus topsoil, however differences aren't statistically significant.

FRACTIONAL DISTRIBUTION OF NOM-LIKE COMPONENTS IN HARD WATERS UNDER NON-OXIDATIVE AND OXIDATIVE CONDITIONS

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Keywords: molecular size distribution, novel photocatalysts, solar photocatalysis, water treatment

Abstract: The major aim of this study was to investigate the influence of photolytic and photocatalytic degradation processes on the molecular size distribution profiles of natural organic matter (NOM)-like matter in hard waters. For this purpose, synthetically prepared hard water samples were exposed to photolytic and photocatalytic degradation processes by using solar simulator. TiO₂ P-25 and ZnO were selected as commercial photocatalysts whereas N-doped TiO₂ and TiO₂/ZnO nanocomposite were nominated as synthesized photocatalysts. Following photolytic and photocatalytic degradation processes, samples were fractionated into appropriate molecular size fractions *i.e.* 100 kDa, 30 kDa, 10 kDa, 3 kDa, and 1 kDa by using stirred cell ultrafiltration system. Changes in humic-like matter with respect to different molecular size fractions were followed by UV-vis and fluorescence spectroscopic parameters as well as dissolved organic carbon content. As an advanced fluorescence technique excitation emission matrix (EEM) in combination with PARAFAC modeling was used for further understanding of hydrophobic, hydrophilic, multi-ligand, and polydisperse character of humic-like matter in NOM composition, that significantly changes with molecular size distribution profiles. Transformation of higher molecular size components into lower molecular size components were noticeably observed by the application of molecular size fractionation procedure as well as EEM fluorescence features. Moreover, EEM fluorescence features in combination with PARAFAC modeling would bring further insight on the understanding transformation of fluorophobic components of water samples exposing to photodegradation and photocatalytic degradation.

FUNCTIONAL MECHANISM AND CONTENT OF HUMIC SUBSTANCES IN SAPROPEL

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Keywords: sapropel, Eastern Latvia, humic substances

Abstract: Humic substances (HS) themselves are not a fertilizing agent because do not contain nutrients necessary for plants in sufficient quantities and in the right proportions. However, they are involved in various functional processes, e.g., promote accumulation of mineral substances in form of humates in soil and stimulate uptake of these elements into plant tissues. They create the most widespread natural organic matter found in sediments, soils and waters. Organic carbon in soil (up to 70%) and peat (up to 90%) usually occurs in the form of HS. Properties and application efficiency of humus depend on the source of HS. Freshwater sapropel is a huge reservoir of HS with superior biological activity, although their total content is lower than in peat. Investigation of HS content in sapropel is significant for the Baltic States and Northern Europe due to wide distribution and availability of sapropel in freshwater bodies. In this research sapropel samples were derived from Lake Pilvelis, Lake Pilcines, Lake Vevers, Lake Liducis and Lake Padelis situated in Eastern Latvia. Content of HS in organic rich lake sediments such as freshwater sapropel varies from 9 mg g⁻¹ to 106 mg g⁻¹, humic acids: 5-95 mg g⁻¹ and fulvic acids 4-11 mg g⁻¹. Sediments more rich in HS are those which consist from peat forming plants, but total organic carbon concentration is higher in HS which are formed from algae and animal remains.

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Global change and natural organic matter flows

STABLE ISOTOPE (δC , δN , δO) COMPOSITION CHARACTERISATION OF PEAT AND PEAT HUMIC MATTER FROM RAISED BOG PROFILE

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Keywords: peat, humic acids, stable isotopes, humification

Abstract: Peat and peat humic substances research provide unique possibilities to study humification processes in peat profiles. Studies of peat profiles provide possibility to analyse impact of precursor biological material, humification conditions and other factors and processes. The aim of this study is to analyse stable isotope (δC , δN , δO) ratios in 3 in-depth characterised raised bog peat profiles and humic acids isolated from them. The stable isotope ratios were compared with peat decomposition, humification indicators, botanical composition, peat elemental composition. The peat humic acids were characterised using element analysis, spectroscopic characterisation, UV, FTIR, fluorescence, ^1H , ^{13}C NMR), functional group analysis. Results of the study indicates good perspectives of stable isotope ratio use for characterisation of peat humification process.

Acknowledgements: This work has been supported by the Latvian Council of Science, Fundamental and applied research project Nr. lzp-2018/1-0009 "Properties and structure of peat humic substances and possibilities of their modification".

COMPOSITIONS AND CONTENTS OF N-ALKANES AND N-METHYL KETONES IN SOILS ALBIC RETISOLS UNDER BROAD-LEAVED FOREST PLANT COMMUNITY

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Keywords: NOM, carbon cycle, biomarkers, GC/MS

Abstract: Soil organic matter (SOM) plays a key role in the ecosystem functioning. Such individual components of SOM lipid fraction as n-alkanes are widely used as biomarkers of vegetation type. n-Methyl ketones are produced during first steps of n-alkanes degradation. Annual dynamic of main alkane homologues ratios – CPI, OEP, LSR, calculated for soil density fractions allows to evaluate the extent of recovery of carbon pools related to different stabilization mechanisms of SOM.

The test plot was selected under lime tree plant community where typical Albic Retisols are developed. Sampling was made from leaf litter, roots of topsoil, soil of horizons AY, AYel, EL, BT, twice in autumn and once in summer. Soil density separation was performed using flotation method in heavy liquid ZnCl₂ ($\rho = 1.60 \text{ g cm}^{-3}$), the two fractions was separated – the free light fraction and the heavy one. In these samples total C and N concentrations were determined with a CHNS analyzer (Elementar). Lipid components were extracted by the method of pressurized fluid extraction in ASE 200 (Dionex). Sample purification and fractionation were carried out in an adsorption column with aluminum oxide. The qualitative identification and quantitative determination of target components were performed by GC/MS Agilent 6890N (Agilent Technologies) with a quadrupole mass-selective detector MSD5973N (Agilent Technologies).

The contribution of the light fraction is about 5% of the organic carbon of the soil according to the results of dense fractions analysis of the upper horizons.

The relative content of n-alkanes in SOM increases for the bulk samples down the soil profile up to 2 times and reaches maximum quantity in the EL horizon -725 $\mu\text{g/gC}_{\text{org}}$. Analysis showed significant seasonal changes in the content and compositions of n-alkanes. In summer their amount in light fraction is about 1-2% of total carbon, and increased up to 4-8% during the autumn. n-Alkane content increases from 195.3 to 360.6 $\mu\text{g/gC}$ in bulk soil with the dominance in the upper part of the profile of long-chain plant origin alkanes (C27, C29) and an increase of the part related to medium-chain in underlying horizons as a result of a greater contribution of bacterial biomass (LSR increases from 8.5 to 10.5).

VARIABILITY OF CONCENTRATIONS OF NATURAL ORGANIC MATTER IN THE DAUGAVA RIVER CATCHMENT

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Keywords: water colour, dissolved organic carbon, total organic carbon, catchment impact, long-term trends

Abstract: Daugava river is the third largest river in the Baltic Sea catchment. Therefore, water chemical composition in the Daugava river affects loads of dissolved and suspended organic matter to the Baltic Sea, where it plays a key role in variety of natural processes. The aim of this study was to evaluate spatial and temporal variability of indicators of natural organic matter (NOM) in the Daugava River basin. Monitoring data of water colour, concentrations of dissolved and total organic carbon (DOC and TOC), general aquatic chemistry and water discharge was obtained from the Latvian Environment, Geology and Meteorology Centre. Water colour in sampling stations on the Daugava river and its largest tributaries varies from 60 to 200 mg Pt/Co and concentrations of TOC are in range from 11 to 26 mg/L. Highest concentrations of NOM indicators are found in tributaries with larger share of wetlands and forests. Most of the TOC are found in dissolved form, and concentrations of DOC varies from 10 to 26 mg/L. Particulate organic carbon constitutes only 1.5-11.3 % of TOC content. Concentrations of NOM indicators have increased since 1990ies as well as their intra-annual variability during 2000ies are higher than that during 1980-1990ies. Similarly, increasing concentrations of NOM in surface waters have been recorded in Europe, North America and elsewhere. Climate change, land-use changes, precipitation chemistry and their impact on hydrological regime are mentioned among factors behind increased concentrations of NOM.



Humic substances in
Nordic environment

BIOSORPTION OF HEAVY METALS ONTO FEN PEAT HUMIC ACIDS

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Keywords: fen peat, biosorption, humic acids, heavy metals

Abstract: Heavy metals are extensively used in the industrial activities, thereby the environmental pollution is inevitable. Heavy metals are not biodegradable hence there is a need in environmental treatment technologies to limit their accumulation and reaching toxic amounts in environment. There is a number of conventional techniques that can be applied for heavy metal treatment, such as, - precipitation, coagulation, ion exchange, membrane filtration or electrochemical technologies. However, these methods are cost-ineffective and difficult to use on large scale. Biosorption using humic acids is a price-friendly alternative. Humic acids are omnipresent in the environment and compose the majority of non-living organic matter. It is known that humic acids are polyfunctional and enabled to interact with metal ions and forming stable complexes with heavy metals. The high surface area, carboxylic and phenolic group content and hydrophobic nature of humic acids work as an advantage in regard to metal adsorption, thus they have high value in biosorption technologies. Moreover, humic acids extracted from raised bog peat are known to have better performance than most other commercially available humic acids. At the same time, the knowledge on fen peat humic acids is limited. This work was carried out to evaluate the efficiency of fen peat humic acids to absorb heavy metals, thereby observing the possibilities of limiting their release further in the environment. In this study we tested fen peat humic acid adsorption capacity in aquatic environment using solutions with chromium ($\text{CrCl}_3 \times 6\text{H}_2\text{O}$), copper ($\text{CuSO}_4 \times 5\text{H}_2\text{O}$) and lead ($\text{Pb}(\text{NO}_3)_2$) at concentrations of 10.0, 50.0, 100.0, 250.0 and 500.0 mg/L. Models that were used to evaluate the adsorption mechanisms were Langmuir and Freundlich. Results show that the high adsorption capacity and high abundance in the environment allow to evaluate the application of fen peat humic acids in biosorption as an equal for commercially available humic acids.

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HUMIC COMPOUNDS AS THE REGULATORS OF HEAVY METAL IONS MOTILITY IN THE ENVIRONMENT

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Keywords: humic compounds, sorption, heavy metal

Abstract: Humic compounds (HC) are one of the most wide-spread nature organic compounds on the Earth. HC take part actively in the redistribution of heavy metals (HM) in nature. They with HM create as sparingly soluble metal humic complexes (MHC) thereby decreasing HM motility, as sedimentation resistant compounds. The aim of the research was to study the formation peculiarities of MHC and their steadiness in in wates media.

It has been established that cations by the activity of its HC connection can be arranged in a row: $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+}$. Regularities obtained are fair as for mono- so for binary solutions although during the change of media reaction the HM sequence in the raw can change.

