CONTENTS

CONTENTS AND STOCKS OF ORGANIC MATTER IN SOME RUSSIAN FOREST SOILS: METHODICAL PROBLEMS AND PERSPECTIVE APPROACHES

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The adequate assessment of the organic matter (OM) content and stocks in Russian soils are complicated by methodical difficulties, which are caused by the reason that method of organic carbon determination in soils are indirect and unprecise. The results of humus determination by Tyurins method depends on the composition of OM and the degree of its transformation, and also influenced by presence of reduction components in mineral horizons. All these reason leads to the changes in OM oxidizability in wide frames. A device is suggested for the determination of the total organic carbon and oxidizability (chemical consumption of oxygen). This devise permits us to analyze precisely real content of OM and the degree of molecular oxidation-reduction. On the bases of these analytical data we can correct the data, obtained with the traditional Tyurins method. The research conducted attest the possibility of revising data on the humus content in podzolic, gray and brown forest soils of European Russia. If we take into account that the organic horizons (litter or peat) encompass an enormous amount of organic carbon, which forms its greatest reserve in pedosphere it is nessesary to deduce the coefficients for the principal types of bog and forest soils in order to adequately assess the condition of these soils to the global budget of organic carbon.

NATURAL ORGANIC MATTER (NOM) AND WASTEWATER DERIVED ORGANIC MATTER (WDOM) IN WATER TREATMENT – SPECTROSCOPIC AND CHROMATOGRAPHIC STUDIES

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Groundwater is the preferable source for drinking water production. However, in many countries river and lake water has to be used as raw water to ensure the increasing demand of drinking water. Concentrations of dissolved organic carbon (DOC) in surface waters can range from 2 up to 40 mg/L, whereas the DOC concentration in groundwater is often around or below 1 mg/L. Due to the influence of waste and wastewater in surface waters, the character of the organic matter (OM) is different compared to groundwater. The presence of OM causes many problems for the process of drinking water treatment. Major problems result from the fact that OM reacts in various ways in treatment processes, and that the effectiveness of water treatment processes in removing OM varies with the nature of the organic material. The aim of the contribution is to study the effect of flocculation, oxidation, adsorption, and chlorination on natural organic matter (NOM) and wastewater derived organic matter (WdOM).

NOM was taken from a brown water lake, whereas WdOM was taken from a secondary effluent from a wastewater treatment plant which serves a moderately industrialized city. The studies were performed with the original samples after filtration and with different fractions. The fractionation was done according to the

IHSS XAD-procedure and with ultrafiltration. Model reactions have been applied to compare the efficiency of OM elimination during the different processes. NOM, WdOM and the fractions were analyzed with several methods before and after treatment. UV-and NMR methods, gelchromatography in combination with UV- and C-detection, and the disinfection by-product formation potential were used for further characterization.

EFFECT OF HUMIC ACID ON METAL PHYTOAVAILABILITY

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The role of humic acid on the distribution of heavy metal in a staple crop was investigated. Hence the effect of varying concentrations of humic acid on the distribution of lead in the shoot and root of corn plant (Zea *mays L)*, grown in a soil culture was investigated. The implication of the addition of a synthetic organic ligand (EDTA) on the metal bioavailability was also assessed. Plant lead uptake increased with humic acid concentration. The performances of HA system, EDTA system and HA+EDTA system on soil metal mobilization or immobilization were evaluated using relevant statistical tools. Suppression of the toxic metal translocation from the plant root to the shoot was recorded with a fraction of the investigated systems.

HUMIC ACID IN NIGERIAN SOILS: AN ENVIRONMENTAL PERSPECTIVE

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Soils suspected to have elevated cadmium, copper and lead levels obtained from three urban environments in the southwest Nigeria were investigated for the metal and humic acid contents. UV/Visible and infrared spectroscopic analyses characterized the latter for basic reactive groups. Ba^{2+} and Standard calcium acetate titration techniques quantified the carboxyl and phenolic hydroxyl groups. Metals were determined by atomic absorption spectrometry. Data generated were subjected to Pearson correlations and ANOVA to establish relationships. Results indicate trace metal levels exceeding the permitted limits. Some degree of statistically significant correlations at $P < 0.05$ between the soil metal levels and the properties of the extracted soil humic acids were recorded. This emphasizes the influence of natural soil organic matter (SOM) on the accumulation or retention of metal cations in a given soil environment which is a function of the reactive group compositions of the SOM and metal type rather than the total SOM.

STUDYING THE EFFECTS OF “DISSOLVED” NATURAL ORGANIC MATTER FROM FRESHWATER SEDIMENTS ON SPECIATION OF ORGANIC CONTAMINANTS: IT WAS SUPPOSED TO BE EASY

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Pore water has been anticipated to be an important route for uptake of contaminants by benthic organisms in freshwater sediments. Natural organic matter (NOM) in pore water affects the speciation and bioavailability of many contaminants in pore water. In order to study the characteristics and functionality of NOM in pore water these have to be separated from particulate components of the sediment. Commonly the separation is made by centrifugation with subsequent filtration. The current study can be divided into two parts. On the one hand we studied the effects of separation procedure (centrifugation speed, water extraction) on the characteristics and functionality dissolved NOM (i.e. defined as material passing through 0.45 μm filter, DNOM). On the other hand we also studied the attributes of NOM in samples separated without filtration. The analyses included for example TOC, SUVA and HPSEC measurements as well as experiments to determine sorption of pyrene. Furthermore, bioavailability of several polycyclic aromatic hydrocarbons in pore waters was tested with two ecologically different aquatic organisms *Daphnia magna* and *Lumbriculus variegatus*. This was done not only to investigate the effects of different characteristics of NOM on bioavailability but also to see whether feeding habits play any role on NOM controlled bioavailability. Separation procedure appeared to affect the attributes of DNOM and more importantly the functionality was also affected. Furthermore, the results indicated that in filtration we may loose larger colloids (or small particles) that are potentially present in pore water and important for speciation and bioavailability of contaminants.

EFFECTS OF CLIMATE CHANGE ON THE MOBILIZATION OF DISSOLVED ORGANIC NITROGEN (DON) – A FIELD EXPERIMENT

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There has been an increasing focus on the effects of climate change on dynamics and mobilization of dissolved organic matter (DOM) during the last years. This is partly due to the observed increases in colour and dissolved organic carbon (DOC) concentrations in lakes and rivers [1,2]. The knowledge of climatic controls on DOC dynamics is limited, and is even more scarce on dissolved organic matter (DON) dynamics. There are also indications of different responses in DOC and DON dynamics to climatic factors [3]. Including DON in studies of DOM dynamics is therefore of great importance.

The objective of the presentation is to examine the effects of changes in climatic factors on DON mobilization, and to investigate possible differences in release mechanisms for DOC and DON. The work is part of the CLUE (Climate change and Land Use Effects) project (http://www.umb.no/ipm/forskning/clue/), where headwater catchments are manipulated. The manipulations are meant to simulate climatic changes that are predicted for Norway. Three types of manipulations are conducted: 1) Addition of artificial precipitation in summer and autumn, to simulate increased precipitation. 2) Snow removal during winter, to simulate the effects of increased winter temperatures. 3) Isolation during winter, to simulate the traditional thick snowpack, for comparison with treatment 2). DON runoff from treated catchments is compared with DON runoff from reference catchments. In addition DOC:DON ratios in runoff from treated and reference catchments is compared.

References

1.Freeman, C., Evans, C. D., Monteith, D. T., Reynolds, B. and Fenner, N. (2001) Export of organic carbon from peat soils. *Nature* 412, 785.
2.Hongve, D., Riise, G. and Kristiansen, J. F. (2004) Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water - a result of increased precipitation? Aquatic Sciences 66, 231-238.
3.Kalbitz, K., Solinger, S., Park, J. H., Michalzik, B. and Matzner, E. (2000) Controls on the dynamics of dissolved organic matter in soils: A review. Soil Science 165, 277-304.

BEHAVIOUR OF PLUTONIUM IN AQUEOUS SYSTEMS CONTAINING HUMIC SUBSTANCES

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The migration of plutonium in aqueous systems is of importance in connection with the safety assessment of high level nuclear waste repositories. Humic Substances (HS) play an essential role in the migration of radionuclides due to their ability to form complexes and to their reducing behaviour.

For the redox speciation of plutonium, Gorleben ground water containing HS was analyzed by online coupling of capillary electrophoresis to inductively coupled plasma-mass spectrometry. Pu(VI) is reduced by humic rich Gorleben ground water to Pu(IV) and Pu(III) and therefore we have focused our studies on the complex formation of trivalent and tetravalent plutonium with HS. The time dependence of the plutonium complexation with Aldrich humic acid was investigated and the complex formation constants of Pu(IV) at different pH values were determined. Different concentrations of plutonium (10^{-6} to 10^{-8} M) and Aldrich humic acid (0.01 to 25 mg/l) were applied. For the determination of log(ß) values the method of ultrafiltration was used.

Ultra-trace amounts of plutonium can be detected by coupling capillary electrophoresis with the highly selective and sensitive resonance ionization mass spectrometry (RIMS). The obtained results will briefly be presented.

EVALUATION AND COMPENSATION OF ION-EXCLUSION EFFECTS DURING GEL-PERMEATION FRACTIONATION OF HUMIC SUBSTANCES

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Size-exclusion chromatography (SEC) is a powerful technique for determination of the molecular weight (MW) distribution of humic substances (HS). However, SEC of HS in aqueous phase is likely to give rise to artifacts. Ionic exclusion is a non-size exclusion effect arising from repulsive interactions between the charged analyte and the partially charged gel matrix. To compensate for ionic exclusion, modification of eluent is needed. The objective of this research was to evaluate the magnitude of ionic exclusion effects during gel-permeation fractionation of HS and to determine the conditions providing compensation for ionic -exclusion effects. SEC-fractionation of HS was conducted with eluents of different ionic strength varying from 0.01 up to 0.13 M. SEC analysis was performed on Abimed system including HPLC pump, autosampler, and UV detector. The column was packed with Toyopearl TSK HW-55S gel. Phosphate buffer at pH 6.8 was used as a mobile phase. For six humic materials tested, it was found that the relationship of partition coefficient versus ionic strength of the eluent reached plateau at 0.06 M. However, polystyrenesulfonates used as calibration standards experienced very substantial sorption at the given ionic strength that made them non-applicable for molecular weight calculation. Recommendations on the optimum SEC fractionation conditions for humics analysis were worked out.

PHYSICO-CHEMICAL COMPOSITION OF LAKE BOTTOM SEDIMENTS IN RELATION TO FOREST CATCHMENT MANAGEMENT

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The aim of this work was to determine the influence of forest catchment management on properties of lake bottom sediments and elemental composition and spectral properties of extracted humic acids. The four lakes located in the Drawa National Park (N-E Poland) were studied. This study shows that there is significant influence of forest catchment (*Pinus sylvestris* or *Fagus sylvatica*) on properties of organic matter in sediments and on properties of humic acids. The content of pigments in littoral and profundal bottom sediments differs in relation to catchment management. Cluster analysis performed for sediment and humic acids parameters divided the samples into four clusters, reflecting the origin of sediments.

APPLICATION OF HIGH-VOLTAGE PLASMA TECHNOLOGY FOR PROCESSING OF ORGANIC MATTERS

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High-voltage plasma technology falls into a class of high technologies and is based on utilization of different interconnected nonlinear dynamic effects and physical phenomena. Plasma filament with high temperature, powerful shock waves, pulse electromagnetic and X-radiations, ultrasound, turbulization of flows occur in a fluid under high-voltage discharge.

Circuit designs and performance data of three types of high-voltage plasma installation are presented (one of them is intended for production of artificial manure from peat). Main units of experimental line for production of artificial manure as well as a sequence of main operations on processing of peat are listed. The results of hotbed agricultural experiments are discussed. Substantial acceleration of extraction of sea-buckthorn oil is achieved. Quantitative output of useful substances from flowers of a calendula, valerian, seaweed was about 88 – 95% (this value exceeds the useful output of many well-known extractions methods). It is possible to receive a sterilized nutritive from peat which further can be used for growing of different species of bacteria.

Yeast has been processed in order to improve its digesting by animals. It is shown, that silt after its sterilization can be used as feed supplement for animals.

Homogeneous sterilized pulp has been produced by this method from fish wastes, and it was used as feed for fur-bearers.

CAVITATION TECHNOLOGY FOR PRODUCTION OF HUMIC SUBSTANCES AND TESTING ON DIFFERENT CROPS

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The results of joint activity of Scientific and Production Firms "Latinvent" and "Intellectual Resources" on designing and application of different types of cavitation reactors for dispersion of organic matters (e.g., peat) are presented.

Cavitation is a fundamental physical phenomenon arising in fluid. It is accompanied with local water hammers, pointwise rise of temperature, shock waves, micro vortexes, etc. Cavitation speeds up chemical reactions, promotes an output of useful product and improves its quality.

Designs of different types of cavitation reactors as well as their advantages and demerits are considered. Performance data of experimental installation for production of humic substances from peat are presented.

Qualitative analysis of humic substances was carried out by laboratory assistant J. Šīre (under scientific supervision of Prof. M. Kļaviņš). The results of analysis are considered.

Biological testing of produced humic substances has being performed during 2 years by Dr. agr. L. Borovko (Institute of Crop-growing, Latvia University of Agriculture).

Positive results of cavitation processing of peat corroborated by biological testing of humic substances show on good prospects of these works.

WATER EXTRACTABLE VERSUS TOTAL ORGANIC MATTER IN A DEEP SOIL PROFILE IN MEDITERRANEAN AREA

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This study was aimed to identify qualitative and quantitative differences of dissolved organic matter (DOM) isolated from each horizon along a deep soil profile and to evaluate any apparent relationship between the water extractable organic carbon (WEOC) and the total organic carbon (TOC) content. The soil profile "Monte Pietroso" is located in the Murge area, Apulia region in southern Italy. Samples from the 8 genetic horizons (Ap1, Ap2, Ab1, Ab2, Bt1, 2B, 2Bt2, and 2B/C) were collected in October 2002. The DOM characterization was carried out by means of UV absorbance, fluorescence spectroscopy in the mode emission and excitation/emission matrix (EEM), and additional spectroscopic derived indexes.

Chemical results indicate clearly that soil organic carbon accumulates in the top horizons (Ap) and, in general, decreases with depth. However, compared to the total soil organic carbon, the water extractable portion, i.e. the DOM, increases with increasing depth.

The aromaticity and the Humification Index of the DOM decrease dramatically towards the lower part of the soil profile, whereas the Fluorescence efficiency index tends to be very high. Fluorescence data show the occurrence of three main fluorophores in the DOM extracts with varying wavelength location and relative intensity. Results suggest the occurrence of DOM transport phenomena along the soil profile, depending on the nature of the organic material and on the chemical and mineral characteristics of the various horizons.

THE INFLUENCE OF VEGETATION ON WATER CHEMISTRY IN HEADWATERS

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The CLUE (Climate change and Land Use Effects) project is manipulating precipitation and temperature in shallow mini-catchments (30-150 m^2) in the Storgama catchment, southern Norway, to predict future consequences of climate change. The objectives are to investigate the effects of altered regimes on the quality of runoff water. Such information is important when trying to model effects of a changed climate on larger catchment scales. Storgama represents a typical headwater catchment in Norway, and the effects of the manipulations are monitored with a special interest in fluxes of dissolved organic N (DON) and dissolved organic C (DOC).