It has been established by the method of the adsorption of acid and the main indicators that Cu^{2+} ions interact with both strongly acidic and weakly acidic HC centers. The low selectivity of HC functional groups during Cu^{2+} ions interactions are due to the high complexing ability of the latter with the majority of HC functional groups even in acid media. This circumstance is fair also for Cr^{3+} cations. For Ni^{2+} ions there is more clear selectivity in an interaction with HC. They interact with functional groups which have a low pK_a meaning and only in a small amount with functional groups with a high pK_a meaning. Co^{2+} cations are able to interact only with strongly acid functional groups. At the same time obtained data unequivocally indicate that the powders of dry MHC contain enough vacant sorption centers. The preparations studied On the decrease of the amount of free centers can be arranged in a row: $\text{H-HC} > \text{Co-HC} > \text{Ni-HC} > \text{Cr-HC} \geq \text{Cu-HC}$.

It is shown that the MHC sedimentation stability is observed till the certain amount of HM in it achieving and depends on the specific content of ionized functional groups which are capable to participate in ion exchange with cations.

ELEMENTAL COMPOSITION AND STRUCTURAL FEATURES OF HUMIC SUBSTANCES IN FOREST FLOOR OF SANDY SOILS WITH DIFFERENT R₂O₃ CONTENT

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Keywords: humic acids, elemental composition, ¹³C NMR, Podzol, pine forest

Abstract: Up to 80% of fine roots can be contained in the forest floor (FF); therefore, the composition and pools of organogenic horizons largely determine the productivity of the trees. The stages of litter transformation in FF are poorly studied. We tested the hypothesis of the influence of R₂O₃ on the quality as of the whole FF as humic substances in FF. The soils of four key plots of dry pine lichen-green moss forests of the Leningrad Region differed in terms of the R₂O₃ content in soil-forming sands (1.7–32.0 mass %) and in forest floor (4.1–17.1 mass%). The age of the main generation of pine was from 100 to 130 years. The FF thickness varied from 7 to 10 cm. Sampling was carried out in fivefold repetitions of L, F, H sub-horizons. The general physicochemical characteristics of the soil and the total elements were determined. Humic substances (HS) isolated from fermented and humified sub-horizons (F and H) have been characterized for their elemental composition (C, N, H). Changes in molar H:C, O:C, C:N and ratio of aromatic and aliphatic fragments have been revealed. Solid-state ¹³C nuclear magnetic resonance spectroscopy was applied to identify the structure of HS. HS of the FF showed low aromaticity and absence of correlation with R₂O₃. The ratio of gross C/N of the F and H sub-horizons of forest floor were from 28-32 to 37-43. The gross C/N and the total Fe₂O₃ content were not correlated. A weak correlation was found with the Al₂O₃ content. More clear dependences were found for C/N of HS with Fe₂O₃ and Al₂O₃ 1) $y_1 = -2.7124x + 35.182$, $R^2 = 0.698$ and 2) $y_2 = -0.728x + 35.431$, $R^2 = 0.719$ correspondingly. Conclusion. The effect of R₂O₃ was revealed only in relation to the nitrogenous part of the HS.

LIGNIN PHENOLS IN SOILS OF THE SECONDARY NORDIC FOREST

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Keywords: lignin phenol, secondary forest, southern taiga, wood tissues

Abstract: The source of lignin phenols in soils are the lignocelluloses (70 to 90 % dry weight of plant tissues). Trees of the Nordic ecosystems contain the highest lignin amount, but they did not play the important role in humus formation. The aim of this work was a detailed characterization of the lignin phenols composition and processes of their transformation in soils of the secondary forest. The objects of investigation were Gray soils of the southern taiga (Russia). An experimental plots (600 m²) with the different types of trees (spruce, birch, pine, aspen, larch, cedar) was created in 1971-1972 (the soil samples were provided by Prof. W. Zech). The grassland (1400 m²) was left as a control. The process of lignin determination in the soils included the alkaline oxidation of a sample using copper oxide at 170° under the pressure in a nitrogen medium. The lignin phenols were divided by a gas-liquid chromatograph. The isolation of lignin oxidation products from the litters of different plant associations showed, that their lignin parameters were similar, but less contrasting than those in plant tissues. The highest content of lignin was found in the spruce forest litter. The composition of the coniferous litters (spruce, fir, pine, larch) was characterized by the accumulation of vanillic phenols and retained tendency toward a decrease in the content of syringic and coumaric structures. The deciduous forest litter (birch, aspen) contained similar proportions of vanillic and syringic phenols and a lower content of ferulic acids. Cinnamic phenols predominate among the lignin phenols of the grass community in the control plot. The presence of cinnamic phenols in the composition of soil lignin in trees ecosystems indicates that 50 years was insufficient for the transformation the difficulty decomposable grass lignin.

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CHANGE OF COLLOID-DISPERSE PROPERTIES OF HUMUS SUBSTANCES UNDER CRYOGENIC IMPACT

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Keywords: humic substances, cryogenesis, colloid-dispersed parameters of humic substances

Abstract: Humic soil substances have a significant role in the formation of soils resistance to external influences. Under the conditions of climate change, the influence of cryogenic processes on the change in the properties of soil humus substances is not well studied.

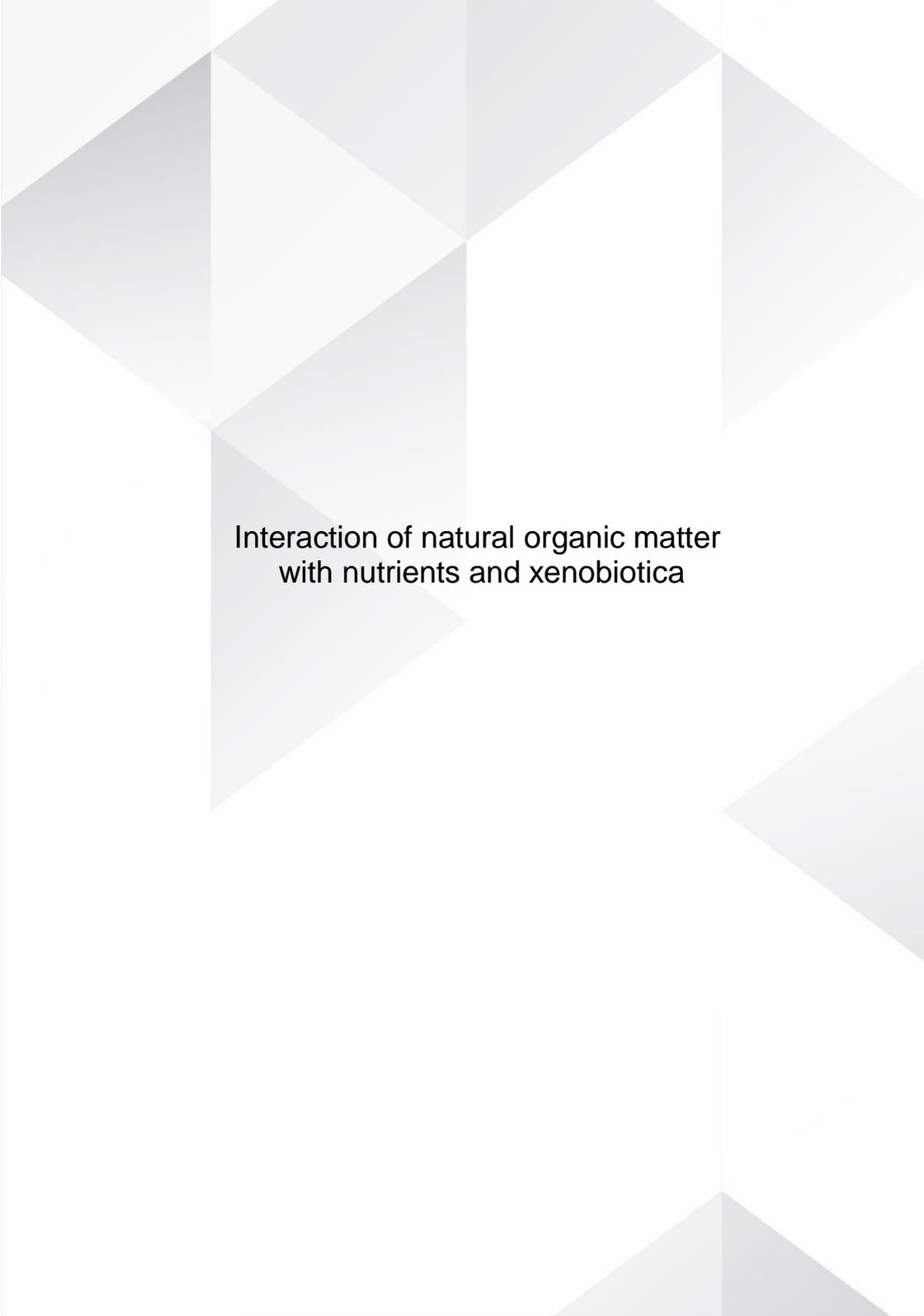
In this paper, based on example of humic substances extracted from the northern taiga podzolic soil (Arkhangelsk Oblast, Russia), the effect of cyclic cryogenic processes on the colloid-dispersed properties of soil humus substances was shown. Extraction of humic substances from the coarse-humus horizon was carried out with using 0.1 N NaOH solution with water ratio of 1:50 during the day without heating. Next, the solution was acidified with a 0.1 N HCl solution to pH 6.5. Cryogenic conditions were modelled by 4 consecutive cycles of "freezing (-18°C) - melting (+4°C)". The measurement of colloid-disperse properties was carried out at a concentration of humic substances of 100 mg/l by the method of quantum correlation spectroscopy with using a Horiba LB550 laser analyser.

The initial sample of humic substances is characterized by high polydispersity. At low concentrations (100 mg/l) in the solution of humic substances are fixed predominantly supramolecular formations of diameter from 80 to 3000 nm, which caused by their functional nature and indicates a high ability for intermolecular interactions.

Under cyclic cryogenic effects gradual destruction of the supramolecular formations of humic substances is observed (decrease in the contribution to the light scattering of the group of large associates with diameter from 500 to 3000 nm). With an increase in the number of freeze-thaw cycles from 1 to 4, there is a redistribution of particle sizes from diameter from 80–500 nm to diameter from 20–100 nm.

Thus, it has been shown that cyclic cryogenic effects on humic substances contribute to the reduction of their colloid-dispersed characteristics due to the partial destruction of macromolecular formations.

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Interaction of natural organic matter
with nutrients and xenobiotica

ECOLOGICAL ASPECTS OF THE HUMIC PREPARATIONS APPLICATION IN AGRICULTURE

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Keywords: Humic preparations, Winter wheat, Herbicides

Abstract: The object of study was the humic preparation BIO-Don, obtained by alkaline extraction from biohumus. Humic preparations contribute to a better development of plants, especially their root systems, increase the intensity of root exudation. As a result, the biological activity in the rhizosphere zone increases, leading to a more complete assimilation of nutrients, both from soil reserves and from fertilizers. Field experiments were performed on winter wheat. The soil was ordinary carbonate chernozem (Haplic chernozem). The control of weeds with the help of the sulfonylurea herbicide Granstar Pro allows to retain the soil moisture necessary for the formation of the crop, and to increase the yield by up to 0.6 t/ha, which is extremely important under the conditions of insufficient moisture. The combination of herbicide with humic preparation provides an increase in winter wheat yield. The research aims to establish the optimal combination of the humic preparation with various doses of the sulfonylurea herbicide when growing winter wheat.