The project introduces a predicted future climate for both the summer- and winter season. To differentiate the effect of these climatic manipulations, an understanding of the influence of vegetation cover in shallow soil (lithosols) area is of vital importance. Eleven mini-catchments are investigated, whereas five are reference catchments. For each mini-catchment there has been generated accurate vegetation maps and vegetation statistics. The maps have been created using a digital image software procedure, and the vegetation data has been related to runoff fluxes and soil characteristics.

CLUE (2003-2007) is a collaboration project between Norwegian University of Life Sciences (UMB), Norwegian Institute of Water Research (NIVA), Norwegian Institute of Air Research (NILU), Norwegian Institute if Soil- and Forest mapping (NIJOS), and Norwegian Institute of Public Health (FHI).

References

Project web site: www.umb.no/ipm/forskning/clue

DISSOLVED ORGANIC CARBON AND DISSOLVED NITROGEN IN SOIL FERTILIZED WITH CATTLE SLURRY

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The objective of the study was to evaluate effects of long-term fertilization of a sandy soil with differentiated doses of cattle slurry as well as its after-effect action on the possibilities of migration of dissolved organic carbon (DOC) and dissolved nitrogen (DNt) down to deeper layers of the soil profile. DOC and DNt were extracted with borate buffer or 0.004 M $CaCl_2$ solution. Evaluation of effects of cattle slurry on the content of DOC and DNt was done in comparison with mineral fertilization. It was shown that the use of cattle slurry in the doses of 100 and 200 $m^3 \cdot ha^{-1} \cdot year^{-1}$ caused a significant increase of labile organic matter in the 0-25 and 25-50 cm soil layers. As compared with mineral fertilization, the application of slurry increased also the amounts of extracted DNt, but only in the surface layer. The DNt content in the deeper soil layers did not depend on the kind of fertilization. Concentrations of DOC and DNt in the extracts depended not only on their content in soil but it was also modified substantially by the extractant used. Concentrations of DOC and DNt found after the extraction with of borate buffer of pH = 7 were higher as compared with extraction with 0.004 M $CaCl_2$.

MOLECULAR SIZE DISTRIBUTION OF HUMIC ACIDS ISOLATED FROM FOREST SOIL

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High Performance Size Exclusion Chromatography (HPSEC) is the most convenient and widely used technique for determination of molecular weight distributions in polymeric materials, both synthetic and natural.

The aim of this work was to determine the changes in properties of humic acids during transformation of organic matter in soil under various forest communities. In these research humic acids isolated from two forest soil profiles (litter and mineral horizons) has been used. Soil profiles were taken under the monocultures of *Abies alba* and *Fagus sylvatica*. Extracted humic acids were analysed for the elemental composition, FT-IR spectra and HPSEC. TSK-GEL 3000 SW 600mm column, sodium acetate at pH = 7 were used in the HPSEC separation.

The main factor determining properties of forest soil organic matter is chemical composition of plant remains. Humic acids, extracted from the litter horizon, in comparison to humic acids from mineral horizons, were characterised by higher values atomic ratio H:C and lower internal oxidation degree. In the FT-IR spectra there appeared additional bands in the region of 1400-1000 cm^{-1}. It is characteristic for „young", newly formed humic acids. HPSEC shown two peaks corresponded to two fractions of humic acids with different molecular weight. Humification process of the litter was connected with the increase of aromaticity and internal oxidation degree and modification of contribution of low and high molecular weight of the humic acids.

BIOLOGICAL FEATURES OF BOG LAKES WITH DIFFERENT AMMOUNT OF HUMIC SUBSTANCES

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Three investigated Lakes, situated in raised bog of Ramsar site Teichi Nature Reserve, Latvia are characterised by different amount of humic substances, low, but different degree of water mineralisation. Lakes are feeding from atmospheric precipitation and practically are without anthropogenic impact. Total bacterial numbers of saprophytic bacteria are tipically low - in bacteriobenthos - approximately 3000-3500 cells G^{-1}. There is not detected clear relationship in taxonomic composition of phytoplankton and amount of humic substances but it was stated clearly relationship in degree of water mineralisation and composition, number and biomass of phytoplankton. Phytoplankton community of lakes investigated are formed by Cryptophyta, Chrysophyta, Bacillariophyta and Chlorophyta. Phytobenthos and periphyton communities in all three lakes are typial for bog lakes and are formed by *Mougeotia* sp., *Ulothrix* sp., *Batrachospermum* spp. Changes in phytoplankton quantity and quality showed definite seasonality. Macrozoobenthos of all three lakes is scanty. The fauna of the profundal of lakes consisit of 1 to 3 taxonomic group dominated by Diptera mainly *Chironomidae* and *Chaoborus flavicans*. The most abundant taxonomic group in all the lakes in coastal zone are *Insecta*, which comprised more than 70% - 80% of the density. It was stated that the effect of high concentration of humic substances leads to a simplification of the species composition and to the formation of monomorphous fauna and flora.

PROPERTIES OF SOIL HUMUS IN RELATION TO GRAIN SIZE FRACTION

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In the model incubation experiment organic fertilisers (cattle manure, vermicompost and wheat straw) were mixed with soil material (sandy texture). The soil samples for testing were taken from 0-20 cm layer (soil material mixed with organic fertilisers) and the 20-35 cm layer (soil material only), after one year and a three years period of incubation. In two grain soil fractions - Ø >0.1 mm (sand fraction) and Ø < 0.1 mm (silt and clay fraction) were determined: total organic carbon (TOC), total nitrogen (TN) and fractional composition of humus (humic acids, fulvic acids and humin contents).

Obtained results showed that fine-grained fraction (Ø < 0.1 mm) accumulate threefold more of organic carbon than coarse-grained fraction (Ø. 0.1 mm). The humus distribution in separated grain fractions depended on the kind of organic material introduced into soil. Humus of the fine-grained fractions were characterised by higher content of TN lower participation of the humic and fulvic acids and higher participation of the humins in comparison with the coarse-grained fraction. The introduction of organic fertilisers into soil increased the content of total nitrogen in both fractions. After three years after introduction of organic fertilisers into soil the migration of carbon and nitrogen compounds in soil profile was not detected.

CHARACTERIZATION OF HUMIC SUBSTANCES OF DIFFERENT ORIGINS OF LATVIA USING PYROLYSIS-GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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The most important part of dissolved organic substances in natural waters are in the form of humic-like organic matter- heterogenous and macromolecular organic acids, which are formed during the degradation of plant and animal derived organic matter as a result of various abiotic and microbial transformation processes. Humic substances (HS) contribute essentially to many processes in aquatic and terrestrial ecosystems: carbon and nutrient cycles, buffer capacity of water and interactions with mineral particles and organic pollutants. But despite of this important role in environment the understanding of their structural chemistry is still insufficient.

In the present study different samples of humic substances were isolated from rivers of Latvia (Daugava, Salaca, Inčupe), lakes (Islienas, Siksalas), peat and groundwater from artificial recharge system. The nominate goal of this study was to find out basic structural similarities/dissimilarities between various humic substances samples.

The chemical nature and structural composition of those samples of humic substances were analyzed with an off-line tetramethylammonium hydroxide (TMAH) treatment procedure followed up with Py-GC/MS. The macromolecules of humic substances in the process of pyrolysis decompose to 200-300 various low molecular compounds. The main degradation products obtained by Py-GC/MS of the off-line TMAH treated different aquatic HM samples were the methyl derivatives of phenols, alkylphenols, phenolic acids and aliphatic acids. These findings allow to compare different humic substances according to their structural composition.

The pyrolysis products of peat humic substances comparing to aquatic HS contain relatively more alkane and alcohol compounds and aliphatic monocarboxylic acids, but pyrolysis of aquatic humic gives relatively more di- and tri carboxylic acids.

QUANTIFICATION OF HYDROXAMATE SIDEROPHORES IN SOIL SOLUTIONS OF PODZOLIC SOIL PROFILES IN SWEDEN

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Siderophores might be of importance for weathering and nutrient uptake in forest soils by their complex forming ability. Selective determination of ferrichrome type siderophores, i.e. ferrichrome, ferricrocin and ferrichrysin, in soil solution at different depths of podzolic soil profiles has been performed for the first time. In four forest soil solutions from north and south of Sweden, ferricrocin was found in all samples from the upper soil layers, i.e. mor layer, eluvial and illuvial horizons, in concentrations up to 12 nM. Ferrichrome was found at lower concentrations, up to 2 nM. In contrast to ferrichrome and ferricrocin, ferrichrysin was not found in any of the studied soil solutions.

For ferricrocin and ferrichrome, the highest concentrations were found in the upper soil layers and declined with depth in similarity to dissolved organic carbon (DOC) and low molecular mass organic acids (LMMOAs). By principal component analysis, the ferricrocin concentration was demonstrated to vary in the same manner as DOC and citric, acetic and oxalic acids. Comparing the two northern and two southern sites, higher ferricrocin concentrations were found in the north. In contrast, the ferrichrome concentrations were similar at all sites.

Although these substances are difficult to separate, utilization of a porous graphitic carbon high performance liquid chromatography column in combination with a preconcentration column, used by column-switching, enabled analysis of soil solution without any prior sample pretreatment. The detection limits were 0.1 - 0.2 nM for ferrichrome, ferrichrysin and ferricrocin by electrospray ionization mass spectrometry (ESI-MS) detection. Further, the structural identities of the siderophores were verified by MS/MS fragmentation.

HUMIC SUBSTANCES IN DRINKING WATER RESERVOIR SYSTEMS OF THE ORE MOUNTAINS (SAXONY): DISTRIBUTION IN THE RESERVOIRS, AND INFLUENCE ON TREATED WATER QUALITY

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During the last decade an increasing input of humic substances in surface waters was to observe in the region of Ore Mountains, Saxony. In wide parts of this region surface water is used for drinking water production. Thereby the rising concentration of humic substances cause increasingly technological and financial problems.

On this account in the year 2001 a project was initiated, which worked on this problem by order of the Federal Ministry of Education and Research, the Saxon Reservoir Administration and waterworks. One of the main target of the project part was to gain insight into quality of NOM in drinking water reservoirs and how it is influenced by water treatment.

To characterise the dissolved organic carbon (DOC) two selected drinking water reservoirs including the waterworks were sampled continuously, and the samples were analysed using a LC-OCD-system. Furthermore experiments in laboratory scale were carried out.

The measurements showed, that the DOC in the reservoir water mainly consist of humic substances. Especially during summer a stratification of humic substances shapes up, with lower concentration at the surface and higher values near the ground. During the seasons the mean water quality inside the reservoir alters, wherefore raw water quality also changes. Treated water is closely correlated to raw waters quality. In times of worse raw water quality with extreme high concentration of humic substances like for instance during the flood disaster in Saxony (2002) the elimination capacity do not suffice to compensate, and thereby a worsening of drinking water quality is inevitable.

INFLUENCE OF MULTIVALENT CATIONS ON GLASS TRANSITIONS IN PRECIPITATED DISSOLVED ORGANIC MATTER

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Interactions between soil organic matter (SOM) and multivalent cations are expected to affect sorbent properties of SOM. Macromolecular structures are discussed for humic substances, and recent studies show the relevance of glass tansitions in whole soil samples [1]. The SOM matrix may be crosslinked by multivalent cations, leading to antiplasticization of the

SOM matrix, which may increase the glassy characteristic and lead to nonideal sorption [2].
Glass transition behaviour has not yet been investigated in precipitated dissolved organic matter (DOM) of whole soils. DOM precipitation by multivalent cations may represent one step in SOM formation, and DOM may be crosslinked in the course of precipitation.

In this study, DOM was extracted from a organic horizon of a spruce forest and was precipitated with different cations (Ca^{2+}, Pb^{2+} and Al^{3+}). We investigated the effect of type and concentration of the cations on the glass transition in the precipitated DOM. Differential Scanning Calorimety (DSC) measurements with different heating protocols were performed with the precipitate. The relationship between the salt type, salt concentration and glass transition behavior will be presented and discussed in this contribution.

References

1. G. E. Schaumann and E. J. LeBoeuf, Environ. Sci. Technol., 39 (2005) DOI: 10.1021/es0490931.
2. Y. Lu and J. J. Pignatello, J. Environ. Qual., 33 (2004) 1314-1321.

RADIOLABELING OF NATIVE HUMIC SUBSTANCES WITH [^{125}I]IODOANILINE

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Humic substances are the main components of none living natural organic matter. Because of their polyfunctional and amphiphilic character the ubiquitous surfactant-like humic substances are in focus of widespread environmental and ecological investigations. However, most techniques gather sum-parameters and can not single out individual interaction processes at the natural concentration level of the humic substances. A promising way to direct measurements of the complex interaction of humic substances is the application of radionuclides. Oftentimes radio-nuclides are used as analogous for metals and their interaction with humic substances. More rare in literature are methods for direct labeling of the backbone chain of humic molecules [1-5]. In this work the known method for preparation of m-[^{125}I]Iodoaniline [6] and for labeling of humic substances via diazotization [3] were combined to a new labeling technique of native humic substances. For this purpose the single preparation steps were further optimized and adapted. Labeling yields of up to 70 % were obtained after optimization of the synthesizing. The stability of the labeling and the unaltered properties of the humic substances were proven by the use of ultrafiltration, precipitation, irradiation and chromatographic methods. As result the known instability of former radioiodination techniques [1, 2] was overcome.

References

1. P. Warwick, L. Carlsen, A. Randall, R. Zhao, P. Lassen, Chem. Ecol. 8(1993)65-69.
2. K. Franke, D. Rößler, H. Kupsch: Use of radioactive tracers for the characterization of humic and fulvic acids in high performance size exclusion chromatography. In E. Ghabbour, G. Davies eds. *Humic substances, Nature's most versatile materials,* New York: Taylor and Francis 2002: 3-8.
3. K. Franke, J.T. Patt, M. Patt, H. Kupsch, J. Steinbach, Radiochim. Acta 92(2004)359-362.
4. J.V.K. Kukkonen: Characterization of ^{14}C labeled humic substances, Proceed. of 20th International Meeting of the

International Humic Substances Society, Boston, USA, p. 121, 2002.
5. G.A. Badun, V.Y. Pozdnyakova, A.V. Kudryavtsev, I.V. Perminova, Bulg. J. Ecol. Sci. 2(2003)26-27.
6. L.A. Khawli, A.I. Kassis, Nucl. Med. Biol. 19(1992)297-301.

PHOTOLYTIC AND PHOTOCATALYTIC TRANSFORMATION OF AQUATIC NOM

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Photochemical processes of NOM are of increasing importance for the understanding of aquatic transformations and for the development of technical methods in water treatment. The aim of the contribution is to present the results of irradiation of dissolved brown water NOM by simulated sun light in the absence and presence of titanium dioxide (TiO_2) as photocatalyst.

Experimentals

NOM from a brown water lake of the Black Forest (Germany) was irradiated using a Oriel Solar-UV-Simulator (Straffort, CT, USA). Photon flux was determined by actinometry. The solutions were analysed for DOC (Shimadzu TOC-5000) and other basic parameters like pH-value, electric conductivity, O_2-concentration and temperature. In addition, the NOM samples were characterized using elemental composition, UV-vis absorption, fluorescence, NMR, ion chromatography, size exclusion chromatography and biodegradation. Organic products were determined chromatographically using different detection systems. Photocatalytic reactions were done after addition of commercially available TiO_2 species (Rutil and Anatase).