It has been established that the complex use of the herbicide and the humic preparation BIO-Don on winter wheat allows to alleviate the toxic side effect when using the herbicide of the sulfonylurea group at doses of 10 and 15 g/ha. The wheat yield was increased by 0.4–1.3 t/ha in different years of research, depending on weather conditions. The joint use of the humic preparation and the herbicide in high doses (20–25 g/ha) in a tank mix provides a reduction in the toxic effect. The alleviation of chemical stress leads to a significant increase in the biological activity of the plant rhizosphere zone. Changes in the number of microorganisms largely depend on the root exudation. The activation of rhizospheric bacteria affects the intensity of biochemical processes and, as a result, increase the content of mobile forms of phosphorus.

Thus, the humic preparation used at a dose of 1 L/ha for treating plants in the tillering and booting stages is most effective as a tank mixture with the herbicide of the sulfonylurea group 'Granstar Pro' at a dose of 15 g/ha and lower. The joint use of the preparations allows to reduce pesticidal load on the soil and other components of an agrocenoses.

THE EFFECT OF THE SEDIMENT ORGANIC MATTER ON CONTENT AND POTENTIAL ECOTOXICITY OF PAHS IN BOTTOM SEDIMENTS FROM ROŻNÓW RESERVOIRS (SOUTHERN POLAND)

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Keywords: bottom sediments, organic matter fraction, PAHs, ecological risk assessment, PCA

Abstract: The aim of the study was to assess the influence of the content of organic matter fractions on the concentration, sources and ecological risk of PAHs in bottom sediments. The Rożnów dam reservoir is located in the Lesser Poland Voivodeship in southern Poland and is one of the largest retention reservoirs in Poland. The samples of bottom sediments were collected at 46 points located along the reservoir. The content of total organic carbon (TOC), humic substances (carbon of humic, fulvic acids and humine), dissolved organic carbon, black carbon and 16 PAHs in sediments was determined. The content of PAHs in the bottom sediments of the Rożnów reservoir was in the range of low and medium values (8.0-980.5 µg/kg). Generally, 4-ring PAHs were predominant hydrocarbons. Most of the sediment samples exhibited the ecotoxicological criterion of level I - the PAH content was below the TEC value. The assessment of potential ecological risk indicated that non-adverse effects on the benthic fauna may occur for sediments from Rożnów reservoirs. Significant positive correlations between PAH content and TOC, humine and black carbon demonstrate that these pollutants have a strong affinity for stable fractions of organic matter in the studied sediments. The identification of above interactions is useful for the prediction of the fate of PAHs in the sediments as well as the assessment of pollution risk.

Acknowledgements: The study was financed by grant no. 2016/21/B/ST10/02127: "Assessment of the bottom sediment organic matter on bioavailability and toxicity of chemical compounds" provided by the National Science Centre, Poland.

THE EFFECT OF UV IRRADIATION ON THE ABSORPTION AND FLUORESCENCE SPECTRA OF HUMIC ACIDS AND THEIR PHOTOCHEMICAL PROPERTIES

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Keywords: humic acids, UV irradiation, excilamps, absorption and fluorescence spectra, photodegradation

Abstract: The absorption and fluorescence spectra of different humic acids (HAs) samples has been investigated. The samples of HAs were prepared from peat of Western Siberia region, other HAs were isolated from Arkhangelsk Region. The comparison of this HAs with the samples of humic acids obtained from Aldrich Chemical Co is carried out. Fluorescence spectra of HAs water solutions of different origins differ from each other to a far greater extent than their absorption spectra. The influence UV radiation from excilamps on the properties of HAs has been investigated. Excilamps as sources of spontaneous radiation are a relatively young family of light sources. The UV radiation can be used for photodegradation of contaminants. This method might be used independently and in combination with other modern technologies. The prospect of using a wide range of excilamps with different characteristics for solving environmental problems is highlighted. It was found that the photochemical properties of HAs depend of their origin. The effects of HAs on the photodegradation of phenoxyacetic acids were investigated. An important point to emphasize is the significance and prospects of optical and photochemical methods in determining the characteristics and functions of humic substances as extremely sensible and informative methods.

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SORPTION OF HUMIC ACIDS ENRICHED WITH Fe_3O_4 NANOPARTICLES IN RESPECT TO EMERGING POLLUTANTS

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Keywords: humic acids, magnetite nanoparticles, sorption, diclofenac, ciprofloxacin

Abstract: In recent years a new environmental problem related to contamination of waters by pharmaceutical products has emerged due to their increased consumption, long-term stability in water and soil, and poor efficiency of recovery at conventional water treatment facilities. Diclofenac (DFC) and ciprofloxacin (CIP) are pharmaceuticals with a broad spectrum of action, which are more often found in surface and wastewaters. One of the most commonly used method for the removal of DFC and CIP from wastewater is adsorption. This study is aimed to estimate surface-dependent effect of humics-conjugated magnetite (Fe_3O_4 -HA) on sorption of diclofenac and ciprofloxacin. The nanoparticles of magnetite were synthesized *in situ* by oxidative alkaline hydrolysis of the iron (II, III) powder precursors into humics medium. The synthesized particles prepared at different humics concentration (10, 20, 40 wt%) were characterized using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Mossbauer and FTIR spectroscopy, DLS and BET analysis. The equilibrium concentration of DCF and CIP was determined spectrophotometrically. The results showed that the size and specific surface of nanoparticles depended upon the humics concentration. XRD results indicate that the addition of HS into Fe_3O_4 nanoparticles media have not changed the crystal structure of nanoparticles, but the intensity of the peaks is reduced with using of HA. The average crystal size of the nanoparticles for the Fe_3O_4 -HA in concentrations of 10-40 wt.% decreased from ~17 nm to ~10 nm, respectively. Fe_3O_4 conjugation with HA lead to increase specific surface from 117 to 142 m^2/g for the Fe_3O_4 and the Fe_3O_4 -HA20 accordingly. The sorbents under study are characterized by a high sorption capacity regarding to DCF and CIP. The results obtained indicate that the adsorption of DCF and CIP by the Fe_3O_4 -HA20 is largely enhanced in comparison with the bare Fe_3O_4 .

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INTERACTION BETWEEN HUMIC SUBSTANCES AND XENOBIOTIC SUBSTANCES: DOES THE ORIGIN AND STRUCTURE OF HUMIC MATTER BE OF IMPORTANCE

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Keywords: humic substances; pharmaceuticals, nanomaterials; interaction

Abstract: Humic substances (HS) form most of the organic matter in soils and waters, and they play a principal role in the turnover of organic carbon. The interaction of humic substances with xenobiotics may modify the uptake and toxicity of these compounds by aquatic and soil organisms, and affect the fate of pollutants in the environment. The interaction between humic matter and trace elements or persistent organic pollutants has been demonstrated on many examples, but the question about significance of such interactions remains of considering emerging pollutants – pharmaceuticals and nanomaterials. Another important aspect of the interaction between humic substances and xenobiotics can be related to the impact of structure of humic substances (their origin, age etc) on the interaction character. To study the impact of origin of humic substances on their interaction with xenobiotics on example of known (trace elements) and emerging (pharmaceuticals and nanomaterials) substances humic substances from in-depth characterized peat profiles, with known composition of precursor living material, age and humification conditions were used as well as reference and synthetic models of humic substances with known major structural elements. As a tool to study the interactions 3D EEM matrix analysis has been used, applying PARAFAC to decompose fluorescence spectra. It has been demonstrated ability of humic substances to stabilise fullerenes in the aquatic phase. In this study the interaction between fullerenes, carbon nanotubes and humic substances has been studied using excitation-emission fluorescence spectroscopy. Humic substances demonstrate appreciable impact on the fate of carbon containing nanoparticles xenobiotics in natural environments. Of the humic substances, the aquatic fulvic acids are the most active in hydrolysis reactions, but the velocity of studied reaction depends also on temperature, the concentration and of humic substances used, as well as presence of surfactants thus indicating possible micellar catalysis presence. The same approach has been used to study interaction of humic substances with pharmaceuticals containing adamantane structures: remantadine, memantine and major precursors of these pharmaceuticals.

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RELATIONSHIPS BETWEEN AGING OF PAHS AND ORGANIC MATTER

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Keywords: organic contaminants, PAH, soil organic matter, aging, sorption

Abstract: Polycyclic aromatic hydrocarbons (PAHs) are specific environmental pollutants which have carcinogenic, teratogenic and mutagenic properties. PAHs are released to the environment mainly by anthropogenic activities (e.g. industry, emission from individual house-heating systems, road transport) during the combustion of solid-phase fossil fuels, which is related to their continuous inflow to the soils.

The aim of the research was to assess the influence of organic matter on aging, dissipation and sorption processes of PAHs in soils. The study was carried as a sorption experiment in strictly controlled water and air conditions.

Four soils with different physicochemical and spectroscopic properties were applied to the study. They were fortified with a PAH mixture containing five compounds differing with properties and number of benzene rings: fluorene-Flu, anthracene-Ant, phenanthrene-Phe, pyrene-Pyr, chrysene-Chry at 20 mg kg⁻¹ of single compound concentration level. The research was conducted as laboratory experiment with incubation times of 0, 1, 3, 6, and 9 months. After each interval time the individual PAH compounds, extractable (E-SOM) and stable organic matter (S-SOM) were measured. PAH were determined in two forms as total concentration (PAH-tot) and residual concentration (PAH-rest) after E-SOM extraction. The rate constants of PAHs losses and half-life times were estimated with the assumption the pseudo first order kinetics.

The amounts of PAH-tot in the soils decreased by an average over 92% while in soil after 9 month of aging, compared with their initial spiking levels. The highest rate of decomposition of individual compounds increased with the decrease of their molecular mass (3-ring > 4-ring PAHs). The amount of the PAHs-rest fraction bounded by the S-SOM after 9 months of incubation varied from 0.9 to 3.5% of total initial PAHs concentration. The hydrocarbon compounds i.e. Flu, Ant, Phe, Pyr exhibited relatively similar $T_{1/2}$ in range from 43 to 59 days, but Chry was characterized by a $T_{1/2}$ much higher and broader than other hydrocarbons, from 67 to 280 days.

The sorption of PAHs by native organic matter structures is controlled by their aging time. Persistence of pollutants depends on their affinity to organic matter fractions and susceptibility to degradation.

Acknowledgements: The studies were supported from the National Science Centre project No UMO-2018/29/N/ST10/01320 "Analysis of the fractional composition and sorption properties of humic substances in relation to various groups of organic contaminants".

INFLUENCE OF HUMIC SUBSTANCES ON THE TRANSFORMATION AND DEGRADATION OF INSECTICIDES IN RICE FIELDS OF BALI ISLAND

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Keywords: Insecticides, Neonicotinoids, Mass-spectrometry

Abstract: The need to intensify agriculture in densely populated areas of South-East Asia leads to the active use of fertilizers and pesticides. For pest management of rice farmers often use insecticides of the group of neonicotinoids. It is known that humic substances affect the behaviour of organic pollutants in the environment. Humic substances are able to bind toxicants, changing their migration ability, as well as to have a stimulating effect on the microbial community of the soil, accelerating the process of decomposition of organic pollutants.