Results

There was a clear bleaching effect in the irradiated samples and a partial mineralization of NOM which was faster at high than at low pH-values. Aromatic and olefinic structure as well as molecular size decreased readily with irradiation time. Low molecular organic acids with one to four C-atoms showed up as products – which were all together better biodegradable after irradiation. The presence of iron accelerated, copper decreased the bleaching effect. In case of particulate TiO_2 addition there was a strong adsorption of the high molecular part of NOM and photocatalytic bleaching especially of the low wavelength chromophores. The resulting reaction products were more hydrophobic and of lower molecular size. The photocatalytic degradation of organic xenobiotics like pharmaceuticals were according to their structure either hindered or stimulated by NOM. The influence of NOM on the photic transformation in aquatic systems is highly obvious.

References

Brinkmann, T., Hörsch, P., Sartorius, D., Frimmel, F. H.: Photoformation of low-molecular-weight organic acids from brown water dissolved organic matter. Environ. Sci. Technol. 37(18), 4190-4198 (2003).

DISSOLVED NATURAL ORGANIC MATTER (DNOM), - PROPERTIES AND ENVIRONMENTAL AND HYGIENIC IMPORTANCE. NEEDS AND MEANS FOR INTERNATIONAL CO-OPERATION

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DNOM is present in all fresh waters and have an effect on all chemical and all biological processes in soil and water. The ecological and hygienic importance of the properties and characteristics of this organic matter will be discussed, first of all in relation to anthropogenic-caused changes.

Ecological properties and potentials

Colour [photo-syntheses]; molecular size [enetration of cell-membranes etc.]; complexation- and ion exchange capacity [uptake and release of “elements”]; electrical charge [ion balance].

Hygienic potentials

Metal complexation [essential elements]; organic- and inorganic micro-pollutant complexation [carrier of pollutants]; chlorination byproducts [intake of mutagenic matter]; smell [taste and odor].

New prospective, relative to improving the international scientific communication on DNOM, will be discussed: Based on the assumption that “no DNOMs are alike” it is important agree on a set of Standard Methods in order to better “speak the same language” in the future.

SORPTION OF DISSOLVED ORGANIC CARBON AND PHOSPHOROUS BY AN AGRICULTURAL SOIL

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Dissolved organic matter (DOM) sorption influences nutrient mobility in soils, and hence leaching of nitrogen, phosphorus and other elements to drain and groundwater. While much has been done on sorption and leaching of dissolved organic carbon (DOC) and nitrogen (DON), especially under forest, clear information about the behaviour of dissolved organic phosphorus (DOP) under agriculture is still lacking.

Therefore, batch experiments were carried out to determine sorption of DOC and DOP to soil samples from Ap, EB and Bt horizons of a cultivated Danish Humic Hapludult in response to pH (5 and 7), DOM concentration (0-4.7 mM of DOC) and time (1 min to 72 h). The used DOM was extracted from the Ap horizon by means of a chelating resin and had a DOC:DOP mole ratio 167:1. DOC was measured by a total organic carbon analyzer (Shimadzu TOC-500), while DOP was taken as the difference between total and inorganic P. Total P was obtained by dissolving the ash left after heating the sample to 550 ^{o}C for 1 h in 6 M H_2SO_4. The concentrations of phosphate in the ash solution (total P) and original sample solution (inorganic P) were quantified by the molybdenum blue method.

The initial DOM sorption was found to be fast with 50-60% of the total DOC and DOP sorption after 72 h occurring within the first minute. In addition to concentration, sorbed DOC and DOP depended on soil samples and pH. More DOP and much more DOC was sorbed at pH 5 than at pH 7 with decreasing sorption in the order Bt > EB > Ap, which is the order of increasing organic matter content. Since the Ap horizon contained most free aluminium and iron oxides, which are the most likely DOC and DOP sorbents in soils, the higher sorption capacity of subsoil than topsoil samples can probably be ascribed to stronger blocking of sorption sites by organic matter in Ap than in EB and Bt samples.
Sorption strongly changed the DOC:DOP solution ratio but in a complex way. At pH 5, stronger sorption of DOC

than DOP decreased the ratio in a similar way for the three soil samples, especially at low concentrations. At pH 7, however, the DOC:DOP solution ratio was substantially higher than 167:1 after reaction with the Ap sample, whereas lower solution ratios were found after reaction with the Bt sample.

Environmentally, the relative DOP enrichment of the solution after sorption found for all three samples at pH 5 and for the Bt sample at pH 7 may indicate an increased risk of organic P pollution of waters from agricultural soils, especially when they are acidic. Increasing pH by liming seems to favour DOP compared to DOC sorption, and may therefore be a tool to decrease organic P pollution of the aquatic environment. More experiments need, however, to be performed before drawing too firm conclusions at this point.

PROPERTIES OF HUMIC SUBSTANCES FROM DIFFERENT SOILS INCUBATED WITH POST-HARVEST RESIDUES

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Current humus content in soil is a result of processes of humus decomposition and the inflow of raw organic matter. The basic sources of organic substances in soils are post-harvest residues left behind in it after the collection of cultivated plants.

The objective of this study was to evaluate the effect of post-harvest residues of maize, rye, sunflower and potato on the properties of humic acids in different soil types. The soils samples from 0-25 layer of Orthic Luvisol, Haplic Phaeozem, Eutric Regosol and Eutric Gleysol were incubated with plant post-harvest residues at the ratio 10:1. The plant material was composed of straw and roots. The samples were incubated at 25°C and constant humidity for periods of 360 days. Humic acids were extracted from samples before and after 360 days of incubation according to the IHSS standard method. The extracted humic acids were analysed for UV-VIS and FT-IR spectra and elemental composition.

Obtained results shown that humic acids extracted from samples incubated with plant materials were characterised by lower absorbance values in UV-VIS region and by higher values of absorbances ratios in comparison with humic acids from samples without additions. FT-IR spectra of humic acids from soil samples incubated with plant materials showed many absorpion bands in the region of 1400-1000 cm^{-1} related to „young” character of humic substances. The changes in spectral properties and elemental composition showed that properties of soil humic acids are determined both by chemical composition of plant residues and soil conditions.

NATURAL ORGANIC MATTER (NOM) FUNCTIONALITY AND DISINFECTION BY-PRODUCT FORMATION

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The size, chemical composition, structure, functional groups and polyelectrolytic characteristics of NOM vary widely depending on the age and origin of the material. Here the functional group distribution will be determined by fractionating UK NOM using a polyvinyl pyrrolidone (PVP) polymer resin. Species absorbed onto the resin at an acidic pH include coloured organic components rich in C=C moieties. The organic components not absorbed are primarily composed of carbohydrates (CHs), proteins, amino acids and uronic acids in solution. By carrying out analyses on each fraction, it should be possible to determine the contribution of the polyphenolic (PP) or CH rich NOM to disinfection by-product formation. Previously spectroscopic techniques such as Fourier Transform – Infra Red (FT-IR) and nuclear magnetic resonance (NMR) have been used to characterise the PP and CH fractions as well as high performance size exclusion chromatography (HPSEC) with UV absorbance detection. Here, HPSEC with UV detection, fluorescence detection and an evaporative light scattering detector (ELSD) will be used for characterisation of the fractions. The ELSD is capable of detecting non-chromophoric molecules whereas the UV and fluorescence detectors are more suitable for detecting chromophoric organic matter.

The work proposed here will be a practical evaluation of the effect that the functional groups present in NOM (character) have on the formation of disinfection by-products and will include a laboratory based evaluation of the polyphenolic and carboxylic groups in UK NOM.

CHANGES IN PROPERTIES OF DISSOLVED ORGANIC CARBON (DOC) DUE TO CLIMATE CHANGE?

- A PRECIPITATION MANIPULATION STUDY

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With a major part of the land area covered by unproductive semi-natural ecosystems, Norway is unusual at the European scale. Climate change can be expected to impose more marked changes in mountains, heathlands and other semi-natural ecosystems compared to forests and cultivated land. For upland ecosystems in Norway, well-designed and -preformed whole ecosystem precipitation experiments are conducted at a realistic spatial and temporal scale. Such whole-catchment scale ecosystem experiments have been shown to be appropriate for the results used in prediction of future climate change effects on surface water quality [1].

Two natural mini-catchments (78 m^2 and 98 m^2) in Storgama (490 m.a.s.l.), a typical southern Norwegian headwater area, has received additional water to imitate predicted climate changes. The artificial precipitation system adds precise amounts of water of a specific quality evenly onto the mini-catchments [2]. Since the predictions of future effects of climate change are based on models, development and testing of models requires basic appropriate experimental data. High-resolution water proportional samples has been analysed weekly, and an increased percentage of high molecular DOC seems to enter the headwaters during episodes with high precipitation. Similar results have also been obtained in resent studies [3], and could explain the increase of colour observed in Nordic waters resent years.

References

1. Carpenter, S.R., Krebs, C.J., Chisholm, S.W., Schindler, D.W., & Wright, R.F. (1995). Ecosystem experiments. *Science* 269: 324-327.

2. Haaland, S. (2005). Precipitation manipulations imitating a climate change in Norwegian headwaters. *In prep.*
3. Hongve, D., Riise, G & Kristiansen, J.F. (2004). Increased coclour and organic acid concentrations in Norwegian forest lakes and drinking water - a result of increased precipitation? *Aquatic Sciences* 66: 231-238.

DETERMINATION OF DOC-WATER PARTITION COEFFICIENTS OF PAHS USING DISPOSABLE SPME FIBRES

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Dissolved organic carbon present in sediment pore waters may have a significant impact on the bioavailability of PAHs and other hydrophobic organic compounds. The measurement of freely dissolved or bioavailable concentrations therefore gives information about the interactions involved in aqueous sorption processes. DOC-water partition coefficients (K_{doc}) for a selection of PAHs have been determined from analysis of freely dissolved concentrations in the presence of DOC extracted from freshwater sediments of varying properties (0.12 - 21.03 % TOC) from the Netherlands, Finland and Sweden. Freely dissolved PAH concentrations were determined using disposable SPME fibres (30 μm PDMS) with increasing concentrations of DOC. Since a significant amount of the PAHs was extracted from solution (3 to 31% for fluorene and benzo(e)pyrene, respectively), the water to fibre partition coefficient (K_{fibre}) was also determined for six PAHs. After equilibrium between water and fibre has been reached (after 10 days at 20°C and 21 days at 4°C), the fibres were desorbed in acetonitrile and analysed with liquid chromatography. The resulting log K_{doc} values were 3.96 for phenanthrene (n=1), 3.17 - 4.23 for anthracene (n=3), 3.44 to 4.62 for fluoranthene (n=4), 3.61 - 4.66 for pyrene (n=6) and 4.82 - 5.97 for benzo(e)pyrene (n=6). This range in K_{doc} values suggests that extracted organic carbon from different sediments shows a variable sorbing potential for the PAHs studied. The effect of temperature on the partitioning of PAHs over water and DOC is also studied to gain more information on the strength of sorption involved.

GLASS TRANSITIONS IN HUMOUS SOIL SAMPLES

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Macromolecular characteristics of soil organic matter are important for sorption and transport processes in soil [1,2]. Until now, glass transitions were detected in isolated humic and fulvic acids [2] as well as in soil samples [3-5]. But the number of studies, investigating glass transitions in whole soil samples, is very low. To judge the relevance of glass transition behaviour in sorption processes in the field, knowledge on the presence and nature of glass transitions is highly important.

The study presented in this contribution shows that glass transition-like behaviour exists in various soil types of different locations. On the one hand, the intensity of the observed glass transitions is correlated to the C_{org} contents of the soils. On the other hand, structural properties of the SOM, like the cross-linking density, which varies with the degree of decomposition, may influence the characteristics of the glass transitions as well.

A surprising result of the study is that the glass temperatures are (61 ± 6) °C for all the analysed air-dried soil samples. This points to a superordinate factor which controls the side chain mobility of the organic molecules. Probably, the water content and the period of time in which the samples gradually approach towards an equilibrium water status are important factors of influence for the observed glass temperatures. Therefore, in improved sorption models, the interactions between water and SOM should be taken into account.

Referenes

1.Xing, B; Pignatello, J J. Environ. Sci. Technol. 1997, 31, 792-799.
2.LeBoeuf, E J, Weber Jr, W J. Environ. Sci. Technol. 1997, 31, 1697-1702.
3.Schaumann, G E; Antelmann, O. J. Plant Nutr. Soil Sci. 2000, 163, 179-181.
4.DeLapp, R C; LeBoeuf, E J. J. Environ. Qual. 2004, 33, 330-337.
5.Schaumann, G E; LeBoeuf, E J. Environ. Sci. Technol. 2005, 39, DOI: 10.1021/es0490931.

SYNTHESIS OF CROSSLINKED HUMIC MATERIALS OF CONTROLLED SIZE

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Crosslinking is a perspective tool for synthesis of humic materials of the controlled size. The promising direction for achieving controlled cross-linking of humics can be incorporation of epoxy cycles. The epoxy cycles can be opened using thermal treatment or via reactions with polyamines. The objective of this study was to test the feasibility and particular features of epichlorhydrine crosslinking of HS. Leonardite humic acids (CHP) were used as the parent humic material. The latter was dissolved in 30% NaOH and added with epichlorhydrine to provide a ratio of 1 mol of CHP phenolic hydroxyls to 5 mols of epichlorhydrine. Heterophase catalyst was used. For opening the incorporated epoxy-cycles, reaction with ethylenediamine; reaction with polyethyleneamine; and heating of the product up to the boiling point were applied. The obtained derivatives were characterized using elemental and functional analyses and size exclusion chromatography. The highest linking degree was observed for the thermally treated derivatives, they were insoluble in water. The derivatives linked with amine-bridges had molecular weight exceeding the value of the parent material. The conclusion was made that the thermal method is preferred for synthesis of humic sorbents, whereas the amine-bridging can be a suitable technique for obtaining humic materials of colloidal size.

CHANGES IN ORGANIC MATTER CONTENT ON ERODED LITHUANIAN ALBELUVISOLS AND INTERNATIONAL CALIBRATION OF ANALYTICAL PROTOCOLS

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Perennial grasses can assist the accumulation of soil organic matter (SOM) and thus soil organic carbon (SOC). Therefore, it is logical that a combination of selected crop rotations, containing different species and configurations of perennial grasses, can help to both sequester SOC and to prevent soil erosion. Research data were obtained on sandy loam Eutric Albeluvisols at the Kaltinenai Research Station of the Lithuanian Institute of Agriculture (LIA) on the undulating hilly topography of the Zemaiciai Uplands of Western Lithuania. Results from 18 years of field investigations show significant increases in SOM content under the grass-grain crop rotations, containing 67% perennial grasses, compared with field and grain-grass crop rotations containing 33% perennial grasses. SOM content was analysed using the Tiurin method, which is not widely known in Western Countries. Therefore, SOM data will be presented also recalculated to dry combustion, Walkley-Black (USDA) and loss-on-ignition (UK) methods. The possibility of data transfer was based on the strength and significance of correlation and regression relationships amongst the five SOM/SOC analytical protocols used in laboratories of LIA and the University of Wolverhampton, UK. The transfer equations were calculated using research data from the scientific pilot project ‘Carbon sequestration in Lithuanian soils’ (F/00630B), which was supported by the

Leverhulme Trust, UK. These transfer functions open the possibility to transfer data between databases. International calibration of the SOM databases in Lithuania and other Central and East European countries will assist in a multitude of tasks. These include international collaborative studies of the role of SOM/SOC in terrestrial ecosystems and the development of effective soil conservation policies.

ANTS – AN IMPORTANT FACTOR FOR DISSOLVED ORGANIC MATTER DYNAMICS AND MICROBIAL ACTIVITY IN DECOMPOSING SPRUCE LITTER?

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Interactions between litter, soil fauna, the microbial community, and easily degradable organic matter delivered by throughfall should strongly affect the composition of organic matter in the forest floor. However, these interactions are poorly understood. In our study we combined the expertise of zoology, microbiology and soil ecology to analyse the effects of ants and aphid honeydew on dissolved organic matter (DOM) and microbial enzyme activities in decomposing Norway spruce litter in field and greenhouse experiments. In the field, low ant densities significantly increased dissolved organic carbon (DOC) concentrations next to a trunk where ants tend to build their nests. This effect disappeared 30 cm away from the

trunk. In a greenhouse experiment, the addition of ants to lysimeters containing spruce litter significantly increased DOC, organic and inorganic N concentrations in litter solutions compared to the control treatment. The simulation of aphid infestation (addition of honeydew) significantly increased DOC, and decreased inorganic N concentrations in leachates. However, increased DOC concentrations were the effects of added DOC by honeydew only. The presence of ants resulted in a changed composition of dissolved organic matter with more aromatic and complex compounds indicating increasing portions of lignin-derived compounds. Activities of 7 microbial exoenzymes involved in C and N cycling were significantly higher in litter from the ant treatment compared to the honeydew and control treatment. However, neither mass loss nor litter composition was affected by ants or honeydew. Our results suggest that ants have a distinct and immediate effect on dissolved organic matter and microbial activity in the litter layer indicating accelerated litter decay whereas the effect of honeydew was insignificant. Dissolved organic matter and the activity of exoenzymes appear to be good indicators for changes in the turnover of organic matter caused by increased activity of the soil fauna.

EFFECTS OF GYTTJA ON SOIL CHEMICAL AND BIOLOGICAL PROPERTIES AND AVAILABILITY OF HEAVY METAL IN SOIL

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Effects of Gyttja (250 kg da^{-1}) on a variety of soil chemical and biological properties, and heavy metal availability were investigated and compared to that of

inorganic fertilization (NP). The influence of Gyttja (G) alone and its combined treatment with mineral fertilizer (G+NP) on soil organic matter, pH, EC, total N, calcium carbonate content, enzyme activities, microbial biomass C, soil respiration and availability of certain heavy metals (Cd, Pb, Ni, and Zn) were examined through a 180 days incubation. A significant increase in organic matter content was observed in the soils treated with G+NP. Compared with G and NP by alone, the G+NP amended soils showed higher values in terms of selected biological properties. DTPA-extractable metals significantly increased with increasing rates of sole NP amendments, however, the addition of G+NP resulted in a considerable decrease in the amount of extractable metals during the incubation period ($P<0.05$). Based on these results, it could be concluded that organic matter applied in the Gyttja led to an increase in the metal absorption capacity of the amended soils. This contribution could be useful to reduce availability and mobility of heavy metals in the soils intensively amended with mineral fertilizers. Combined treatment of G and NP could therefore be considered as an alternative approach in the applications of organo-mineral fertilization.

SORPTIVE CONTROL ON DISSOLVED ORGANIC MATTER EXPORT FROM SOILS IN FOREST TUNDRA ECOSYSTEMS

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To test the hypothesis of sorptive control on the release of dissolved organic matter (DOM) from soil systems affected by permafrost in northern Siberia we examined the sorption of DOM (obtained from the respective organic layers by extraction with water) by mineral soils. The tested soils were Gelisols and Inceptisols with varying depth of the active layer. Water-soluble organic matter in the O layer of the Gelisols was less (~400 mg C kg^{-1}) and comprised more carbon in the hydrophobic fraction (HoDOC) (~70%) than that of the Inceptisols (~700 mg C kg^{-1}, ~45% HoDOC). All A and B horizons adsorbed DOM strongly with a preference for HoDOC. Inceptisol C horizons, having a weak overall DOM sorption, retained carbon in the hydrophilic fraction (HiDOC) stronger than HoDOC, probaby because their high pH (>7.0). A horizons released large amounts of carbon with a large share of HiDOC. The results indicate that soils with deep active layer, i.e. Inceptisols, may release little DOM. These results are in harmony with the situation observed for streams at lower latitudes. Where the active layer is thin, i.e. in Gelisols, DOM rich in HiDOC can pass the soil and enter streams. This is in agreement with the large DOM concentrations in more northern catchments. However, as the Inceptisols, the Gelisols preferentially retain HoDOC which dominates the DOM in streams towards north. This discrepancy can be explained by additional seepage water from the organic horizons discharged into streams without intensive contact with the mineral soil.

DETOXIFYING ABILITY OF THE HYDROXYLATED HUMIC DERIVATIVES WITH RESPECT TO COPPER

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The objective of this study was to evaluate detoxifying ability of the hydroxylated humic materials with respect to copper. The hydroxylation procedure included subsequent oxidation-reduction of the aromatic structures present in the parent humic material - leonardite humic acids. Three oxidizing agents were applied: Fenton reagent, Elbs reagent and Fremy's salt. The oxidized derivatives were reduced using sodium sulfite. Detoxifying ability of the oxidized and oxidized-reduced humic derivatives was assessed using seedling technique. The results of biotests were treated to calculate toxicological binding constant of copper to humic material (K_{OC}^{tox}, L/kg OC). K_{OC}^{tox} values ranges from 5.2×10^4 to 5.6×10^6 L/kg OC. K_{OC}^{tox} values for five out of six derivatives were an order of magnitude higher than K_{OC}^{tox} of the parent material. In addition K_{OC}^{tox} values preparations obtained by Elbs reagent increased after reduction from 7.0×10^4 to $4.0\ 10^5$ L/kg OC. Similar effects were not registered for other preparations. Hence, the undertaken hydroxylation brought about a substantial increase in detoxifying ability of the parent humic material. The proposed approach can be considered as a promising tool for producing humic detoxicants efficient against heavy metal pollution.

ENVIRONMENTAL CATALYSIS BY HUMIC SUBSTANCES

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I. INTRODUCTION

Humic substances (HS) improve soil fertility, and they play a principal role in the turnover of organic carbon. Humic substances form the major part of the organic component of soil, peat and natural waters, and they affect groundwater properties and the formation of fossil fuels. Humic substances can complex heavy metals and persistent organic xenobiotics. The catalytic activity of humic substances has been little analyzed. However, they contain many groups and structures which in similar macromolecules are responsible for their catalytic activity or may increase reaction velocity due to structural conformation of the macromolecules. The main factor responsible for removal of organic xenobiotica (pesticides, PCB's, PAH's and many other substances) is considered to be microorganism activity, and in this regard the role of humic substances may have been unduly neglected. Considering the high concentrations of humic substances in natural environments and their potential catalytical activity, they may indeed be significant in the fate of different xenobiotics. Of the different reactions, it may be expected that the velocity of hydrolysis and condensation reactions can be influenced by the presence of humic substances. These reactions may be particularly important in the hydrolysis of xenobiotica, as many environmental pollutants contain ester linkages.

The aim of the present study was to study the catalytic activity of humic substances of different origin in the reactions of hydrolysis of esters and condensation reactions.

II. MATERIALS AND METHODS

Humic (HA) and fulvic (FA) acids were isolated from soil and peat by extraction with 0.1M NaOH, and from water by a modification of the Malcolm and Thurman method. The concentrations of functional groups in humic substances were determined by standard methods. Commercial humic substances were used for comparison (Aldrich). UV spectra were obtained on a Hitachi 850 spectrometer. The velocity of the reaction was estimated using a spectrometer HACH DR/2000.

Reaction kinetics

p-nitrophenylacetate in dioxane (2 ml, 2 mole/l) was added to HS solutions in phosphate buffer (100 ml, 0,05 mole/l, pH= 8), with or without a catalyst. Quartz cell absorption (A_τ) of p-nitrophenol (400 nm) was measured at 20^0 C as a function of time. After at least 10 half-lives, the absorption for complete reaction was measured (A_∞). Catalysis by buffer only (blank) was measured in the same fashion.

The measured data were treated as first-order kinetics by plotting (A_∞-A_t) on a log scale vs. time on a linear scale. The plots were straight lines for 70 % conversion or more. The slope was taken as $k_{measd.}$. The solvolysis of substrate $k_{measd.}$ is the composite of the catalyzed ($k_{obsd.}$) and the uncatalyzed reaction. k_{obsd} is therefore obtained by subtraction $k_{obsd.} = k_{measd.} - k_{blank.}$

The kinetics of p-dimethylaminobenzaldehyde condensation with hydrazine was studied similarly.

III. RESULTS AND DISCUSSION

The humic substances selected for catalytic activity studies represented the common types of HS and were comparable with reference samples. The humic substances were isolated from soil, peat and water in Latvia and their properties were within the ranges common for humic substances. The highest aromaticity was for peat and soil humic substances, and the lowest for aquatic humic substances. The molecular mass of the studied humic substances varied from 850 (aquatic fulvic acids) to ~ 10 000 (peat humic acids).

We examined the well-known p-nitrophenylacetate hydrolysis reaction in the presence and absence of a catalyst, as well as the condensation reaction between p-dimethylaminobenzaldehyde and hydrazine. Both were considered as pseudo-first order reactions. The reaction kinetics showed that all of the tested humic substances acted as catalysts, with fulvic acids showing the highest catalytic activity. The reaction velocity depended on the pH and the concentration of humic substances.

The velocity of p-nitrophenylacetate hydrolysis reaction increased up to a concentration of humic substances of ~ 50 mg/l (a concentration rarely exceeded in the natural environment). As at higher concentrations the reaction rate decreased, the interaction of humic substances with the reaction product was studied. The hydrophobic groups of humic substances allow association with low-molecular weight organic molecules. It can be supposed that the hydrolysis rates of humic substances will decrease significantly after association with organic compounds. We found that a substantial part of the reaction product may be associated with the catalyst- humic substances. The highest association coefficients were obtained for soil and peat humic and fulvic acids, which had the largest number of hydrophobic structural elements. The nonlinear character of the reaction velocity in response to the catalyst concentration in this case may involve the participation of a micellar catalysis mechanism in the overall catalytic process.

An increase of ionic strength was found to decrease the rate of hydrolysis and also condensation reactions, similarly to the effect of surfactants. This effect can be explained by the possible destruction of micelles of humic substances, which provides further evidence for the micellar mechanism of the catalysis.

The results showed that humic substances (soil humic acids) are poorer catalysts than sodium dodecylsulphate. While their catalytic activity is variable (compared with commercial HA), they are true catalysts and the activity is superior to that of nonionic surfactants and cationic surfactants. Thus, they behave as substances with acidic functional groups and exist in form of micelles in aquatic media. The velocity of reaction depends also on pH, being highest at low pH values.

An increase of HS concentration substantially increased the velocity of condensation reaction. Also, the velocity of the condensation reaction depended on the origin of the humic matter, with the highest catalytic activity observed for fulvic acids and the lowest in humic acids isolated from peat.

The condensation reaction kinetics of the three studied reactions showed general similarity with the micellar catalysis of anionic surfactants. The micelle structure of humic substances in aqueous solutions, their surfactant properties, and the determined critical micelle concentrations suggest that the micellar properties of humic substances can influence their catalytic activity. The clear dependence of the reaction velocity on the hydrophobicity of humic substances, and the inverse dependence on the presence of carboxylgroups, confirm that both these properties are important for their catalytic activity. This may be possible by influencing the association of hydrophibic reactants with humic molecules and reactions with participation of acidic functional groups.

IV. CONCLUSIONS

The results showed that humic substances from water, soil and peat exhibit considerable catalytic activity in colour fading and condensation reactions and thus may influence the fate of pollutants in environment. The rate of the studied reactions depended on the nature and concentration of humic substance, pH and temperature. The maximum catalytic activity was characteristic for aquatic fulvic acids, and the reaction mechanism possibly involves micellar catalysis in aquatic media.

TRIHALOMETHANE FORMATION POTENTIAL IN DRINKING WATER SUPPLY SYSTEM IN LATVIA DEPENDING ON PROPERTIES OF HUMIC SUBSTANCES

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Drinking water quality is amongst aims essential for human life. However existing water treatment technologies requires disinfection of water before providing to consumers. Since the pioneering work of Rook in 1974**,** it is known that the use of chlorine for disinfection purposes of drinking water leads to the formation of many byproducts potentially harmful for human health. Epidemiological studies suggest that probable health effects of these compounds in humans may be related to cancer and birth defects. Among all the chlorinated by-products trihalomethanes (THM) (chloroform ($CHCl_3$), dichlorobromoform ($CHCl_2Br$), dibromochloroform ($CHBr_2Cl$) and bromoform ($CHBr_3$) which exhibit a potentially carcinogenic activity, are most widely investigated during the last 20 years. The mechanism of THM formation from the chlorination of humic substances is not well understood. The yield and composition of chlorination byproducts very much differs depending on origin of humic substances .

Previous studies have shown the importance of many parameters for the formation of THM, such as dose of chlorine, pH, temperature, content and type of the humic substances. A number of researchers have tried to correlate humic substances or raw water characteristics to trihalomethane formation potential (THMFP) in an effort to find a useful surrogate parameter for THM or to better understand the chemical nature of THM formation from natural organic matter.

The aim of the present study is to evaluate the impact of structure of humic substances on the yield of THM and evaluate factors affecting THM formation in drinking water supply system in Latvia.

In this study the major drinking water utilities of the Riga were considered. As far as source for the drinking water supply are groundwater, groundwater after artificial recharge of surface waters and surface waters are been used, differing technologies for removal of humic material and disinfection are applied. The water distribution systems in Riga do have comparatively high residence time in the distribution systems and in general the water from different sources is mixed, but still dependence on water source can be observed. To study THM in drinking water, seasonal sampling from representative sites has been done and THMs and concentrations of humic substances have been determined.

The THM results showed some seasonal variation and usually both their concentration, and individual THM concentrations in drinking water of city dominantly supplied by treated River Daugava waters increased during autumn and winter and this pattern may be directly linked to changes in the concentrations of humic substances and their seasonal pattern of changes.

Humic acids commonly have much higher carbon concentrations than fulvic acids, but at the same time oxygen, carboxyl group concentrations are higher in fulvic acids. In humic substances from, concentrations of carboxyl groups and phenolic hydroxyl groups are lower, than in humic substances from aquatic sources and peat. The most dominant functional groups in the structure of humic substances are carboxyl and phenolic hydroxyl groups. The concentrations of carboxyl groups are higher in fulvic acids (3.5-6 mmol·g^{-1}), while humic acids have more phenolic hydroxyl groups (1.0-1.5 mmol·g^{-1}). The slope of the adsorption curves as measured by the ratios of UV absorbancy at 465 and 665 nm, have been suggested to be inversely related to the condensation of aromatic groups (aromaticity), and also to particle size and molecular weight. The higher E_4 /E_6 ratios measured for the aquatic FA, with respect to those of soil origin, are in general agreement with data in the literature and suggest a lower degree of condensed aromatic systems and smaller particle sizes or molecular weights than for aquatic HS. The E_4/E_6 ratio for fulvic acids is higher than for humic acids, thus this ratio correlates with the changes in molecular mass of humic substances. Humic substances from soils and peat have a high degree of aromaticity (as determined by ^{13}C-NMR) and molecular mass than humic substances from aquatic sources.

Table.

THM potential formation potential for water, soil and peat humic substances

Humic substance	CHJ$_3$, μg / μg HS	THMFP, μg THM4/ μg DOC
HA-Baltezers Lake	0.432	97
HA-Groundwater	0.346	43
HA-Daugava River	0.610	135
FA-Daugava	0.351	53
HA-IHSS	0.265	37
HA-Typical podzol.	1.246	210
FA- Typical podzol.	0.471	104
HA-Typical brown soil	0.908	155
FA-Typical brown soil	0.502	110
HA-Peat	1.582	260
FA-Peat	1.017	136
HA-Aldrich	1.786	352

It has been found that basic descriptors of both molecular mass or aromaticity of humic substances can be correlated with THMFP. Aromaticity of humic substances studied can be correlated to THMFP however weak correlation is found in respect to THM values.