The aim of our work was to assess the effect of humic product on the transformation and migration of pesticides in soils. The object of the study was widely used on the island of Bali drugs based on neonicotinoid insecticides: thiamethoxam, Imidacloprid and fipronil. During the model experiment, soil samples with insecticides and humic preparation were incubated for 14, 28, 56 days at a temperature of 25°C. Humic preparation was introduced as a solution with a concentration of 0.25% (5 ml per 25 g of soil). During the experiment, the indicators of the microbial state of the soil (basal respiration, nitrogen fixation, methane formation) were measured. The method for determining pesticides in soil is based on acetonitrile extraction and subsequent determination on a chromat-mass spectrometer (HPLC-Q-TOF).

The results show an increase in methane formation in the soil on day 7, which can be associated with a significant number of methanogenic bacteria in flooded rice cakes. As a result of the experiment, after 14 days, a decrease in the content of Imidacloprid in the variant with the introduction of humic substances by 30% was revealed. The decrease in the detectable pesticide in soil may be due to the specific effect of humic preparation on certain groups of microorganisms.

THE FUNCTION OF CARBOXYL GROUPS ON THE INTERACTIONS OF HUMIC ACIDS WITH ORGANIC DYES AND SURFACE ACTIVE AGENTS

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Keywords: humic acids; methylation; osmosis; interactions; transport properties

Abstract: The interactions of humic acids (Leonardite Humic Acid Standard 1S104H) with ionic compounds (organic dyes and surface active agents) have been deeply studied using unconventional diffusion (dialysis) techniques. Standard humic acids have been modified by selectively blocking of carboxyl groups by methylation to clarify the role of these essential functional groups in the interactions with ionic compounds. The results of dialysis experiments confirm the strong affinity of humic acids towards ionic compounds (organic dyes as well as surface active agents). Surprisingly, the effect of humic acids methylation is minor than it could be expected because the modified humic acids had almost equally approved the similar affinity towards ionic compounds comparable with their non-modified equivalent. To conclude the presence of carboxyls in the structure of humic acids is not important considering the interactions with ionic compounds.

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DETOXIFYING EFFECTS OF HUMIC SUBSTANCES IN RADIOACTIVE SOLUTIONS. ASSESSMENT VIA LUMINESCENT BIOMONITORING

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Keywords: Humic substances, radiotoxicity, bioassays.

Abstract: Bioluminescence is glowing of living organisms; it is based on chemiluminescent enzymatic reactions. Marine luminous bacteria and their enzyme reactions are widely used as bioassays for monitoring the environmental toxicity; main tested physiological parameter here is a bioluminescence intensity. In this work, we used cellular and enzymatic bioassays based on luminous marine bacteria *Photobacterium phosphoreum* and their enzymes to study the detoxifying effects of humic substances (HS) in radioactive solutions.

The BL intensity was monitored in solutions of alpha-emitting radionuclide Americium-241 ($\text{Am}(\text{NO}_3)_3$, 0.4–6.7 kBq/L) and beta-emitting radionuclide Tritium (0.3–500 MBq/L) under the conditions of chronic low-dose irradiation. Tritium was used as a component of tritiated water. Bioluminescence activation and inhibition were revealed under low-dose exposures to Americium-241 and Tritium. These effects were attributed to adaptive and toxic responses of the bioassays, respectively.

To study the HS detoxification ability, the HS were added to the model radionuclide' solutions. Detoxification coefficients (D) were calculated to characterize the changes in activation and toxic effects of the radionuclides under the action of HS:

$D = I_{HS}^{rel} / I^{rel}$, where I_{HS}^{rel} and I^{rel} are relative bioluminescent intensities in the radioactive solutions in the presence and absence of HS, respectively. The range of detoxifying HS concentrations, as well as maximal and minimal D -values were determined in the radioactive solutions of alpha- and beta-emitting radionuclides. Detoxification mechanisms under conditions of low-dose ionizing radiation are discussed with chemical, biochemical, and cellular aspects conditioning those. Role of reactive oxygen species in the detoxification mechanisms is under consideration.

COLLOIDAL ASPECTS OF THE INTERACTIONS BETWEEN HUMIC ACIDS AND SURFACTANTS

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Keywords: aggregation, dynamic light scattering, interaction, humic acids, surfactants

Abstract: Humic acids are ubiquitous natural substances, which can interact with various substances e.g. metals, surfactants, dyes, pesticides, creating from them a universal sorbent with possible applications in remediation processes of soils and waste waters treatment plants. Surfactants represent a group of substances, which are artificially introduced in the nature by human driven applications causing the undesirable foaming of waters and enhancing the solubility of hydrophobic organic pollutants such as highly toxic polycyclic aromatic hydrocarbons. The present work is focused on the study of colloidal aspects of the interactions between selected representatives of surfactants and humic acids, as the example of a promising sorbent and flocculant. For purposes of present work Hexadecyltrimethylammonium bromide, Tetradecyltrimethylammonium bromide, and Carbethoxypendecinium bromide were used as selected cationic surfactants, Sodium dodecyl sulphate as anionic and TWEEN-20 as a non-ionic. The interactions between the components were studied mainly by using a combination of dynamic light scattering (determination of the changes in particle size distributions) and electrophoretic light scattering (zeta potential – stability investigate) in titration mode of their measurements. This set-up provided us the determination of the critical aggregation concentrations of the surfactant-humic acid system, which corresponded to its phase separation. Moreover, the interactions between the components were confirmed also by routine physico-chemical methods (e.g. thermogravimetry and Fourier transform infrared spectroscopy). The batch sorption experiments were also used to describe the potential to form the interactions with the surfactants and to immobilize them into the insoluble form of humic–surfactant precipitate. We believe that the outcomes of our work will help to shed a new light on the phenomenon of the formation of the interaction between surfactants and humic acids and will provide the crucial insight in the broader utilization of humic acids as the universal sorbent for surfactants mainly from the waste waters.

COOPERATIVE SORPTION OF PHENOLIC ACIDS ON MODIFIED KAOLINITE UNDER BATCH AND DYNAMIC CONDITIONS IN THE PRESENCE AND ABSENCE OF LACCASE

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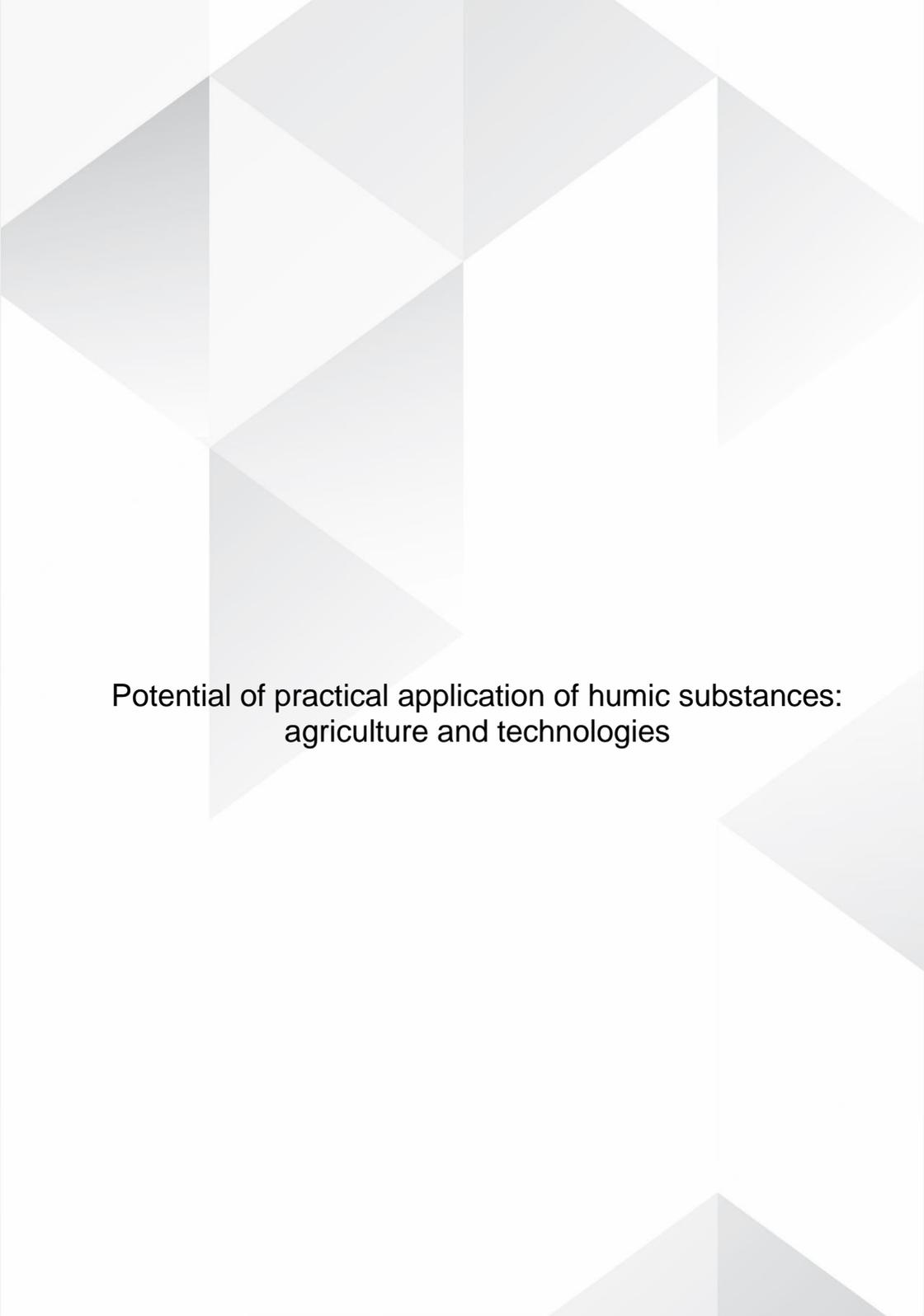
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Keywords: organic-mineral interactions, phenolic compounds, biocatalyst, continuous-flow conditions

Abstract: Phenolic acids (PA) are important products of lignin breakdown. Their interactions with minerals and oxidative enzymes lead to accumulation of aromatic compounds in soil organic matter. Little is known on cooperative sorption of PA by mineral phases under environmentally relevant concentrations and on the impact of phenoloxidases, ubiquitous at soil interfaces, on this process. In the present work the sorption of an equimolar mixture of phenolic acids by kaolinite modified with amorphous aluminium hydroxide has been studied in the presence and absence of fungal laccase in Na-acetate buffer (pH 4.5). Teflon flow-through column equipped with peristaltic pump has been used for simulation of dynamic conditions and reversed-phase HPLC for acids determination. Phenolic acids sorption was 3-4 times lower in 50 mM buffer than in 5 mM buffer, suggesting competition among PA and acetate ions for binding sites. The sorption of gallic and protocatechuic acids exceeded the sorption of p-hydroxybenzoic, vanillic, syringic, and ferulic acids by an order of magnitude. Phenolic acids competed for binding sites on kaolinite-Al(OH)_x. The sorbed gallic acid displaced the other acids, which passed into solution in the following order: p-hydroxybenzoic acid > vanillic acid > syringic acid > ferulic acid > protocatechuic acid. In the presence of inactivated fungal laccase PA sorption decreased by 1.2-1.4 times suggesting that the protein reduces the number of available active sites on the mineral. Sorption of gallic, protocatechuic and syringic acids in the presence of active laccase increased and the surface of the mineral became darker, suggesting oxidation/oligomerization of PA in the presence of laccase. Results of the study show selectivity in PA sorption; potential importance of o-substituted phenols and syringyl structures in SOM formation; importance of oxidative enzymes for aromatic C sequestration in soils.