APPROACHES FOR DERIVATIZATION OF HUMIC SUBSTANCES

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Humic substances (HS) are major refractory product of decay of living organic matter and as natural compounds they are abundant in soils, peat, sediments, some fossil fuels and waters all around the world. The suggested chemical network structure of HS contains hydrocarbons, aromatic and heterocyclic structures, carboxyl groups, phenolic and alcoholic hydroxyls and possess many active bonding sites making them chemically reactive. This allows explain binding ability of HS not only with metals and organic molecules, but also incorporation into the molecular structure of humic substances also persistent xenobiotica.

Humic substances do have high potential in their modification. Modification of HS has been used at first for structural studies of HS to protect labile functional groups. In the same time there are many possibilities to develop modification possibilities of humic substances, to search for new areas of application of modified HS. Modified HA can contain much weakened links between structural units of HA and can be of importance to uncover structures of HA. On the other hand, modification of HA can allow to obtain HA derivatives with significantly modified properties and of definite applied interest.

The aim of this study is to develop methods that can be used for derivatization of humic substances and to study properties of obtained derivatives.

In this study several approaches for derivatization of humic substances has been compared:

a) alkylation with CH_3I in presence of K_2CO_3, with Ag_2O/CH_3I in methanol, alkylation in presence of phase transfer catalyst 18-crown-6alkylation with dialkylsulphates or with alkylhalogenides in ionic liquids;

b) synthesis of thiolderivatives of humic substances;

c) synthesis of sulphoderivatives either using direct sulphonation or treatment with 1,3-propanesultone;

d) synthesis of silylderivatives;

e) modification of humic substances with diolgroups;

f) synthesis of trimethylammonio derivatives;

The degree of derivatiozation much depends on the reactivity of the used agents and reactivity of reactive groups in structure of humic substances. If the alkylation, nitration and sulphonation can been done with quantitative yields then other derivatization procedures gives only partial substitution of functional groups. The obtained derivatives of humic substances has been characterized by their elemental, functional analysis, IR, UV, NMR spectra. The molecular mass and its changes during the derivatization procedures have been followed. For some derivatives their ability to complex metal ions as well as ability to influence surface tension has been studied.

All alkylation products are soluble in $CHCl_3$ and CH_2Cl_2. In the same time their hydrophobicity as expressed by octanol/water partition coefficient vary quite significantly, indicating that in some cases the derivatization has not been quantitative. obtained methylderivatives are a complex mixtures partly soluble in water partly in hydrophobiv organic solvent. Quite significant reduction in the molecular mass and polydispersity of the humic molecules during the derivatization process has been observed and partly it can be explained with destruction of the more labile structures during the derivatization on one hand, but also possible can be dissociation of higher mass units into smaller, but more uniform structures.

FLOWS OF DISSOLVED ORGANIC MATTER AND THEIR CHANGES IN RIVERS OF LATVIA

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Dissolved organic matter plays a significant role in aquatic environment influencing mineral weathering, nutrient cycling, metal leaching as well as pollutant behavior and toxicity. Measurements of water color and chemical oxygen demand (COD) can be used as indirect estimates of humic substances since in many undisturbed rivers usually 40-65% of the COD is contributed by humic substances. Within this study both spatial and temporal changes of chemical oxygen demand (COD) and water color are analyzed. Both the spatial and seasonal variability of concentrations of organic substances in surface waters of Latvia can be considered to be comparatively high. The highest COD concentrations are usual for rivers in the Lielupe and Aiviekste basins, and also in eutrophic and bog lakes. Export values of COD varies between river basins in Latvia by nearly twice (from 5226 kg/km^2/year for the Mūsa River up to 12731 kg/km^2/year for the Iecava River, both rivers of the Lielupe basin. High loading of dissolved organic matter comes also from the Salaca

River basin. Higher export values of organic matter are typical for river basins with large bog areas. Spatial differences in loading are determined by land-use patterns, soil properties and anthropogenic activities within the river basin.

Investigations revealed that long-term changes (1977-2002) of COD and water color values have an oscillating pattern thus indicating the importance of natural processes in geochemical cycling of organic matter. Increasing values of COD and water colour during the last 10 years, coupled with a reduction of antropogenic loading suggest that natural processes play a dominating role in the actual flows of organic matter.

NATURAL ORGANIC MATERIAL AND BIOAVAILABILITY OF ORGANIC CONTAMINANTS IN AQUATIC ENVIRONMENTS

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Interaction of hydrophobic contaminants with natural dissolved organic material or particulate organic material plays a major role in contaminant distribution and bioavailability in the aquatic environments. For non-polar organic compounds the binding affinity is generally directly related to the hydrophobicity of the contaminant and the organic content of a sorbent such as particles. However, partitioning and bioaccumulation studies indicate that contaminant sorption and bioavailability may also be affected by different forms of natural organic material. Partitioning between water and particles has been described in multi kinetic processes that appear as two differentially bioavailable pools: one in a reversible pool and another in a resistant pool. The fraction of contaminant that resides in each of these pools changes, depending upon the sorption duration. During this equilibration phase, contaminant bioavailability can also be expected to change with time. The extent to which humus-associated contaminants are biologically available and bioaccumulated is important in order to assess their direct effects on organisms. More well designed studies are required to determine the potential for bioaccumulation that can be interpreted and modelled for predicting the impact of accumulated chemicals. This is a demanding work because bioavailability of any given contaminant is not a constant factor but rather an organism and system dependent parameter.

ASSOCIATION OF LACCASE WITH HUMIC ACIDS

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Laccase (Lc, EC 1.10.3.2) is an extracellular multicopper oxidase widely presented in soils. In the environment Lc behavior is determined mainly by its association with humic acids (HA). This study was aimed to provide direct evidence for the complex formation and to get deeper insight in its chemical nature. Lc from *Coriolus hirsutus* and coal HA was used. The Lc-HA complexes were prepared by incubation of Lc and HA in phosphate buffer. An additional peak corresponding to a component with molecular weight exceeding that of both Lc and HA was observed in size-exclusion chromatography (SEC) profiles of Lc-HA complexes, what was evident for Lc-HA complex formation. The finding was confirmed by measuring enzyme activity profile as the additional peak contained nearly 80% of total Lc activity applied. Assuming stability of Lc-HA complex under conditions provided compensation of partial negative charge of both Lc and HA, one can exclude ionic interaction as mechanism of complex formation. On the other hand, isoelectrofocusing (IEF) data allowed concluding on non covalent binding as complex was unstable under electrophoresis conditions. Association between Lc and HA by weak dispersive forces such as hydrophobic, van der Waals, π-π etc. was therefore hypothesized.

PARAMAGNETIC PROPERTIES OF HUMIC ACIDS EXTRACTED FROM ALBELUVISOLS OF NORTH-EASTERN EUROPEAN RUSSIA

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Free radicals content has been determined in humic acids (HA). Samples of HA were collected from soil horizons along a gradient of increasing hydromorphology. The soils sampled were: a Siltic Albeluvisol, a Silti-Stagnic Albeluvisol, and a Stagni-Histic Albeluvisol (Siltic) (FAO, ISRIC and ISSS, 1998). The sampling site was located on a hilltop, 6 km west from the city of Syktyvkar. The site was at the Maksimov field station of the Institute of Biology, Komi Science Center, Ural Division of Russian Academy of Sciences (61º39.6', 50º41.0').

Free radicals content in HA molecular structure increases with increasing soil moisture. The high free radicals concentrations in HA from all the horizons of the Stagni-Histic Albeluvisol (Siltic) are apparently caused by biohydrothermal conditions of humus formation in Stagni-Histic Albeluvisol (Siltic). Under these conditions all biochemical processes are hindered, which favors free radicals accumulation in HA molecules. It has been found out that in all studied soils free radicals content in HA decreases downwards the soil profile; this proves a higher thermodynamic stability of the HA molecules from mineral horizons as compared to those from organic horizons. An exception are HA extracted from litters, in which free radicals content is much lower than that in the HA from the underlying horizons.

POTENTIAL ANTIALLELOPATHIC ACTIVITY OF HUMIC SUBSTANCES ON CAFFEIC, FERULIC AND SALICYLIC ACIDS DURING EARLY GROWTH OF LETTUCE AND TOMATO

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Plant allelopathy is a phenomenon that occurs in the vicinity of plant roots, i.e., the rhizosphere, and consists in the stimulation or inhibition of growth, development and reproduction of plants, microorganisms, and animals. Allelopathy is produced by plant secondary metabolites called “allelochemicals” that are mainly of phenolic nature, and include several benzoic and cinnamic acid derivatives. The ubiquitous presence of humic substances and their capacity to react with a wide range of organic molecules suggest their possible involvement in the regulation of this phenomenon.

In this study, the capacity of a leonardite humic acid (LHA), a soil humic acid (SHA) and a soil fulvic acid (SFA), belonging to the Standard and Reference Collection of the International Humic Substances Society

(IHSS), was investigated in modulating the allelopathic potential of caffeic acid (CA), ferulic acid (FA) and salicylic acid (SA) on early growth of lettuce (*Lactuca sativa* L.) and tomato (*Lycopersicon esculentum* Mill.). The adsorption process of the three allelochemicals onto SHA was also studied in order to elucidate the mechanism(s) by which the antiallelopathic activity may occur.

Germination and early growth was examined by adding lettuce or tomato seeds with the following aqueous solutions or suspensions: (i) distilled H_2O, (control); (ii) SHA, SFA, or LHA at concentrations of 20 and 200 mg L^{-1}; (iii) CA, FA and SA at concentration of 20 mg L^{-1}; (iv) mixtures of SHA, SFA, or LHA and CA, or FA or SA at the above concentrations. Root and shoot lengths of seedlings were measured after 4-day germination. The residual concentration of CA, FA, and SA was also measured during germination in the presence or absence of seedlings and in the presence of seedling exudates collected previously. Adsorption kinetics and isotherms of CA, FA, and SA onto SHA were determined by using the slurry-type method. Allelochemical analyses were achieved by HPLC with UV detection at 280 nm.

Lettuce showed a sensitivity greater than tomato to CA, FA, and SA phytotoxicity, which was significantly reduced or even suppressed in the presence of SHA or SFA, especially at the highest dose, but not LHA. In general SFA was slightly more active than SHA¸ and the efficiency of the action depended on their concentration, the plant species and organ examined, and the allelochemical. The daily-measured residual concentration of CA and FA decreased drastically and that of SA slightly in the presence of germinating seeds of lettuce, which were thus able to absorb and/or enhance the degradation of CA and FA. The CA, FA, and SA adsorption onto SHA followed a linear model and no saturation was reached in the concentration range from 1 to 50 mg L^{-1}. The adsorption capacity of SHA was small for the three allelochemicals, and decreased in the order: FA > CA > SA. These results suggested that adsorption can be a relevant mechanism but not the only one responsible of the “antiallelopathic” action of HA.

THE EFFECT OF CROPPING AND FERTILIZER MANAGEMENT ON SOIL HUMUS CONTENT AND COMPOSITION

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Experiments were carried out on clay loam *Endocalcari – Endohypogleyic Cambisol* during 1986-2002 with a view to identifying the effects of preceding crops and biomass introducing for green manure and different fertilization systems – mineral, organic - mineral and organic on humus accumulation in the soil, its quality and crop productivity. In the mineral fertilization system, an average annual mineral fertilizer rate was $N_{56}P_{48}K_{60}$, the soil humus content remained close to the initial level. In the organic-mineral fertilization system application of 40, 60 and 80 t ha^{-1} of farmyard manure and NPK fertilizers as much as in the mineral fertilization system resulted in the following increases – soil humus content by 8.7; 11.7and 10.2 per cent respectively. In the organic fertilization system application of only 80 t ha^{-1} of farmyard manure, compared with mineral fertilization system, resulted in a humus content increase in the plough arable layer by 5.8 per cent. Analysis of humus fractional composition showed that its content was rather stable, however, a slightly higher content of mobile humic acids was found after lucerne as a preceding crop when green manure or farmyard manure had been applied. The ratio of humic and fulvic acids (C_{HA}:C_{FA}) did not differ much after various preceding crops, it was a highest after lucerne – 0.71.

ORGANIC AND MINEROGENIC ACIDITY IN FINNISH RIVERS IN RELATION TO LAND USE COVER

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To look at the role organic acidity might play in controlling the pH levels in Finnish rivers we determined total organic carbon (TOC), organic anion and non-marine sulphate ($^*SO_4$) from Finnish main rivers and their sub-catchments, (altogether 86 catchments) situated along a latitudinal gradient (60°N to 69°N) and covering 297 322 km^2, 88 % of the total area of Finland. The area of the catchments ranged from 73 to 56 500 km^2. For each catchment the percentage of different land use cover was derived from Environment Data System of Finland. Majority of the catchments was covered by coniferous forests and peatlands. The proportion of the land area covered by upland forests ranged from 29 to 64 % and the proportion of peatlands from 3 to 60 %. The percentage of peatland was highest in the northern Finland, whereas the forest proportion increased to the south. The proportion of agricultural land was on average 12 %. The sampling frequency of the rivers was between 12 and 32 per year during the study period 1995 – 1999. Some of the small rivers and sub-catchments were sampled less frequently. The high proportion of peatlands in the catchments and the high TOC concentrations decreased pH values in the river water, whereas no correlation between the $^{*}SO_4$ concentrations and pH was found. The average organic anion concentration exceeded the average non-marine sulphate concentration in 17 northern rivers, while $^{*}SO_4$ concentrations were higher in basins located in areas containing acid sulphate soils.

PYROLYSIS GC-MS ANALYSIS OF HUMIC ACIDS EXTRACTED FROM LAKE SEDMIENTS

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Homological composition of carboxylic acids in humic acids extracted from lake sediments was analyzed. The pyrolysis products were analyzed by gas chromatography in combination with mass spectrometry. It among carboxylic acids in studied KH esters of methylic fatty acids, esters dimethylic $\alpha\omega$-fatty acids and esters of methylic methoxybensoesic acids were identified was. Straight chained fatty acids methyl esters were found a major group of compounds, in which C_{18} and C_{22} homologues predominate.. The C_{18}/C_{22} ratio can testify about predominant part the phytoplankton in creating the organic components of organic matters. The concentration the carboxylic acids are insensibly larger in KH from sediments deposited in the maximum depth of lake than in KH from sediments of coastal zone.

MYCOTOXINS IN SOILS

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Mycotoxins are secondary metabolites often formed by fungi on cereal crops in the field or during storage. These metabolites are highly toxic to animals and humans, and high contents have been measured in cereal crops. In this project, the focus was on the occurrence of mycotoxins in agricultural soils and the fate of these toxins in the soil-water-plant system. Four different mycotoxins were selected: nivalenol (NIV), deoxynivalenol (DON) and zearalenone (ZON) produced by species of *Fusarium* or *Aspergillus*, and ochratoxin A (OTA) produced by species of *Penicillium.* We developed analytical methods for determination of these toxins in soil. Nivalenol and DON were extracted with acetonitrile:water (84:16), purified with florisil SPE columns, and derivatised with trimethylsilylate before determination by gas chromatography coupled to mass spectrometry (GC/MS). Zearalenone and OTA were extracted with methanol - water (9:1) and purified with C8 SPE columns), and determined by HPLC with fluorescence detection. All field soil samples contained DON at µg/kg levels. Degradation of the four mycotoxins was followed in pot experiments during 225 days. The degradation consisted of an initial fast degradation followed by a slower transformation step and was described well by a sum of two first-order kinetic equations. The slowest degradation was measured in soil rich in clay. Half-lives ($t_{½}$) were 6.4 – 11 days for ZON, and 0.2 – 1 day for OTA. No mycotoxins were detected after 225 days in any of the soil types. These results are the first records of the presence of

mycotoxins in soil-water systems, and an ongoing project.

QUANTIFICATION OF NOM FLUXES IN FORESTED DRINKING WATER CATCHMENTS IN THE LOW MOUNTAIN RANGE “ERZGEBIRGE” GERMANY

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Since the beginning of 1990ies increased NOM (Natural Organic Matter) flux into surface runoff and drinking water reservoirs were observed. These dissolved organic compounds mostly are characterized by humic matters. The investigation detected as responsible reasons a multi-causal complex of endogen and exogen ecosystem conditions. Dependent on the catchment characteristics (e.g. peat bog share in areas) we measured different loads and fractions of humic substances on NOM. Large storage of organic carbon in the peat layers, different rapidity in water movement due to ditches or short-term variability of water table in restored bogs and strong frequency of extreme climate events causes enhanced NOM export from catchments.

The investigation about sources and drivers of NOM dynamics in forested drinking water catchments aims to support the water treatment companies in planning for future steps in water treatment and catchment management. The use of the catchments referring to rising NOM fluxes is an important factor in this context.

The characteristic of NOM fluxes and approaches for modelling of NOM transfer will be discussed in the presentation.

The water balance model SWAT was adjusted for catchments with peat bogs. NOM quantifications are based on the water balance calculations and our measurements of DOC concentrations and humic substances in rivers. Our investigation showed a strong correlation between catchment characteristic and NOM load. We identified the variation in NOM concentration and load at different time scales (e.g. yearly, seasonal, during defined weather phases). Development of a humic matter transfer model is the main target of our research work.

AN INFLUENCE OF THE TREATMENT PROCESS ON THE NITROGEN CONTENT IN HUMIC ACIDS EXTRACTED FROM SEWAGE SLUDGE

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Humic acids were extracted from sludge from three sewage treatment plants with different treatment technology. Investigations of the extracted humic acids were carried out by means of elementary analysis and spectroscopic methods.

Results of elementary analysis show that percentage content of nitrogen is different for humic acids extracted from sludge derived from the following treatment stage. The influence of the treatment process on the nitrogen content also were observed. The percentage content of nitrogen were high and it enclose in the range from 5.05 % to 8.99 %. The highest value for humic acids extracted from sludge at the nitrification and denitrification chamber were obtained.

The spectroscopic methods confirmed the presence of nitrogen functional groups.

THE EFFECT OF HEAVY METALS AND AROMATISATION PROCESS ON g-FACTOR OF HUMIC ACIDS EXTRACTED FROM SEWAGE SLUDGE

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The aromatisation degree and the presence of heavy metals forming complexes with humic substances can influence on g-factor value. This effect was investigated for humic acids, extracted from sludge at the biologic-mechanical sewage treatment plant in Jastrzębie Zdrój by means of spectroscopic methods (EPR, NMR, IR, ICP). Sludge samples for studies were taken from the primary settling tank, the sludge nitrification and denitrification chamber, the sludge digestion chamber and the sludge drying bed.

The value of g-factor at each process stage were determined. The mean g-factor of the studied humic acids from sludge were low in comparison with the values obtained for humic acids originated from the other sources.

The low value of g-factor could be caused by the formation of metal complexes and aromatisation process. The ^{13}C NMR indicates that the aromatisation of the humic acids from sludge at the sewage treatment plant in Jastrzębie Zdrój increases during treatment process and it is relatively high. The presence of metals was confirmed by ICP. IR spectroscopy shows that the dissociated carboxylic groups in humic acids occur. Relative intensity of asymmetric bands, originated from carboxylic and dissociated carboxylic groups, change.

These facts indicate that complexes of transition metals could be formed.

THE INFLUENCE OF SIZE DISTRIBUTION ON COLOUR PROPERTIES OF DOM IN LOW IONIC FOREST LAKES E-NORWAY

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Studies in a forest lake area, E-Norway (1983-2004), have shown that increases in water colour and dissolved organic matter (DOM) are related to increased amount of precipitation. Furthermore, changed water pathways with increased leaching through the upper forest floor influence the spectroscopic properties of DOM, as DOM are, generally, more coloured (high colour:DOC ratio) at high compared to low flow conditions. As optical properties of water often are used to quantify the concentration of organic carbon, increased knowledge on factors influencing the spectroscopic characteristics of DOM are needed. The major objective of the present study was to investigate how the size distribution of DOM influences the colour properties (spectroscopic properties in the visible region of the spectrum) of freshwaters in low ionic forest lakes.

Water samples were collected from the surface layer (0 - 2 m) of 24 non-limed lakes during the autumn circulation period in 2004. The same lakes have previously been investigated in 1983, 1996, 1997, 2000 and 2001 and analysed for organic carbon, colour, pH and ionic composition. Water samples from the year 2004 were ultra filtered by means of a Centriprep concentrator method (Amicon YM 10) with a nominal molecular cut off of 10 kDa. Both unfiltered and ultrafiltered water samples were investigated for absorption properties at 254 nm, 410 nm, 465 nm and 665 nm. Generally, the absorption per mg DOC increased with increased amount of high molecular weight forms of DOC. Hydrological factors influencing the properties of DOM will be further discussed.

ELEMENTAL AND STRUCTURAL REGULARITIES OF THE INDIVIDUAL MOLECULES IN A FULVIC ACID MIXTURES AS DETERMINED BY SIZE EXCLUSION CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY

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The application of electrospray ionization-mass spectrometry (ESI-MS) offered new possibilities to investigate fulvic acid mixtures. With highly sophisticated FT-ICR-MS single fulvic acid molecules and their molecular formulas could be determined [1]. We have recently shown that a more commonly found quadrupol-time of flight mass spectrometer (Q-TOF-MS), if coupled to size-exclusion chromatography (SEC), allows to determine and to investigate individual fulvic acid molecules [2].

Using SEC-Q-TOF-MS we detected remarkable regularities at three different levels for the molecules in Suwannee River fulvic acid (SRFA):

1. SEC separated SRFA into three fractions and the respective MS data suggest that fulvic acids show a polymer like character, as high mass molecules appear

to consist of subunits that are identical to lower mass molecules [3].

2. On the level of molecules we determined more than 220 molecular formulas within a mass range of 190 – 350 Da. These formulas could be arranged in three superimposing homolog series of a) hydrogenation, b) alkylation and c) oxidation.

3. On the level of molecular structures the product ion spectra generated by Q-TOF-MS revealed striking structural regularities molecules between the individual fulvic acid molecules.

These data outline that fulvic acids are a complex but homogenous class of compounds with a remarkably high degree of elemental and structural regularity. Furthermore this compound class appears to be structurally independent from any other class of biogenic material yet investigated.

References

1. Stenson, A.C., Marshall, A.G., and Cooper, W.T. (2003) Exact masses and chemical formulas of individual Suwannee River fulvic acids from ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectra. Anal. Chem. 75: 1275-1284.
2. These, A., Winkler, M., Thomas, C., and Reemtsma, T. (2004) Determination of molecular formulas and structural regularities of low molecular weight fulvic acids by size-exclusion chromatography with electrospray ionization quadrupole time-of- flight mass spectrometry. Rapid Commun. Mass Spectrom. 18: 1777-1786.
3. Reemtsma, T. and These, A. (2003) On-line coupling of size exclusion chromatography with electrospray ionization-tandem mass spectrometry for the analysis of aquatic fulvic and humic acids. Anal. Chem. 75: 1500-1507.

VARIABILITY OF ORGANIC CARBON AND NITROGEN STORAGE IN A SMALL CATCHMENT AT

THE FOREST TUNDRA ECOTONE, NORTHERN SIBERIA

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This study addresses the effects of ecosystem differences at the catchment level on the permafrost pattern and the storage of organic carbon (OC) and nitrogen (N) in soils. The case study was carried out in the 0.44 km^2 catchment Grawikja creek located in the forest tundra north of Igarka at the lower Yenisei region, Siberia. Based on a grid mapping and using GIS techniques, the spatial distribution of vegetation pattern, percentage of canopy closure, exposition and slope inclination, organic layer thickness, depth of the active layer, and OC and N storage in soils was assessed, and analyzed by discriminance and canonical correspondence analysis.

Forty three percent of the catchment was underlain by permafrost within 90 cm soil depth. Little active layer thickness occurred at northern slopes of weak inclination and with plateau situations, whereas soils developed in south facing slopes usually had no permafrost within 90 cm. This indicates the role of solar radiation and of drainage for the active layer thickness. At plateau situations, pronounced permafrost degradation by thermokarst erosion is occurring. The permafrost thickness can be well predicted by vegetation parameters. Further, thick organic layer providing insulation for the soil concur with high permafrost. Soil OC stocks varied between 5 and 95 kg m^{-2}, and are closely related to the permafrost regime, as are N stocks. High permafrost leads to particularly larger OC storage in the organic and moss layers and in between 20 - 90 cm soil depth. This suggests that high permafrost increases SOM storage by decreasing decomposition of organic matter due to high water contents in the surface soil, whereas in the subsoil this is due to conservation by freezing. ^{14}C analysis indicated bog formation in the holocene about 3.700 yrs ago and a C age of 29.000 yrs in the frozen mineral subsoil.

The results suggest that permafrost degradation in soils of the catchment correspond with a decrease in SOM storage. In well-drained terrestrial soils this process develops gradually, and concurs with a shift to drier and deeper soils providing better growth conditions for the vegetation. In bog areas, however, permafrost degradation is a rapid process. Since we measured large methane emissions in the thermokarst lakes formed, thermokarst degradation of bogs and associated mobilisation of old carbon leads not only to the release of CO_2 into the atmosphere but also of CH_4, which is a much more potent greenhouse gas than CO_2.

THE UNEXPECTED ROLE OF WATER IN SOIL ORGANIC MATTER FROM A MACROMOLECULAR POINT OF VIEW

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In the field, soil components are subjected to subsequent changes of their water content. These are expected to alter physicochemical properties of soil organic matter (SOM). Very little is known about the process of hydration of SOM and its effect on SOM physicochemistry.

This contribution aims to eludicate the role of water from the macromolecular point of view, in which SOM is regarded as amorphous polymer consisting of glassy and rubbery regions [1], with a glass-to-rubber transformation at the glass transition temperature (T_g) upon heating. Theory expects that water acts as plasticizer in the SOM matrix, i.e. the glass transition temperature decreases with increasing water content.

Recent studies showed that SOM reveals principal macromolecular characteristics in a variety of humous soil samples [2,3]. However, glass transition behavior does not fully match theoretical expectations. Glass transitions in water containing soil samples are observed only in hermetic systems and reveal a very slow reversing component [3]. Water reveals a short-term plasticizing function (days) as well as an unxepected slow antiplasticizing function (weeks, months or more) [3,4].

In this contribution, an overview on the peculiar effects of hydration on SOM will be given, and possible explanations and consequences for the ecological relevance of the SOM-water interactions are discussed. Non-equilibrium and matrix relaxation are considered the rule rather than the exception in nature and underline the ecological relevance of hydration, the relevance for sorption and transport phenomena was well as possibly for soil development.

References

1. E. J. LeBoeuf and W. J. Weber Jr, Environ. Sci. Technol., 31 (1997) 1697-1702.
2. J. Hurraß and G. E. Schaumann, Environmental Sci. Technol. (2005) submitted.

3. G. E. Schaumann and E. J. LeBoeuf, Environ. Sci. Technol., 39 (2005) DOI: 10.1021/es0490931.
4. G. E. Schaumann, Colloids Surfaces A: Physicochem. Eng. Aspects (2005) submitted.

STABILISATION OF DISSOLVED ORGANIC MATTER BY FORMATION OF DOM-AL-PRECIPITATES

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Precipitation of dissolved organic matter (DOM) by aluminium is one process of DOM retention in acidic forest soils. However, the contribution of DOM-Al-precipitates to the formation of stable soil organic matter has not been investigated so far. The aims of our study were to quantify the microbial stability of DOM-Al-precipitates in dependence on (i) the source of DOM, (ii) Al speciation, and (iii) the Al/C ratio.

Aluminium-DOM precipitates where gained by adding $AlCl_3$ in varying amounts to DOM-solutions from 2 forest floor horizons of a spruce and a beech site. To include the effect of different aluminium speciation, pH-values of 3.8 and 4.5 were used. The precipitates were incubated for 7 weeks and organic matter stabilization was quantified by CO_2 measurements. We analyzed changes in organic matter composition induced by precipitation and its subsequent mineralization applying spectroscopic methods (UV, fluorescence, FTIR, NMR). Furthermore, we quantified the microbial activity by enzyme assays and described the spatial colonisation of the precipitates by micro-organisms using laser scanning microscopy.

DOM-Al-precipitates proofed to be very stable and showed much smaller mineralization than DOM itself, e.g. C mineralization declined from 50% for one DOM sample to 3% of the corresponding DOM-Al-precipitates. The spectroscopic measurements indicated a preferential precipitation of aromatic compounds supporting the idea that mainly per se stable compounds of DOM tend to precipitate. Organic matter stabilization was less with increasing percentage of Al-hydroxides species. Surprisingly, the stability of DOM-Al-precipitates decreased with increasing Al/C ratios which was affirmed by measured enzyme activities. These combination of different chemical, spectroscopic, microscopic and microbial methods allows the conclusion that precipitation of DOM in acidic forest soils could be a major driving force of organic matter stabilization.

NOM QUALITY AND TRANSFER FROM PEAT BOGS DUE TO ENVIRONMENTAL CHANGES IN THE MOUNTAINS “ERZGEBIRGE” (GERMANY)

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In the mountains “Erzgebirge”, located between Czech Republic and Germany, there were many drinking water reservoirs and flood protection dams established. Since the 1990ies a changed natural organic matter (NOM) quality and flux from peat bogs into surface waters was observed, and also the raw water quality in the reservoirs was concerned. In the same period changes in climatical and emission situations were measured. Recently, there is an increase for example at the pH values in the precipitation or at the frequency of heavy rain events. The management strategies in the catchments changed as well.

For the determination of the causes for the changes in quality and transfer of NOM water sampling networks were sketched. By this taken water samples were analysed organic parameters like NOM fractions by Liquid-Chromatography with OC-Detection (LC-OCD). Furthermore soil samples were investigated on the parameters organic carbon, nitrogen and phosphorus, in addition, the decomposition degree and the saturated water conductivity within different peat layers. With peat samples laboratory experiments were accomplished, in order to determine the potential mobilizable organic matters.

In the lecture it will be shown, in what responsibility the properties of catchments are connected with the matter discharge. The effects between changes in the peat characteristics due to environmental changes are discussed by NOM quality and transfer.

THE EUROPEAN CARBON BALANCE AND THE POSSIBLE ROLE OF HUMIC SUBSTANCES

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The European carbon balance as measured by top-down approaches via inverse modeling and via bottom-up approaches from inventories shows a gap of about 70 Tg C/year, which is ± 20% of the average. Regionalizing the continental budget indicates that the Baltic countries are a major Carbon source, due to the trade of peat. Any of these budgets do not contain dissolved organic C (DOC) or the export of Inorganic C (DIC). In this overview, the role of different land use types on the terrestrial carbon budget will be discussed. The sampling procedure at European scale will be explained. This sampling design underestimates Eastern Europe and the Baltic states. Also, the problems of measuring long-term changes in Soil Organic Matter will be discussed. At this point, the stabilization mechanisms of SOM, and the fate of DOC in the soil profile and its exchange with DIC remains unclear. The lecture summarized work that was initiated by the European project CarboEurope-IP.