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Potential of practical application of humic substances:
agriculture and technologies

CO-COMPOSTING OF SEAWEED WITH LIGNOCELLULOSIC SUBSTRATUM: EFFECT OF COMPOST COMPOSITION ON COMPOST HUMIC SUBSTANCES

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Keywords: compost, algae, spectrum, monosaccharides, humic substances

Abstract: The seaweed is one of underexploited Latvian natural resource. The dominant macroalgae in the Gulf of Riga in autumn was brown alga *Fucus vesiculosus* and green algae *Cladophora glomerata*. Green and brown algae collected after stranding on beaches were co-composted with lignocellulosic substratum – grass and/or hardwood sawdust. Six different compost composition were prepared. Composting was carried indoor in autumn-winter season at room temperature around 10 °C. Obtained composts correspondence to the national and EU legislation were evaluated. Best results were obtained for compost prepared from algae, grass and sawdust mixture. Composts and compost humic substances were characterized by elemental analysis, UV and Fourier transform infrared spectroscopy (FT-IR) and monosaccharides analyses. Compost humic substance composition was depend on compost raw materials. UV spectra of compost humic substances were described by absorbance ratios E_4/E_6 and E_2/E_6 . The lowest E_2/E_4 and E_2/E_6 ratios indicate on higher molecular weight of humic substances of algal-grass-wood compost. FT-IR spectra of humic acids of algal-wood compost and algal-grass-wood compost showed a fairly well-defined lignin absorption band pattern, in contrary humic acids of algae compost and algae-grass compost. Humic acids of algal compost contained around 8% monosaccharides. Fucose is deoxy sugar typical for brown algae not higher plants and can be used as chemical indicator of brown algae biomass in compost. Fucose/glucose ratio of algal compost was lower than that in brown algae. These results show that compost humic acids constituted of recognisable algae and plants biomolecules structures, included lignin-derived structures and carbohydrates.

EFFECTS OF HUMIC SUBSTANCES APPLICATION ON STARCH FORMATION IN POTATO

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Keywords: potato yield and quality, humic products, agriculture and technologies, fertilization

Abstract: Taking into account advantages of using of humic substances in environment (incl.: prolonged accumulation of nutrients and trace elements necessary for growth, improve nutrient circulation in plant and the productivity of photosynthesis thus resulting in increased productivity) in this study, we examined the effect of commercial humic products on formation of starch in potato tubers. Experiments were carried out during the period 2011 – 2014 at the Priekuli Research Centre of the Institute of Agricultural Resources and Economics on a soddy podzolic light loam soil with organic matter content 1.9 – 2.1% and pHKcL 5.8 – 5.9. The liquid organic fertilizer concentrate obtained with a special cavitation method from high quality Latvian peat on two different maturity (medium early and medium late) potato varieties ('Lenora' and 'Brasla') plantations were tested. Prior to trial in spring, the soil in the field was levelled and loosened. Potatoes were mechanized-planted in the 3-rd decade of May. Spacing between tubers was 25 cm, row spacing – 70 cm. Humic product was used for the treatment of plant material directly before planting, sprayed onto leaves after germination and in the beginning of butonization, accordingly methodology. Application of humic product tended to have a positive impact on formation of starch in potatoes. In all product application options, the starch content in potatoes was higher than in the control variant.

HUMIC ACIDS IN FEN PEAT: PROPERTIES AND RELATION TO THE SOURCE MATERIAL

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Keywords: fen peat, peat accumulation, humic acids, functional groups

Abstract: Fen peat is insufficiently used on industrial scale, while raised bog peat is intensively excavated – thereby degrading mire ecosystems, limiting natural renewal of peatlands and adding to the greenhouse gas emissions. Yet balanced use of local natural resources, especially expanding new and innovative applications for fen peat use, not only can benefit the environment, but also is good for the economic growth and can promote worldwide recognisability of the country. Humic acids are the part of peat that is most refractory and recalcitrant to organic matter degradation. Humic acids form the major part of peat organic matter and our study shows that a kilogram of dry fen peat contains up to 700 grams of humic acids, making fen peat a notable source for their extraction. Humic acids have no defined composition as it is based on the source material, on site environmental factors and the method of their extraction. Thus, fen peat humic acids show both similarities and differences when compared to organic material of different origin. This work was carried out to overview fen peat humic acids and their properties, thereby giving the scientific background for new possibilities of their application in environmental technologies and products with high added value. Amongst the parameters that were determined was elemental composition, major functional groups, humification indicators, major fluorophores, stable isotopes and more. Each parameter was evaluated for humic acids of different depth range and age. Results show comparative differences in humification indicators with raised bog peat humic acids, indicating significant differences during formation of humic acids. Moreover, fen peat humic acids contain different amounts of carbon, oxygen, nitrogen and hydrogen, resulting in differences in such parameters as functional compounds and isotopic ratios.

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HUMIC SUBSTANCES AND THEIR INFLUENCE ON THE ENVIRONMENT

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Keywords: humic substances, fulvic acids, sewage sludge, agricultural,

Abstract: Humic substances (HS) are the most widespread group of organic compounds in nature. They are commonly found in water, groundwater, soils, sludge, peat bogs and swamps. HS are used in agricultural, industry, veterinary, construction, ecological economy and in removing soil pollution. HS play a very important role in the whole ecosystem, they regulate global cycles of carbon and nitrogen. Based on numerous studies have been proved that humic acids (HA) are found mainly in groundwater, where they determine the intensity of its colour, while FA predominate in surface waters and are responsible for their oxidation. HS improve soil structure, stimulate plants and prevent high losses of water and nutrients. They play negative as well as positive influence on the environment. Discrepancies between the positive and negative impact of HS on the environment are really big. Practically in most of their places of occurrence they show positive and negative features. It has been widely accepted that HS play a positive role in soils while negative in surface and underground waters, but it is a big simplification and it is not as obvious as it might seem what author prove in this work. The paper presents negative and positive influence of the HS and the possibilities of using them in specific branches of industry and agriculture. According to many scientists, products based on HA are future direction due to economic and ecological solutions for the economy their importance and influence on the environment will increase.

TARGETED TRANSFORMATION OF ORGANIC MATTER IN THE TECHNOLOGICAL PROCESS OF LIGNOHUMATE® SYNTHESIS

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Keywords: humic-like substances, elemental content, FTIR, ¹³C-NMR, bioassay, PCA

Abstract: Conversion of lignin-containing organic matter into qualitative organic fertilizers is an important task of the present. LTD RET Company has developed and patented an industrial technology for the conversion of technical lignosulfonate with following synthesis of a number of humic-like biologically active substances (HLS), which finally compose the commercial humic product Lignohumate® (LH). Depending on the technological regimes used (alkali content, changes in temperature, pressure, oxidation rate and time), composition and properties of the obtained product are different. The objectives of the study were: (1) to characterize chemical composition and biological activity of the product in a number of LH samples taken at different times during the technological process; (2) to reveal differences in LH composition as a function of time and to determine the optimum duration of the process for obtaining a high-quality product. Samples of LH were taken from the heated working mixture at 0, 15, 30, 45, 60 and 120 min from the start of the oxidation process. Chemical parameters (elemental content, functional groups, carbohydrate content, MW, FTIR, ¹³C-NMR) were determined, biological activity was evaluated in phytotests as an increment of oven-dry biomass of shoots and roots of radish. Principal component analysis (PCA) was carried out considering set of chemical data and root biomass. Data on chemical parameters and biological activity combined with PCA show that LH-samples can be divided into three groups, depending on the duration of synthesis: initial raw material (0-time sample); "young" HLS (15-30 min) and "mature" HLS at 45-120 min of treatment. Starting from 15 min, content of HLS, elemental composition, content of functional groups, molecular weight distribution, character of IR and ¹³C-NMR spectra change. After 45-60 minutes the composition stabilizes, the share of high molecular weight fraction increases, and biological activity reaches maximum. At that stage further synthesis can be stopped.

DETERMINATION OF LIGNOSULFONATES IN HUMATE FERTILIZERS BY INFRARED SPECTROSCOPY

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Keywords: humate fertilizer, lignosulfonate, IR spectroscopy

Abstract: Lignosulfonates (LS) are wood-processing byproducts. They serve as stabilizers of fertilizers and plant-growth stimulants based on humic substances (HS) due to similar properties but show lesser effects on plant growth. Thus, HS-based fertilizers require standardization and control procedures, as the final properties depend on the HS source and other components including LS contents. However, the analytical procedure development for this task is hindered as both HS and LS are complex macromolecular mixtures of variable composition, molecular weights, and irregular structure.

Existing gravimetric, chromatographic, and spectrophotometric techniques are not selective and sensitive enough and require labor- and time-consuming sample-preparation stages to separate the components. For functional-group identification and assessment of both HS and LS, FTIR-spectroscopy is used; however, their quantification in a single sample was not proposed.

The aim of this study was to develop a procedure for LS assessment in aqueous HS samples by ATR-mid-IR spectroscopy as it is suitable for solid and aqueous samples with minimum sample preparation. Several commercial preparations of HS, LS, and fertilizers were investigated. A Bruker Vertex 70 spectrometer with a diamond-crystal ATR attachment was used.

ATR-IR spectra of dry fertilizer samples and their aqueous solutions have multiple characteristic but overlapping bands. LS-only bands selected for the quantification are 1266, 1192, 1093, and 1042 cm^{-1} . Silicate impurities in humates interfere with LS quantification; thus, they were precipitated by centrifugation. Different-ratio LS/HS solutions were prepared. LS bands at 1192 and 1093 cm^{-1} show the maximum sensitivity and precision: up to 25 g/L and for LS:HS = 1:2, the determination error reaches 50%; for a 1:1 ratio, 20%; and for a 4:1 ratio, it does not exceed 10%. It is possible to assess both LS and HS from a single sample by the bands that corresponds to S=O and C-O-C vibrations.

STUDY ON EXTRACTION TECHNOLOGY OF HUMIC ACID BY ULTRASONIC-KOH

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Keywords: Ultrasonic; Joint Extraction; Weathered Coal; Humic Acid

Abstract: Weathered coal is one of the main sources of humic acid. The extraction process of humic acid directly influences the extraction effect. To improve the extraction rate of humic acid from mineral sources, the ultrasonic pretreatment method was used in this study to extract humic acid from weathered coal together with KOH solution. The effects of KOH solution concentration, water- coal mass ratio, ultrasonic power, extracting temperature and time on the extraction rate of humic acid in weathered coal were studied, and the extract was characterized by infrared spectrum. The results showed that the optimum parameters of extraction of humic acid was treated in a 2% KOH solution at a 1:8 solid-liquid ratio for 30 min in ultrasonic power 150 W and 45°C. Under these conditions, the water- soluble humic acid content was 22.81%, the extraction yield was 65.32%. The results can provide theoretical basis for the extraction and industrialization development of humic acid from mineral sources.

SULPHUR CONTAINING DERIVATIVES OF HUMIC SUBSTANCES AND THEIR USE FOR REMEDIATION OF CONTAMINATED ENVIRONMENTS

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Keywords: humic substances; modification, functional groups

Abstract: Humic substances (HS) are high molecular weight refractory polycationites formed during decay of living organic matter and through biosynthesis of low molecular weight organic substances (metabolites or decay products of living organisms). Humic substances usually are considered as refractory and inert, but they do have numerous functional groups which influence their behaviour in the environment. Humic substances do contain carboxylgroups, phenolic and carbohydrate hydroxylgroups, aminogroups, quinonic groups and reactive positions in aromatic structures. Presence of many functional groups in the structure of humic substances determines their ability to interact with metal ions forming stable complexes and influencing metal ions speciation in the environment and mobility, behaviour and speciation forms in the environment. Considering the complex forming properties of humic substances, they are suggested for use in remediation of environments contaminated with metals. Considering presence and high concentrations of many functional groups in structure of humic substances their derivatization can be done, unless use of many derivatization reagents is of limited use, considering low solubility and presence of labile structures in their molecules. Derivatives of humic substances containing sulpho, and thiolgroups were synthesized and their properties were analyzed for their elemental composition; functional group content changes in spectral characteristics. The derivatives of humic substances showed significant differences in the number and in ability to interact with the metal ions, which were reflected in their complexation properties towards metal ions. FTIR spectra gave evidence of the presence of metal ions, strongly bound and protected in inner sphere complexes. The obtained derivatives of humic substances can be used for remediation of environmental contaminated with heavy metal ions.

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MULTIPROXY ANALYTICAL COMPARISON OF INDUSTRIALLY PRODUCED AND REFERENCE HUMIC SUBSTANCES

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Keywords: humic substances, authentication, stable isotopes

Abstract: Humic substances nowadays are not only topic of basic research, but also they are a industrially in amounts of tons produced substances, at first for application in agriculture. Considering diversity of functions there is a high potential of application of humic substances also for other aims, such as food additives, applications in cosmetics etc. However, as humic substances can be obtained from diversity of different sources using different extraction, concentration and purification methods their properties and structure have high variability. All these factors can influence properties and thus also application areas. The aim of the study is to compare properties of industrially produced humic substances with properties of humic substances of known origin (soil, peat, water etc.). Another aim of the study is to develop authentication methods of humic products, based on identification of their origin. As known humic substances in the study were used potassium humates, humic acids and fulvic acids isolated from well characterised and known sources: low rank coal, peat of different origin (low moor, raised bog peat), soil, compost, vermicompost and others. The methods used for characterisation includes element analysis, spectroscopic characterisation, UV, FTIR, fluorescence, ¹H, ¹³C NMR), functional group analysis, stable isotope (δ C, δ N, δ O) and others. The results of the study indicate possibilities to identify sources of industrially produced humic substances.

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SORPTION OF PHARMACEUTICALS BY CLAY-HUMIC SUBSTANCES COMPOSITE MATERIALS

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Keywords: clay composite materials, pharmaceuticals' sorption, environmentally friendly technologies

Abstract: Pollution caused by pharmaceuticals has become an increasingly serious issue, therefore innovative and cost – effective methods of pharmaceutical's removal must be studied. Clay – humic acid composite materials can be considered as prospective and low cost sorbents for contaminants. The aim of this study is to develop clay mineral and humic acid composite materials and to characterise their possible applications. For this research, three types of clay minerals (montmorillonite, kaolinite and bentonite) were modified with three types of humic substances: technical humic acid from lignite, humic substances extracted from raised bog peat and technical K humate from lignite. The obtained material was characterised by various multi-parameter methods (FTIR, SEM, XRD, BET) and tested for sorption of pharmaceuticals (chlorpromazine hydrochloride, ibuprofen and estradiol). The obtained results characterise clay mineral and humic acid composite materials' possible applications as sorbents for removal of pharmacologically active substances.

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EFFECT OF BIOCHAR ON STABILIZATION OF HUMUS COMPOUNDS AND ENZYMATIC ACTIVITY OF SANDY SOIL

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Keywords: soil, biochar, humus compounds, enzymatic activity

Abstract: Due to the indisputable significance of humus in many biochemical processes as well as its increasing deficit particularly in light soils, alternative sources of substrates for the reproduce of this constituent should be sought. Considering the physical, chemical and biological stability, the solid product of thermal transformation of biomass called biochar may be such a source. The natural mediators and catalysts of many important processes related to the transformation of organic matter including egzogenic origin are soil enzymes. Determination of enzymatic activity and understanding of its regulating factors is necessary to characterize the metabolic potential, fertility and quality of the soil and useful for the assessment of the amount of microorganisms. The aim of this study was to evaluate the effect of the addition of poultry litter and biochar obtained from this biomass on quantitative and qualitative parameters of humus compounds and dehydrogenase and urease activity. A micro-plot field experiment was established on an *Eutric Cambisol* with five treatments: soil without fertilisation, mineral fertilisation (NPK), NPK + poultry litter at a rate of 5 t ha⁻¹ DM, NPK + poultry litter biochar at a rate of 2.25 t ha⁻¹ DM and NPK + poultry litter biochar at a rate of 5 t ha⁻¹ DM. Given the need to create comparable conditions, the following rates of mineral fertilisers were used in the experiment: 100 kg ha⁻¹ N, 40 kg ha⁻¹ P and 120 kg ha⁻¹ K. After additions of biochar to the soil, the Corg. soil content significantly increased compared to the control soil and soil with mineral fertilization. The addition of biochar to the soil decreased the share of humic acid carbon in the Corg. content. The content of non-hydrolysing carbon significantly increased in the soil with biochar. The application of biochar in different ways influenced the enzymatic activity. The addition of biochar obtained from poultry litter to the soil in amounts equivalent to 2.25 t and 5 t DM ha⁻¹ increased dehydrogenase activity and decreased urease activity compared to the soil with mineral fertilisation.

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EFFECT OF COAPPLICATION OF BIOCHAR AND MINERAL SALTS ON THE CONTENTS OF Cu, Cd, Pb AND Zn IN MOBILE AND ORGANIC MATTER-BOUND FORMS IN SANDY SOIL

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Keywords: soil, biochar, humus compounds, heavy metals

Abstract: The speciation of heavy metals and the determination of the mechanism of their uptake in soil is of fundamental importance for the assessment of their potential environmental toxicity. Biochar can be used to mitigate the effects of soil contamination with inorganic compounds, including limiting the mobility of heavy metals. The aim of the study was to evaluate the impact of wheat straw and *Miscanthus giganteus* straw biochars on the content of Cu, Cd, Pb and Zn in organic matter-bound forms in sandy soil. The process of thermal transformation of plant biomass was carried out on the stand for thermal transformation of biomass with limited air access (1-2%). The temperature in the combustion chamber was 300 ± 10 °C. The pot experiment was carried out in the greenhouse of the University of Agriculture on soil with a loamy sand texture collected from 0-20 cm layer. The experiment included 6 treatments carried out in 3 replications: 0 – control soil (soil without additives), MF - soil with addition of chemically pure mineral salts, WSB - soil with addition of mineral salts (MF) and wheat straw biochar in doses of 1% (WSB 1%) and 2% (WSB 2%), and MSB - soil with addition of mineral salts and miscanthus straw biochar in doses of 1% (MSB 1%) and 2% (MSB 2%). The nutrients were introduced into the soil as mineral salts at the following doses: 0.10, 0.04 and 0.12 g kg⁻¹ DM of soil, for N, P and K, respectively. After the application of biochars and mineral salts and mixing them with the soil, the seeds of *perennial ryegrass* were sown. During the experiment, the humidity of soils was maintained at a constant level of 45% of the WHC. Application of organic materials caused considerable reduction of soil acidification. Application of wheat and miscanthus straw biochar, depending on the quantity added, caused a decrease in mobility of copper, cadmium, lead, and zinc. Cu, Cd, Pb and Zn content. The obtained results indicate that, compared with the content determined in soil from the control treatment, the 2% amendment of organic materials to the soil had a greater effect on the content of Cu, Pb and Zn in the organic fraction than the 1% amendment. The applied organic materials did not affect content of cadmium in the fraction bound to organic matter of the soil.

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OLIVE HUSKS BIOCHAR: IMPROVEMENT OF SOIL CHEMICAL AND BIOLOGICAL PROPERTIES

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Keywords: Olive oil industry by-products, biochar, pyrolysis, soil improvement, carbon sequestration

Abstract: Olive oil is a major agro-industrial production with increasing worldwide consumption and, at the same time, increasing attention to the issue of by-products and wastes. Specifically, solid residues generated by the olive oil industry represent an important issue both for the productive process and the environment. Hence, conversion techniques and innovative technological approaches are needed to reduce the possible impact of solid residues on the environment. Pyrolysis is a carbon-negative thermo-chemical process commonly adopted for energy production. At the same time, pyrolysis has the additional advantage of producing biochar, which is a carbon-rich, recalcitrant solid material showing a dual potential in enhancing soil quality and mitigating greenhouse gas emissions. This study aims to investigate the use of pyrolysis as a technological approach for the conversion of olive pomace into biochar and to characterize this product in order to demonstrate its potential application as environmental and agricultural enhancer. Fresh olive pomace was thermochemically converted into biochar by slow pyrolysis at 450 °C. The resulting biochar was characterized for its physical, chemical and morphological properties. Olive pomace biochar had a high carbon content and was rich in surface functional groups capable of retaining cations, which are important properties for fertilization management. But, is also predictable that olive pomace biochar exerts a positive effect on the microbial community due to the wide specific porosity and to the volatile matter content. Moreover, the olive pomace biochar seems to show physical characteristics that can positively affect soil aeration and water retention. In conclusion, olive pomace biochar presents numerous characteristics that make it a valid soil improver and a valuable environmental enhancement tool. Moreover, in terms of circular economy, its production represents an excellent management strategy for waste biomasses and for a more sustainable energy production.

TRACE ELEMENTS INTERACTION WITH NATURAL AND MODIFIED HUMIC ACIDS

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Keywords: trace elements, humic acids, oxidation, adsorption

Abstract: New technologies for cleaning of the environment from chemical contamination require the development of efficient materials characterized by high absorption capacity, selectivity, eco-friendly etc. Humic substances are ubiquitous in the environment and comprise the most abundant pool of non living organics. Their structure contains numerous functional groups and organic fragments, which enables them to interact with pollutants.