ACID-BASE PROPERTIES OF WATER-SOLUBLE ORGANIC MATTER OF PODZOLS IN THE NORTH-EAST EUROPEAN RUSSIAN TAIGA

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Systemic research of soil organic matter is justified by a variety of its composition, forms, and ecological functions. An important component of soil humus is organic matter water-soluble fraction. Being of a non-homogeneous character and also differing by molecular-weight composition, its various functional groups are responsible for a unique role of these compounds for formation of genetic horizons of podzols.

Acid-base properties of water-soluble organic matter of podzols have been studied. Five groups composed of different substances with pK values around 3.6; 4.8; 6.7; 8.7 and 9.7 have been identified. The pK values from 3.6 to 6.7 are typical of low weight acids, such as formic, oxalic, citric, maleinic acids. Higher pK values attribute to phenols and water-soluble aluminum (III) compounds.

Each group includes soluble fulvic acids, which pK values often lie within an interval of 3.0 - 7.0 but mostly 4.0 - 5.0. Besides, contribution of the components with pK 9.6 ÷ 9.8 equals 41%.

Testing the composition and properties of soluble soil fraction, it is to be taken into account that when it is isolated from non-soluble soil matter, some water-soluble substances remain in soil and do not pass into the solution. Most firmly adsorbed in soil are water-soluble components with pK 9.6-9.8.

EFFECT OF HUMUS ENRICHED PHOSPHORUS APPLICATION ON THE YIELD AND NUTRIENT UPTAKE OF RICE AND SESAME IN COASTAL SALINE SOIL

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India has a coast line of about 8000 km and soils along the coast are severely degraded. The soil suffers due to salinity, sodicity , poor organic matter status, light texture and low CEC which causes deficiency of nutrients especially Phosphorus. Mono cropping of rice coinciding with the monsoonic rain is the common practice in coastal India with very poor rice yield of 1.5 – 2.0 t ha^{-1}. Sesame (*Sesamum indicum* L.) being other crop grown with poor yield realization (250 – 300 kg ha^{-1}). Hence, with a view to increase the productivity of these crops in coastal saline soils , Green house and field experiments were conducted using humus enriched phosphorus application on the growth, yield and nutrient uptake of rice and sesame. The experimental soil was saline sodic with pH 8.74, EC 2.84 dS m^{-1} and ESP

28.74. The alkaline $KMnO_4$- N and Olsen-P were low. The treatments studied were Control (100 % recommended NPK for the crop), 75 and 50 per cent recommended P with substitution of 25 and 50 per cent P through lignite derived humic acid enriched P and enriched Farm yard manure constituting five treatments replicated four times in a randomized block design. The results of the various experiments indicated the beneficial effect of application of 75 per cent of the recommended P with 25 per cent P substitution as lignite humic acid derived P in increasing the growth, yield and nutrient uptake of both the crops investigated. There was a yield increase to the tune of 22- 26 per cent in rice and 18 – 23 per cent in the case of sesame in coastal saline soil. Humic acid application also increased the availability of soil nutrients and microbial activity of soil.

RISK ASSESEMENT OF TOXICITY OF HUMIC SUBSTANCES

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Humic substances form most of the organic component of soil, peat, lignite, natural waters and their sediments. Considering their high chemical and biological persistence, they can be considered as essentially non-toxic, and as such, humic substances have been evaluated during long history of their research. The humic substances have properties, which determine their environmental roles and their importance in agriculture, but also some significant areas of their potential use, for example as fertilizers and animal food additives, in medicine and cosmetics, as anti –

inflammatory agents, hormone – like substances, human food additives, etc.

As humic substances containing products are new and innovative, risk of their use have to be assessed.
Recent studies have indicated comparatively significant impact of humic substances on immune and reproductive systems. In the same time there are very few studies of toxicity of humic substances. Tecently started large-scale production of humic substances requires new level of knowledge about properties of humic substances, including also their toxicity:

1. New findings of humic matter properties clearly indicating wide range of biological activity, and impact at first on regulatory properties;
2. Industrial production of humic substances can develop new routes of exposure and thus they may influence human health and living organisms.

HUMIC BASED WOOD AND PAPER COLORS

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Humic substances are the dominating naturally occurring organic substances. Humic substances (HS) form most of the organic component of soil, peat and natural waters, they influence the process of formation of fossil fuels, they play a major role in the global carbon geochemical cycle. The humic substances may be regarded as a valuable substance which may found manifold uses for different purposes. Due to multifunctional character (presence of numerous carboxylic and phenolic, but also keto-, and aminogroups) humic substances are able to complex heavy metals and persistent organic xenobiotics, but they do have also comparatively high chemical reactivity.

Considering relatively low costs of industrially produced humic substances, their brown colour and their bacteriostatic properties there are definite options to develop humic based colorants for paper and wood.

The aim of this study is to develop approaches for synthesis of humic based colorants for paper and wood. As basic tool has been selected approach of modification of humus structure with secondary amines and triazoles, also oxidizing them to N-oxides.

Using this approach it is possible to obtain humic based wood colorants. The introduced color is stable in respect to washing and light interaction and with reasonable wood protecting capacity

THE USE OF ELECTROSPRAY – ION TRAP MASS SPECTROMETRY IN THE STUDY OF AQUATIC HUMIC MATERIAL

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The humic material in water is build up of highly heterogenic compounds with various structural features. The molecular weight of the material has been determined with various methods such as size exclusion chromatography and ultrafiltration. Recently, the applicability of soft ionization methods for mass spectrometry has received interest as a tool for both molecular mass distribution studies and for structural studies. In the respect of structural studies, the ion trap mass spectrometer should offer great possibilities due to the inbuilt feature for performing MS^n.

In this work, we have studied the humic material in water using ion trap MS and electrospray ionization. In both the negative and the positive mode, the mass distribution was found to be lower than previously reported in the literature. When negative ions were recorded, ions from about *m/z* = 150 to 700 were observed and the most abundant ions were those around *m/z* = 350 – 400. These ions are mostly due to proton abstraction from parent compounds with acid functionalities ($[M - H]^-$), and thus the mass spectrum gives information about the molecular weight distribution of organic compounds with acid functionalities. In the positive mode (basic functionalities, $[M + H]^+$), ions of near equal abundance were observed between *m/z* = 100 – 600. MS/MS studies showed the predominant fragmentation to be the loss of water and CO_2 from the parent ion.

THE RELATIONSHIP BETWEEN THE COMPONENTS OF HUMIC SUBSTANCES IN THE SOIL AND CROPS GROWN

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In the present study we have provided the findings from the field and laboratory tests on the effects of cereal crops (winter wheat and barely) and perennial grasses on the build up of humic substances in the soil. Humic substances were characterised by dividing its substances into fractions using the chemical fractionation method (Ponomarieva-Plotnikova modified Tyurin method). The statistical analysis of data revealed that there was a significant increase in the concentration of total humic acids (∑HA) when barley and perennial grasses were grown after winter wheat. While estimating the changes in the composition of humic substances one should pay attention to the ratio between the fractions of soluble, so-called “mobile” or “active” humic substances and bound with soil mineral part. For the purposes of practical agriculture it is necessary to estimate the effect of the above-mentioned forms of humic substances on the performance of crops. Experimental evidence revealed a direct relationship between HA1 fraction in the soil determined in the spring and crop yield in the same year, and this proves the importance of mobile humic acids. This direct correlation was described by pair regression equations.

THE EFFECT OF LONG-TERM MINERAL FERITILIZATION ON FRACTIONAL COMPOSITION OF ORGANIC MATTER OF ALBIC LUVISOLS

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Soil material of a long-term experiment settled in 1974 was used in the study. Two separate ferilization systems were used, i. e. nitrogen fertilization (factor I) and potassium fertilization (factor II) without organic fertilization and liming. A crop rotation good for fodder and industrial applications was used (maize green, winter rape, winter wheat, rye as aftercrop).

Soil samples were analysed for organic carbon (C_{org}), total nitrogen (N_{tot}) content, and pH in KCl. Fulvic and humic acid fractions were isolated and C_{org} and N_{tot} concentrations were assayed.

The results indicated that significant changes were triggered by uniform mineral (nitrogen-potassium) fertilization. Soil reaction shifted to considerably more acidic values, and the more, C_{org} content decreased what was accompanied by an increase of N_{tot} values. Fractional composition of organic matter indicated its degradation. Another phenomenon observed was a domination of fulvic acid fraction over the humic acid fraction.

CHARACTERIZATION OF HUMIC ACIDS EXTRACTED FROM HAZELNUT HUSKS AND HAZELNUT HUSKS AMENDED SOIL

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Changes in the soil humic acid (HA) fraction resulting from composted hazelnut husk (CHH) application have been investigated by comparing the chemical properties and FTIR characteristics of the HAs extracted from the original hazelnut husks (UCHH), composted hazelnut husks (CHH) and composted hazelnut husks amended soil (CAS). C and O content of HA samples were found to be 41.4 - 50.8 %, 37.8 - 50.5 %, respectively. The high percentage of C content obtained for all materials except CHH-HA indicates humification and high degree of condensation of aromatic rings. The nitrogen content of the HAs are in the expected range for HAs which is 2-6 %. During the composting process changing in C and N content of the hazelnut husk samples HAs (from 17.1 to 12.1) make C/N ratio similar to that of native soil humic acid.

Comparison of FTIR spectra of UCHH and CHH HAs shows that both exhibit similar series of IR bands, indicating the presence of the same functional groups in both samples. The only difference in the spectra seemed to be a decrement in the peak intensities of composted sample compared to uncomposted one. The similar differentiation of the intensities of IR bands of compost applied soil sample (CAS-HA) has also been observed. The FTIR spectral results show that the characteristics of composted material tend to become similar to that of soil HAs characteristics in time.

DEVELOPMENT AND APPLICATION OF FUNCTIONAL ASSAYS FOR FRESHWATER DOM

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A series of 11 standardised, reproducible, assays have been developed of physico-chemical functions of dissolved organic matter (DOM) in freshwaters. The assays provide quantitative information on light absorption, fluorescence, photochemical fading, pH buffering, copper binding, benzo(a)pyrene binding, hydrophilicity and adsorption to alumina. To obtain DOM for the assays, a 45 litre sample of filtered freshwater was rotary-evaporated to reduce the volume to ca. 500 cm^3. The concentrate was then passed through a strong cation-exchanger , in the Na$^+$ form, to remove alkaline earth cations, and then through 0.7 and 0.2 μm filters. Eight samples, two each from four surface waters, were processed, and the yields of dissolved organic carbon (DOC) ranged from 70 to 107 % (average 91%). The samples of DOM, stored in the dark at 4°C, retained their functional assay characteristics for up to 7 months.

When assaying the concentrates, parallel assays were performed with Suwannee River fulvic acid, as a quality control standard. For most of the assays, the results for 8 freshwater DOM samples are similar to those obtained with SRFA. The chief exception is that the DOM samples are appreciably more hydrophilic than SRFA. For 8 of the assays variability among the DOM samples is significantly ($p < 0.01$) greater than can be explained by analytical error, i.e. by comparison with results for the SRFA quality standard. The three exceptions are photochemical fading, copper binding and benzo(a)pyrene binding. Two DOM samples from a eutrophic lake gave assay results that differed from streamwater DOM samples. DOM optical absorbance was negatively correlated with hydrophilicity and positively correlated with adsorption to alumina.. Buffer capacity was positively correlated with fluorescence.

STRUCTURAL IDENTITY OF LMW FULVIC ACIDS OF DIFFERENT ORIGIN AND HINTS FOR THEIR FORMATION

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The complexity of fulvic acid mixtures has long hampered the investigation of individual fulvic acid molecules. For the same reason the comparison of fulvic acids of different origin was limited to the average properties of fractions of these mixtures. Now, that the elemental composition and the structure of individual fulvic acid molecules can be investigated by means of electrospray ionization-high resolution-mass spectrometry [1] we can also compare the molecules in fulvic acid mixtures of different origin.We investigated fulvic acid isolates from different locations and environments with SEC-Q-TOF-MS and determined the molecular formulas of several hundreds of molecules of their LMW fraction [2]. We recognized that the sets of molecules of the different isolates were virtual indistinguishable in terms of their elemental composition and structure. The only difference was the relative frequencies of the various molecules in each of these isolates. It will be discussed whether these relative compositional differences can be linked to the origin of the respective isolate and the suggested conditions of their formation.

In a second study we tested three different approaches to generate fulvic acid molecules in the laboratory from different precursor substances and the product molecules were analyzed by SEC-Q-TOF-MS. The mass spectrometric data proved that several oxidative approaches were suitable to form a series of fulvic acids that were identical to those found in natural isolates.

Based on these results we suggest that fulvic acid formation may not require one specific biogenic precursor material or formation process but that various processes from different source materials may be suitable to form fulvic acid molecules.

References

1. These, A., Winkler, M., Thomas, C., and Reemtsma, T. (2004) Determination of molecular formulas and structural regularities of low molecular weight fulvic acids by size-exclusion chromatography with electrospray ionization quadrupole time-of- flight mass spectrometry. Rapid Commun. Mass Spectrom. 18: 1777-1786.
2. Reemtsma, T. and These, A. (2004) Comparitive investigations of fulvic acid of different origin by SEC-Q-TOF-MS - new insights into structure and formation. subm.

MODELLING HG INTERACTIONS WITH NATURAL ORGANIC MATTER USING WHAM

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The transport, retention and bioavailability of mercury in the natural environment depends to a large extent on the interactions of mercury species with the organic matter of soils, waters and sediments. A number of authors have reported quantitative data on Hg-organic interactions under defined laboratory conditions. The purpose of the work described here was to analyse these data within a consistent framework, using the WHAM / Model VI chemical speciation model. Model VI uses a structured formulation of discrete, chemically-plausible, binding sites for protons, in order to allow the creation of regular arrays of bidentate and tridentate binding sites for metals. Metal aquo ions (Al^{3+}, Cu^{2+}, Hg^{2+} etc) and their first hydrolysis products ($AlOH^{2+}$, $CuOH^{+}$, $HgOH^{+}$ etc) compete with each other, and with protons, for binding, characterised by a single intrinsic equilibrium constant for each metal. The intrinsic equilibrium constants are modified by empirical electrostatic terms. The speciation of inorganic forms of the metals are also taken into account. The 10 published data sets for Hg binding by organic matter cover a wide range of conditions (Hg concentrations, pH). The model gives reasonably consistent results in 7 cases, cannot be applied in two cases, and in one case the data do not agree with the model's assumptions. At low Hg concentrations, competition for binding by Al and Fe(III) might be significant. Of the three published data sets for MeHg, two agree with one another, while a third gives conflicting results. The implications for field situations are discussed.

PHOTODEGRADING PROPERTIES OF COMPOST HUMIC-LIKE MATERIALS

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Humic-like substances (HLS) can be provided by recycling of organic wastes after composting. However their photochemical properties (transformation of organic polutants under monochromatic or polychromatic irradiation) still remain unknown. HLS were extracted from a mixture of sewage sludges and trimmings (70 - 30 %, w/w) after different times of composting. They were found to significantly enhance the pesticide Irgarol 1051 photodegradation either in artificial and natural solar light. An increase of the photoinductive properties with composting time that paralleled the increase of absorbance and emission intensity 365/460 (λexc/λem) was observed. Elemental analyses showed a relative stability in atomic composition whatever the time of composting. Using 2-propanol as hydroxyl radical scavenger shown that around 25 % of Irgarol degradation was due to the oxidation by hydroxyl radicals. The ability of HLS to photogenerate the production of such highly oxidant species may be used for organic pollutants elimination.