In the present study we investigated a sorption of four trace elements (Pb, Zn, Cu, Ni) by natural and chemically modified humic acids from mezotrophic peat. Two different methods of chemical modification were used. The first is oxidation of humic acids by potassium persulfate (K₂S₂O₈ persulfate oxidation). The second is the introduction of dibenzoylmethane molecule into the structure of humic acids. Natural humic acids have high sorption capacity in relation to all trace elements. Metal adsorption is satisfactorily described by the Langmuir equation. The maximum adsorption values were 318.2 mmol/kg for lead, 286.5 mmol/kg for copper, 225.0 mmol/kg for zinc and 136.8 mmol/kg for nickel, respectively. Obtained oxidized derivatives possessed an increased binding ability to all studied trace elements due to carboxyl groups and quinoid fragments increasing (NMR ¹³C data). Lead absorption increased by 16.3%, nickel - by 14.2%, zinc - by 10.6%, copper - by 6.9%. The introduction of dibenzoylmethane molecule into the structure of humic acids improved the metals adsorption also.

So, binding interactions of natural and modified humic substances with trace elements are of particular importance in remediation, as such interactions reduce concentrations of freely dissolved metals and as a result leave the offending contaminant less available to living organisms.

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SPECTROSCOPIC INDEXES CAN REVEAL ABILITY OF MICROSCOPIC FILAMENTOUS FUNGI TO TRANSFORM HUMIC SUBSTANCES

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Keywords: industrial humic substances, soil filamentous fungi, pathogens and antagonists, transformation, absorbance spectroscopy

Abstract: Humic substances (HSs), both natural and industrially manufactured, provide various effects: as agents for remediation of degraded soils, as plant biostimulants and others. Potential benefits of HSs can be associated with direct nutrient values, plant physiological mechanisms, modifications in physical, chemical or biological components of soil health. Soil filamentous fungi are involved in HS turnover. The study of interactions between HSs and soil filamentous fungi can help us to understand the sustainable soil functioning. The aim of the work was to perform multifaceted laboratory experiments on the transformation of various HS samples (industrial HSs and extracted humic acids) by soil filamentous fungi using a set of spectral indices. As a potential agent for HS decomposition, we used three strains: melanin containing phytopathogenic *Alternaria alternata*, non-pigmented phytopathogenic *Fusarium solani*, and antagonistic *Trichoderma harzianum*. As spectral indices, we estimated absorbance ratio A_{250}/A_{365} , emission wavelength of the humic-type fluorescence, and fluorescence quantum yield measured with excitation at 355 nm (QY_{355}). The transformations of HSs under cultivation of *A. alternata* led to increase of A_{250}/A_{365} ratio, shortening of the emission wavelength, and growth in QY_{355} . Under cultivation of *F. solani* and *T. harzianum*, we did not find remarkable transformations of HSs. A positive correlation was observed between the accumulation of fungal biomass and the degree of HS decomposition. The obtained results show that fungi *A. alternata*, *F. solani* (phytopathogens) and *T. harzianum* (which is antagonistically active against alternaria and fusaria) have different patterns of interaction with HSs, and this fact should be considered when humic-based biostimulants are used.

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LIGNIN TRANSFORMATION IN SOILS UNDER THE IMPACT OF SOIL PLOWING AND DRAINAGE

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Keywords: lignin phenol, arable lands, drainage, soil plowing, agrogray soils.

Abstract: Lignin is one of the difficultly decomposable compounds of plant tissues. The content and composition of lignin phenols that are the main matrix for the humus formation in Agrosoils affect greatly the transformation their organic matter. The aim of this work was a detailed characterization of the lignin phenols composition and processes of their transformation in soils under the impact of soil plowing and drainage in dynamic during last 30 years.

The objects of investigation were Agrogray soils of the Moscow district, where an experimental reclamation test arable area was created in 1987 (in three variants for each impact).

The process of lignin determination in the soils included the alkaline oxidation of a sample using copper oxide at 170°C under the pressure in a nitrogen medium. The lignin phenols were divided by a gas-liquid chromatograph.

It has been established that, the yield of agricultural crops has always been lower in non-drained land than in drained soils. In the average humidity years, the yield of spring crops due to the use of drainage was higher by 10-12%, of winter crops - by 18-20%. The total lignin content decreased from 13 mg/g C_{org} in drained soils up to 9.0 mg/g C_{org} - in non-drained soils as a result of increased microbiological activity. Microbial activity is diagnosed by increasing the length of the fungal mycelium from 84 to 120 m/g, and biomass from 0.033 to 0.050 mg/g. However, in drained soils, the degree of biopolymer oxidation (the ratio of acid to aldehydes) increases. According to the values of the lignin/N ratio in Agrosoils, there is also an accumulation of metabolic carbon in humic acids over aromatic carbon. Drainage caused a deep transformation of lignin in the Fe-Mn nodules.

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SYNTHESIS AND FOLIAR APPLICATION FOR *TRITICUM AESTIVUM* L OF NANO- $\text{Fe}_{3-\Delta}\text{O}_4$ @HS/DMSO

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Keywords: Iron deficiency, bioavailability of iron oxide nanoparticles, foliar application, magnetite, dimethylsulfoxide

Abstract: Iron deficiency of plants is a vastly common agricultural problem. One way of its treatment, which is notably cheap, rapid, and efficient, is direct spraying of aquatic aerosol with suspended bioavailable iron compounds onto the leaves. The main objective of this work in search for such compound is synthesis of iron (II), (III) oxide nanoparticles core in shells of humic substances (HSs) and dimethylsulfoxide (DMSO). Highly dispersed suspended iron oxide compounds presumably allow for controllable high content of iron; HSs benefit plant growth as well as being surfactants which reduces nanoparticle coagulation; and DMSO is used as a solvent, stabilising agent and adjuvant. The tasks of this work are to assay for physical-chemical properties of products as well as their bioavailability by testing on *Triticum aestivum* L seedling shoots.

Synthesis of nano- $\text{Fe}_{3-\delta}\text{O}_4$ @HS/DMSO by the co precipitate method of mixing ferrous and ferric chloride DMSO-solutions and aqueous ammonia solution of HS was carried out. Samples obtained were assayed by Mössbauer spectroscopy, DLS, UV-visible spectroscopy, X-ray powder diffraction phase analysis, and magnetic susceptibility measurement. Properties on solution content dependence was studied. HSs presence allows for smaller particle size while that of DMSO affects stoichiometry of the product.

Shoots uptake assay of obtained sample while compared to agricultural iron deficiency treatment standard, which is ferric EDTA (FeEDTA), as well as ferrihydrite-HS (fhHS) based compounds, was carried out. Seedlings were treated by spraying with previously mentioned suspended compounds aerosol as well as HS and DMSO solutions and distilled water (Blank). After 7 day application, ashing and analysis of iron content by ICP-AES followed. It was shown that foliar application of nano- $\text{Fe}_{3-\delta}\text{O}_4$ @HS/DMSO results in four times higher (441 mg kg^{-1}) iron uptake than that of FeEDTA (98 mg kg^{-1}), and two times higher than application of fhHS (212 mg kg^{-1}).

UNIVERSAL ORGANIC FERTILIZERS “ELDOROST” BASED ON HUMIC SUBSTANCES

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Keywords: humic substances, organic fertilizer, agriculture, crops, yield

Abstract: Seventy percent of Kazakhstan land is subject to desertification. Today some 14 mio ha out of 182 mio ha of Kazakhstan pasture lands are completely non-usable, and the total degradation area exceeds 50 mio ha, which is explained by intensive and very intensive desertification. One of the most efficient methods used to increase soil fertility and crop yield is the use of organic fertilizers. They help increasing the content of humus in soil, soil structure and avoiding many adverse consequences caused by the use of chemicals. In general, environmental balance cannot be maintained without the use of organic fertilizers for farming purposes. Therefore, development of new high-efficiency and low-cost multipurpose organic fertilizers with complex features (regulating, antistress, immune-stimulating, moisture-retaining, etc.) on the basis of humic acids becomes very urgent since the need in high-efficiency phyto regulators is growing day in and day out. The purpose of this work is the creation and introduction of a new domestic integrated high-performance organic fertilizer for modern technologies to restore soil fertility, forests, reduce land degradation in arid areas of Kazakhstan and increase the yield of agricultural cultures. We have produced an innovative domestic plant growth regulator from highly oxidized brown coal and lowland peat by extraction using alkali solutions adding a set of aminoacids, natural phytohormones and micro- and macroelements. The distinguishing feature and scientific novelty of the proposed project as compared to the traditional ones is the use of natural aminoacids, phytoharmones extracted from vegetable raw materials and addition of micro- and macroelements in certain proportions. In-depth laboratory and demonstration field (microplot) comparative tests on cereals, vegetables and other crops demonstrated a high efficiency of the new domestic multipurpose organic plant growth regulator.

THE PRODUCTION TECHNOLOGY OF HUMATE SUBSTANCES BASED ON THE CLOSED-LOOP PRINCIPLE FROM PEAT

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Keywords: peat, humic acids, extraction, cavitation

Abstract: Peatlands cover the estimated area of about 6 600 km², which is about 10% of total Latvia's territory. Most valuable deposits were found located in the eastern plains and near capital city Riga. Researchers regard the amount of about 230 million tons as a suitable source of fuel out of the estimated total peat deposits of 1 500 million tons. A difference in the structure and properties of analysed extracted humic substances depends on the source location of the organic components of peat.

Aims of this study were to characterize the humic substance consisting of the set of potassium humate compounds (K-HS) and the technological aspects of extraction from Seda's peatland. Main stages in the extraction of chemical substances, such as homogenization, thermal treatment, and separation were discussed in the present work. The innovative method of peat suspension homogenization induced by hydrodynamic cavitation effect was introduced and developed with the help of rotational disperser. The effect of physical treatment of peat suspensions, such as paddle mixing was described and analyzed. The application of humate extraction byproduct in the production of another valuable material - granulated soil improver was proposed in the present study.

Nowadays, the globally growing demand for agricultural production, cheaper thermal and electrical energy resources causes nonpoint and point sources of pollution in the atmosphere, forests, lakes, and rivers that do not meet quality goals. Global agreements and local governments tend to limit allowed polluting emissions, which causes the sustainable development without rest. The extraction of various valuable substances from peat inevitably leads to loss of energy and collection of byproducts, i.e., remaining substances and contaminated water. The adaptation of closed-loop principle in the production of K-HS reduces the energy consumption and provides more efficient extraction of K-HS. Proposed application of byproduct may help to reach zero waste goal. Such approach matches the circular economy principles and provides a green solution for industrial production of the humic substance.

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METABOLIC ROLE USING A FEED ADDITIVE OF HUMIC NATURE "HUMILID" ON THE ORGANISM OF ANIMALS

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Keywords: humic substances, metabolism, adaptation processes.

Abstract: Humic substances are products of biotransformation of organic matter under anaerobic conditions. When applied to animals, they do not accumulate in the body, and they are metabolized to the end products due to the heterocyclic structure of their molecules and the presence of a large number of functional groups. Therefore, the purpose of this study is to determine the effect of the feed additive humic nature "Humilid" on the physiological state, qualitative and quantitative performance indicators in farm animals and adaptation processes in laboratory rats in model experiments.