STRUCTURAL COMPONENTS OF SOIL HUMIC ACIDS FRACTIONATED BY TANDEM SEC-PAGE

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The IHSS soil humic acid (HA) standard and three HAs from soils of very different origin have been fractionated by tandem size exclusion chromatography-polyacrylamide gel electrophoresis (tandem SEC-PAGE). From each HA three fractions with different molecular sizes (MSs) and electrophoretic mobilities were obtained and investigated. The tandem SEC-PAGE allowed to obtain HA fractions with the clear differences in terms of electrophoretic mobility, MSs, elemental composition, amino acid content, UV-visible spectra, fluorescence, photoinductive properties, plant and microbial fatty acid distribution from different soil HAs, sampled in soils with extremelly different genesis, climatic conditions and geographic regions. This method seems could help to shed the light on the structural components and organization of soil HAs in relation to their genesis and climatic conditions.

OCCURRANCE AND REMOVAL OF NATURAL ORGANIC MATTER (NOM) IN DRINKING WATER TREATMENT

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This work is made of interest into NOM and its effects of drinking water treatment with respect to treatability by different technologies. Unit operations studied during the research have been coagulation, disinfection with clorine dioxide and ozone, as well as activated carbon (AC) filtration and nanofiltration (NF). The sizing of NOM on different molecular size fractions and the removal and transformation of these fractions has been studied with high-performance size-exclusion chromatography (HPSEC).

According to HPSEC results, the raw water consisted mostly of high and intermediate molar mass (HMM and IMM) NOM. The HMM matter disappeared almost completely and the IMM substances decreased considerably in the surface water treatment process. Coagulation with ferric sulphate was noticed to remove about 10 % more NOM than aluminium sulphate coagulation according to different measuring techniques. Especially the removal of IMM NOM was approximately 25 % more efficient according to HPSEC. The AC filtration could not remove no more the HMM substances but reduced the amount of IMM and low molar mass (LMM) matter. LMM and IMM matter were noticed to remove about 30 % and 20 %, respectively, after coagulation The regeneration of the AC filters enhanced the removal of organic matter right after regeneration by about 20% more compared to the situation before regeneration. NF removed, in general, 100-49% and 85-47% of remaining organic matter after traditional treatment train, according to HPSEC and TOC measurements, respectively. Removal of different molecular size fractions with diverse studied membranes varied between 100-56%, 100-54% and 88-19%, regarding HMM, IMM and LMM organic matter, respectively.

THE ROLE OF DECAYING ORGANIC MATTER IN CU SORPTION BY *PHRAGMITES AUSTRALIS* A KINETIC STUDY

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Following shoot senescence and death most of the plant aquatic biomass enters the particulate organic matter pool. Trace metals are strongly associated with these particulate phases in aquatic environments. The objective of this study was to determine if non-living biomass from the aquatic macrophyte *Phragmites australis* could be used to recover metals from contaminated effluents. Effects of decay time on adsorption capacity were also studied.

Leaves and stems at different breakdown stages (freshly collected or subjected to decomposition during five months in synthetic waste-water), were used to study the adsorption dynamics of *Phragmites australis.*

Batch adsorption experiments were performed using 0.1 g of plant material (leaves or stems) with 50 ml of $CuSO_4$ aqueous solutions (Cu content: 0.01, 0.05, 0.1, 1, 5 mg/l). After the target contact time was reached (6 h, 24 h, 96 h and 192 h) suspensions were filtered and analyzed for Cu(II) ions using an ICP-OES (Varian Vista MPX, Varian, Palo Alto, CA). The amount of Cu(II) adsorbed onto *Phragmites australis* was determined from the difference between the concentrations of initial and final solutions. The Langergren pseudo-first-order model, Ho and McKay's pseudo-second-order model, Elovich equation and two diffusion models (Weber-Morris and an intra-particle diffusion model) were fitted to the experimental data.

Sorption kinetics observed for the four plant materials at the different metal concentrations were similar in shape, showing a fast initial sorption ($t<6$ h) followed by a slow sorption proceeding continuing for several days ($6<t<192$ h). Adsorption capacity was significantly different between fresh and decomposed leaves ($P<0.05$) as well as between fresh and decomposed stems ($P<0.05$). However, there was no significant difference on adsorption capacity between the different organic material after 192 h within decay time ($P<0.05$). The overall adsorption process could not be described by the selected first order reaction or the Elovich equation ($r^2<0.8$). The sorption system was best described by second order kinetics (r^2~0.99) but the intra-particle diffusion model fitted the data only slightly less ($r^2>0.95$). The results showed that *Phragmites australis* can be used for Cu removal.

A NOVEL APPROACH TO THE DESCRIPTIVE EVALUATION OF OXIDIZED HUMIC SUBSTANCES BY FLUORESCENCE SPECTROSCOPY

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Characterization of natural organic matter, mainly humic substances is an important task in order to elucidate its reactivity during water treatment processes. Numerous studies address the use of spectroscopic techniques such as UV-vis and fluorescence. However, there is still a need for the continued development of new analytical methods and approaches for the characterization and analysis of humic substances.

With the purpose of improving the understanding of the structural and functional properties of humic substances from aquatic and terrestrial sources as well as of determining the relationships during and after photocatalytic oxidation, a set of fulvic and humic acids of different origins were studied. The spectral changes of humic substances during oxidation processes were investigated focusing on their analysis by fluorescence spectroscopy in the emission and synchronous scan modes and three dimensional fluorescence spectroscopy in the form of an excitation–emission matrix (EEM) of fluorescence intensity as a function of excitation and emission wavelengths. The spectroscopic differences between humic substances of various origin were outlined and compared with that of photocatalytically oxidized humic substances.

FRACTIONATION OF SOIL HUMIC ACID BY MEANS OF CAPILLARY ZONE ELECTROPHORESIS

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Humic substances can be described as a heterogeneous mixture of polyelectrolite-like molecules which differ in chemical composition and size. Different fractionation techniques based on different properties of humic macromolecules have been used for their characterization, however detailed information on charge distribution in humates and their mobility depending on pH is still poorly understood. These data are important for understanding of the mechanisms of HS interactions with mineral and organic compounds and predicting HS behavior in natural processes. Our aim was to study applicability of capillary zone electrophoresis for fractionation of HS on the charge basis. Humic acid (HA) extracted from soddy-podzolic soil was used for this purpose. It was shown that HA consisted at least of three fractions that differed by their electrophoretic mobility at given pH. This can be explained by different content of functional groups with different acid-base properties in each HA fraction. With pH decreasing from 11.0 to 3.0 the electrophoretic mobility of HA fractions decreased to $30 \cdot 10^{-3}$ $cm^2/V \cdot s$. This value corresponded to the beginning of precipitation of HA components in the fraction. The pH of the beginning of precipitation can be used for preliminary assessment of isoelectric point of HA.

EFFECT OF BIOLOGIZATION OF AGRICULTURE AND MEANS OF SUSTAINABILITY ON SOIL ORGANIC MATTER CHANGES

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Organic matter is one of most important factors for clay soil protection from its degradation. Seeking to increase the content of organic matter in soil and to improve its quality by means of agriculture's biologizations and by application of sustainable soil tillage systems complex investigations were carried out at the Lithuanian Institute of Agriculture's Joniskelis Research Station on a glacial lacustrine clay loam *Endocalcari-Endohypogleyic Cambisol.*

The results of investigations suggest that expansion of longer vegetation wintering crop area on heavy soils, as biological mean had positive effect on organic carbon content, amount of humic acids, degree of humification. Application of the sustainable soil tillage system, especially in combinations with organic manure, resulted in a reduction of organic matter mineralization and in on increase of humus and humic acids.

CHANGES IN NOM CHARACTERISTICS THROUGH WATERCOURSES FROM HEADWATERS TO HIGH ORDER STREAMS

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There are large variations in properties of natural organic matter (NOM) in surface waters. The spatial variation is often seen to be larger than the seasonal oscillations, though fluctuation with runoff intensities (especially in low order streams) is believed to be the main factor governing the observed differences.

Despite larger spatial variation in headwater brooks then in high order rivers it is commonly found that on average the DOC and the specific color of NOM decreases downstream in the same way as pH and alkalinity increases. Probable causes for these trends are the mixing of different watercourses, in-stream processes (biodegradation, photo-bleaching, coagulation) and the effect of more mineral- relative to organic soil (% mire and groundwater). Unraveling the main factors governing these trends is a prerequisite for assessing the impact by likely future perturbations to the NOM.

Variation in several physical and chemical characteristics of Nordic NOM has been found to be empirically correlated to total S-deposition, H^+ concentration, growing season, vegetation type, site elevation and TOC concentration, as well as climate, nutrient status and catchment size. Most of these parameters change in a more or less uniform manner down through a watershed. It is therefore natural that also the quality of NOM changes in a similar way.

POLYMERIZATION OF PHENOLIC COMPOUNDS ON THE SURFACE OF HYDROXYALUMINUM-KAOLINITE COMPLEX, CATALYZED BY IMMOBILIZED FUNGAL LACCASE

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Humic substances comprise the major part of stable organic matter in the diversity of the environments. They are formed during transformation of organic residues of biotic origin and important step in their synthesis is oxidative co-polymerization of polyphenols with proteins, tannins, carbohydrates etc., catalyzed by oxidative enzymes. It is supposed that in soils formation of humic polymers is followed by their binding to mineral compounds, that protects them from microbial decomposition. Using fungal laccase, immobilized on hydroxyaluminum-kaolinite complex and several phenolic acids and their mixtures with amino acids we have shown that condensation of phenolic compounds into humic-like polymers can occur directly on the surface of soil minerals. Molecular weight of the polymers formed from gallic and caffeic acids on $Al(OH)_x$-kaolinite complex under the action of laccase was over 75 kDa. Such high-molecular weight products did not formed in the absence of mineral matrix, when the same concentration of phenolic acids and the same laccase activity were used in liquid homophasic system. It was concluded that stable organo-mineral complexes can be the primary form of soil humus.

HUMIC ACID REDUCES FROG OOCYTE HORMONE-INDUCED MATURATION ACTIVITY

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The specific stimulatory effect of sturgeon *Acipenser güldenstädti* Br. gonadotropic hormone (GTH) on frog *Rana temporaria* L. oocyte maturation activity in vitro was investigated in relation to humic acid (HA) concentration. Commercial HA (Aldrich) was additionally purified according to the International Substance Society recommendations and transferred to the H^+ form on the strong cationite KY-23.

Chromatographically pure standard sturgeon GTH was isolated from pituitary glands according to a standard procedure.

The frog oocyte in vitro maturation test was employed to assess specific stimulatory effect of GTH on the oocytes maturation activity in the test-system “oocyte–hormone”at the different HA concentrations. The oocyte sensitivity to the hormone was expressed as the minimal dose of the GTH that produced 50 % test-oocyte maturation (D_{50}). Also, D50 served as the hormone activity indicator.

The investigation was carried out in two variants. In the first variant the test-oocyte portions (30 oocytes) were preincubated for 48 h with the following HA concentrations: 12,5; 25 and 50 μg •1^{-1} at 5º C in Petri dishes in Ringer solution, pH 7.5. After that oocytes were washed five times with fresh Ringer solution to wash off of the residual HA. GTH was applied in following doses: 0.1; 0.3; 0.5 and 1 µg •1^{-1} to estimate the hormone sensitivity of the HA-pretreated oocytes.

In the second variant the intact fresh oocytes were biotested for 48 h using the same GTH doses in the same test system wich contained the said HA concentrations in the test medium.

The results indicated that the GTH activity decreased depending on the used HA concentrations in the test medium, by 20 to 30% in comparison with that found in experiments with the oocytes preincubated with the same HA concentrations. So, it is obvious that HA may effect not only the oocyte follicular membrane, but also the GTH molecule thus producing more deep negative influence on the oocyte–hormone interaction in whole.

Thus, for the first time frog oocytes was successfully used to assess the effect of HA on both hormone-depending maturation ability of the amphibian reproductive cells and the specific hormone function. It was showen that HA, depending on concentration, can produce an inhibitory effect on oocytes, reducing their ability to respond to the specific hormone impact. The range of inhibiting doses of HA causing a decrease of oocyte maturation ability was determined.

Author Index

Gondar, D.
Gonet, S.S.
Goslan, E.H.
Grabe, M.
Grunewald, K.
Guggenberger, G.

H
Haaland, S.
Haftka, J.J.H.
Hansen, H.C.B.
Hansen, S.
Holmström, S.J.M.
Hongve, D.
Hurraß, J.

I
Ilyukhina, E.A.
Iversen, A.

J
Jankauskas, B.
Jankauskiene, G.

K
Kaiser, K.
Kalbitz, K.
Karaca, A.
Kaste, Ø.
Kawahigashi, M.
Kayran, C.
Kholodov, V.A.
Kita, A.
Kļaviņš, M.,
Kokorīte, I.
Koroleva, O.V.
Kortelainen, P.
Kovalenko, A.N.
Kratz, J.V.
Kreišmanis, J.
Kristaponyte, I.
Kronberg, L.
Kuczewski, B.
Kudryavtsev, A.V.
Kukkonen, J.V.K.
Kulikova, N.A.
Kulovaara, M.
Kupsch, H.

L
Lankes, U.
Lebedeva, G.F.
Lehtonen, T.
Lepistö, A.
Lesage, E.
Lodygin, E.D.
Loffredo, E.
Lundström, U.S.
Lyytikäinen, M.

M
Maiksteniene, S.
Matilainen, A.
Mattsson, T.
Meers, E.
Miano, T.M.

Mielnik, L.
Moberg, M.
Monaci, L.
Mortensen, K.
Murawska, B.

N
Ndahi, N.P.

O
Owolabi, O.

P
Parele, E.
Parsons, J.R.
Parsons, S.A.
Patt, J.
Pavlik, D.
Perminova, I.V.
Peuravuori, J.
Polak, J.
Ponomarenko, S.A.
Popov, A.I.
Prasath, V.

R
Räike, A.
Reemtsma, T.
Richard, C.
Riise, G.
Rodinov, V.
Rodionov, A.
Ryazanov M.A.

S
Saiz-Jimenez, C.
Schaumann, G.E.
Scheel, T.
Scheithauer, J.
Schmidt, W.
Schramm, A.
Schulze, E.-D.
Senesi, N.
Serné P.
Shamrikova E.V.
Shkinev, V.M.
Simanskaite, D.
Singaravel, R..
Šīre, J.
Slätis, T.
Slepetiene, A.
Smoliński, S.
Sözüdoğru Ok, S.
Springe, G.
Spychaj-Fabisiak, E.
Stadler, B.
Stepanova, E.V.
Stoffers, S.
Strobel , B.W.
Stuanes, A.
Styczen, M.
Sułkowski, W.W.

T
Tack, F.
Tamer, N.

Thacker, S.A.
These, A.
Tipping, E.
Tobiasova, E.
Trautmann, N.
Trubetskaya, O.
Trubetskoj, O.
Tsvetkova, E.A.
Tuhkanen, T.
Tuikka, A.
Tureli, F. C.
Turgay, O.C.

U
Unamuno, V.R.
Uyguner, C.S.

V
Vanchikova E.V.
Vanifatova, N.G.
Velykis, A.
Vogt, R.D.
Vose, V.

W
Warwick, P.

Z
Zaujec, A.
Zavarzina, A.G.
Zenkevičs, H.
Zicmanis, A.
Ziemelis, R.
Zsolnay, A.