The studies were carried out on rabbits of Hyplus, of black African ostriches and broiler chickens of the Cobb-500 cross on the basis of production complexes. In these animals, were determined an indicators of protein, lipid, carbohydrate metabolism and performance. Under the conditions of the model of water-immobilization stress (VIS), the adaptive capacity and the state of hemostasis system were determined in rats.

Was found that used "Humilid" contributes to the normalization parameters of the hemostasis system and more active processes of adaptation of the organism to the damaging factors under the influence of VIS. In productive animals, "Humilid" has shown an improvement in the physiological state of the body due primarily to the activation of the erythrocyte system and the protein-synthetic processes. The activation of metabolic processes in the body as a whole is due to an increase in the muscle tissue of the experimental animals of the content of total protein, essential amino acids, essential fatty acids, a decrease in the fat content. As a result increase of biological value of meat products.

Using of "Humilid" promotes the improvement of the overall functional state of the animal organism and the increase of quantitative and qualitative indicators of their productivity and the basis for more rapid adaptation to various stress factors.

EFFECT OF HUMIC ACIDS ON MAGNETITE/SiO₂ NANOPARTICLES: STRUCTURE AND BIOACTIVITY

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Keywords: iron oxides nanoparticles, humic acids, structure, bioactivity

Abstract: This study is aimed to control aggregation behavior of humics-coated magnetite nanoparticles, which is essential in controlling the biofate and transport in the environment. We have simulated the oxidation process of magnetite to maghemite in HA and HA-free medium. Mössbauer spectroscopy identified transformation Fe₃O₄ in γ-Fe₂O₃ species even so in humic shell.

Mitigating effect of HA on bioactivity of Fe₃O₄ and γ-Fe₂O₃ to *Paramecium caudatum* and *Sinapis alba* were investigated with a focus on the oxidation effect. As a result, the growth inhibition of NPs to both test-species increased with an order: Fe₃O₄ < Fe₃O₄/HA < γ-Fe₂O₃/HA.

The toxicity nature of NPs from the released ions or NPs itself arises were investigated in terms of endpoints (EC50) and threshold level (EC20). Solutions of Fe(II), Fe(III) salts clearly demonstrated increased toxicity with respect to root length of *S. alba* seedlings and mortality of *P. caudatum*. Combination of Fe (II and/or III) with HA lead to mitigation of toxicity. The Fe₃O₄ in some concentrations stimulated the survival of ciliates and the growth of higher plants. For both Fe₃O₄ and Fe₃O₄/HA the toxicity more largely depend on the treatment concentration.

To form additional protective layer for magnetite-HA from oxidation we grafted Fe₃O₄ with SiO₂ and HA. The XRD pattern for all samples proved that magnetite is main phase. The sequential layer-by-layer grafting demonstrated an logical increase in the hydrodynamic diameter (measured by dynamic light scattering) and the polydispersity index of a dispersion in the row: Fe₃O₄/SiO₂ < Fe₃O₄/SiO₂/HA. The bioactivity of samples demonstrated higher toxicity for Fe₃O₄/SiO₂/HA in compare with Fe₃O₄/HA. To clarify why composites with humic end-surface in both cases give different bio-responses, the surface charge and other colloidal characteristics for NPs-HA are performed.

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POTENTIAL USE OF FULVIC ACID ISOLATED FROM SAPROPEL IN SKIN CARE

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Keywords: fulvic acids, antioxidant activity, skin regeneration

Abstract: Skin is the first physical barrier protecting our body from harmful environment. Due to aging, stress, damage and other negative factors skin loses its protective abilities and functionality over time. To decrease the loss of functionality, medical and cosmetic products and applications can be used. For many decades sapropel have been used as a part of medicinal procedures treating various skin diseases and to improve overall wellbeing of skin and body. Although sapropel as medicinal mud is used worldwide, due its diversity and place of origin, information regarding properties of sapropel is varied and inconsistent. To evaluate quality of sapropel samples from Latvia and their potential use in medical applications, fulvic acids were selected as one of the testing parameters. Fulvic acids are a minor fraction of sapropel composition, however they have been attributed to play an important role in forming therapeutic properties and showed an antioxidative properties.

Our study uses fulvic acids obtained from sapropel samples of 3 different lakes in Latvia. The aim of this study was to assess fulvic acid effect on skin cell proliferation in vitro and evaluate optimal concentration of fulvic acid that could further be used in cosmetic formulations. For this purpose, immortalized human keratinocytes (HaCaT) and dermal cell lines were used as test system. Skin cells were supplemented with solution of different concentration of fulvic acid. Also a total phenolic content was determined spectrophotometrically according to the Folin–Ciocalteu's method and total antioxidant capacity was evaluated according with the decolourization of the ABTS radical cation (ABTS^{•+}) according to their concentrations and antioxidant capacities.

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IMMOBILIZATION POSSIBILITIES OF HUMIC SUBSTANCES

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Keywords: humic substances, immobilization, sorbents

Abstract: Humic substances in environment can interact with wide range of different substances such as organic pollutants, pesticides, they also can bind and transport trace metals. Humic substances can change the toxicity of xenobiotics, and influence pollutants fate in environment.

The immobilization of humic substances on solid carriers is an approach for investigation of their interaction with various substances. Although immobilization has shown its usefulness for investigation of the structure, catalytic activity and other properties of proteins, nucleic acids and other macromolecules, in the case of humic substances there are few publications. Immobilized humic acids can serve as sorbents for organic and inorganic substances, enabling study of their interactions.

This study has mainly focused on immobilization methods based on inclusion of humic substances in polycondensation reactions with formaldehyde and substances that are capable of forming phenol-formaldehyde resins. For immobilization two different types of humic acids were used: commercially available coal humic acid and humic acid extracted from peat from Latvia peat bog.

The study of the properties of the obtained polymers indicate that they can act as efficient sorbents both for organic substances both for sorption of heavy metal ions. In the same time the obtained polymers can be used to study the interaction between humic substances and xenobiotics.

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APPLICATION OF HUMIC SUBSTANCES IN PRECISION FARMING

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Keywords: humic substances, rhizosphere, precision farming, soil bacteria

Abstract: Increasing world population and changing quality of life has justified the use of disruptive high-external input agriculture. As a response, the trend of precision agriculture has developed which, among other includes fertilizer application at a variable rate regarding the need. Biological inputs, such as humic substances and soil bacteria as substitute for chemical fertilizers can contribute to transition to even more environmentally friendly agriculture. Rhizosphere process management provides an opportunity to harmonize crop productivity and environmental impact. These strategies are based on maximizing the efficiency of root and rhizosphere processes in nutrient acquisition and use by crops rather than depending on excessive application of chemical fertilizers. The strategies mainly include manipulating root system including localized application of nutrients synchronizing rhizosphere nutrient supply with crop demands. The beneficial effect of humic substances on soil fertility is well known as is the role of soil bacteria. However, the number of studies which have focused on combined use of humic substances and plant growth promoting microflora is very low and thus, such products are not readily available on the market. We have developed a granulated product, containing humic substances, which are gradually released from granule once in the soil, designed to be applied at the time of sowing, using the same agricultural machinery. This technology ensures that the humic substances are not applied at random all over the field but instead occur in the direct vicinity of the seed. The gradual release ensures the formation of beneficial rhizosphere around the growing seedling and its maintenance throughout the season. The plant root-soil interface is a dynamic region in which numerous biogeochemical processes take place mediated by soil microorganisms. The effectiveness of this granulated product is ensured by humates as a nutrient transport vehicle and their beneficial effect on soil microbes.

BLOOD REDOX-BALANCE AS A SENSITIVE TEST-SYSTEM FOR ASSESSING THE HEALTH STATUS OF THE POPULATION

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Abstract: The purpose of our study was to evaluate redox balance of the population of various points in the Chiatura district in Georgia, living in villages characterized by varying degrees of environment pollution.

The redox balance of the blood of residents of the Chiatura district (both sexes) living in villages characterized by different degrees of environmental contamination (Khreyiti - low, Perevisa - medium, Rgani - high) has been studied. The redox blood balance was determined by means of modified DPPH (2,2-diphenyl-1-picrylhydrazyl) test.

The results of comparison of the ecological contamination degree in the villages and the level of the antioxidant potential of inhabitants' blood show the particularly low value of the blood redox potential in residents of Rgani. That should be due to the high level of contamination of this area and the inactivation of the antioxidant protection system of the body. A significant increase in the redox balance of blood in the residents of Perevisa indicates the presence of body's redox-active processes inductor and sufficiently high antioxidant potential of blood in conditions of moderate contamination.

It was concluded that the blood redox system is a sensitive marker reflecting both the degree of environmental pollution and the compensatory ability of the body's antioxidant defense system. The results obtained suggest the method used to determine the redox blood balance as a sensitive test system for population-based health research.

HEALTH RISKS AND ITS MOLECULAR AND CYTOGENETIC CORRELATES IN DIFFERENT ECOLOGICAL ZONES

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Abstract: The purpose of our study was to identify the nature of the cause-effect relationship between the risks of developing of Chronic Obstructive Pulmonary Disease (COPD) and Cardio-vascular Disease (CVD) in patients residing in the villages of Chiatura district, characterized by varying degrees of environmental stress.

The residents (n=400) of the Chiatura district living in the villages, Khreiti, Perevisa and Rgani were examined. The villages are characterized by different degrees of ecological tension (the villages differ both in their remoteness from sources of environmental pollution - manganese mining quarries and the scale of its extraction, which allows them to rank according to the degree of environmental tension: Khreiti - low, Perevis - medium, Rgani - high). In the patients the blood general redox balance and genetic parameters (the number of micronuclei in the scrapings of the oral mucosa) were studied.

In the zone of moderate environmental stress (the village of Perevisa), a significant increase in the indicator of the total antiradical activity of blood plasma and an increase in the frequency of micronucleated buccal cells were revealed in comparison with the zone of low environmental stress (the village of Khreiti). In residents of the village of Rgani, characterized by the highest level of pollution, the indicator of the total antiradical activity of blood plasma decreases sharply, the number of micronuclei decreases, the presence of various types of damage to the nucleus is noted, which is characteristic of intensive apoptosis.

Under the conditions of moderate air pollution, observed mobilization of protective anti-radical and replication mechanisms in the body are aimed at preserving the stability of the somatic cell genome. Identified oxidative stress can also act as mediators of secondary alteration and the development of the inflammatory process in the circulatory bed, resulting in an increased risk of arterial hypertension (AH) against the background of a relatively high risk of chronic nonspecific obstructive pulmonary diseases (COPD). High level of environmental pollution contributes to the development of permanent intense oxidative stress in the affected tissues of the respiratory tract. That contributes to the development of predominantly nonreparable changes in the cell genome, apoptosis and intensification of secondary oxidative stress, which, under conditions of depletion of antiradical protection, causes preferential defeat of the microenvironment of apoptotic cells, the development of local effects, reflected in a sharp increase in the risk of COPD.

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