14th European Meeting on Environmental Chemistry

DECEMBER 4th to 7th 2013, BUDVA, MONTENEGRO

BOOK OF ABSTRACT

HOSTED BY CHEMICAL SOCIETY OF MONTENEGRO

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14^{th} EMEC PROGRAMME

4. December 2013

12^{00} –18^{00}	Registration of participants
19^{00} –	Welcome reception (coctail)

05. December 2013

9^{00} - 9^{20}	**Opening ceremony**
9^{20} -10^{20}	**Plenary lecture:** **George Cobb** Inorganic Nanomaterial Effects on Aquatic Organisms *Chair person Željko Jaćimović and Branimir Jovančićević*
10^{20} -10^{45}	**Coffee break**
10^{45} -11^{00}	**Albert Lebedev, Olga Polyakova, Dmitry Mazur, Viatcheslav Artaev** Fast, cheap, safe and reliable GC/HRMS analysis of priority pollutants in water samples *Chair person Polonca Trebse*
11^{00}-11^{15}	**M. Kranjc, M. Pflieger, T. Jug, M. Franko** Stability and retention of sulfamethoxazole and ciprofloxacin in soils
11^{15}-11^{30}	**L.Dsikowitzky, D. Dwiyitno, E. Heruwati, F. Ariyani , J. Schwarzbauer** Organic contaminant burden in water and sediment from Jakarta Bay, Indonesia, and its implication for seafood consumption
11^{30}-11^{45}	**D. Vione, E. De Laurentiis, M. Minella, V. Maurino, C. Minero,** Linking surface-water photochemistry with climate change: A model aprouch
11^{45}-12^{00}	**A. Turner** The geochemistry, bioavailability and toxicity of thallium in the aquatic environment
12^{00}-12^{15}	**V. Antoniadis, E. Golia, A. Prapas, and A. Dimirkou,** Sorption of Cu and Zn in 21 soils as influenced by soil pH

12^{15}-12^{30} **J. P. Coelho, A. I. Lillebø, D. Crespo, S. Leston, M. Dolbeth**
The effect of the alien invasive bivalve, *Corbicula fluminea*, in nutrient dynamics under climate change scenario – a mesocosm experience

12^{30}-12^{45} **E. De Laurentiis, D. Vione, M. Pazzi, C. Minero, V. Maurino, M. Brigante, G. Mailhot**
Photosensitised processes of atmospheric significance for the formation of humic-like substances (HULIS) from phenolic compounds

12^{45}-14^{30} **Lunch**

14^{45}-15^{00} **N. Urien, E. Uher, L. Fechner, O. Geffard, J. D. Lebrun**
Modeling Pb, Cd and Ni bioaccumulation in *Gammarus pulex*: Application to realistic environmental conditions and importance of water chemistry
Chair person Jan Schwarzbauer

15^{00}-15^{15} **Anatoly Verenchikov, Alexander Kolosov, Boris Kozlov, Yuri Khasin**
GC-TOF with Soft Ionization and High Resolution for Analysis of Complex Mixtures

15^{15}-15^{30} **Passananti M., Gaetano D, Vinatier V, Deguillaume L, Delort A.-M, Mailhot G, Brigante M.**
Iron-organic complexes photochemistry under atmospheric aqueous phase conditions: from the hydroxyl radical generation up to the formic acid transformation

15^{30}-15^{45} **H. T. Chon, M. Sager, L. Marton**
The Emission and Pollution Level of Platinum, Palladium and Traffic-Related Elements in Road Dusts from Seoul, Korea

15^{45}-16^{00} **J. Čáslavský, M. Vávrová, L. Zouhar, P. Komárková**
Contamination of waste waters by synthetic fragrances

16^{00}-16^{15} **K. Ilijević, Đ. Ranić, I. Gržetić**
WDXRF and ICP-OES analysis: biomonitoring of toxic metalswith different conifer species

16^{15}-16^{30} **Coffee break**

16^{30}-16^{45} **George P. Cobb, Emily Bigorgne, Leanne F. Baker,**

Shawna L. Nations and Cole W. Matson
Inorganic Nanomaterial Effects on Aquatic Organisms
Chair person D. Vione

16^{45}-17^{00} **M.-C. Leroy’, M. Legras, V. Moncond’huy**
Comparison of three macrophytes to remediate co-contaminated soils with Polycyclic Aromatic Hydrocarbons (PAHs) and Trace Elements (TEs), implications for green urban infrastructures

17^{00}-17^{15} **M. Vaitilingom, L. Deguillaume, V. Vinatier, M. Sancelme P. Amato, N. Chaumerliac, A.-M. Delort**
Potential Impact of Microbial Activity on the Oxidant Capacity and the Organic Carbon Budget in Clouds

17^{30}-18^{30} **Poster session:** Chemistry of water soil and atmosphere, Biodegradation and bioremediation , Analytical methods for environmental science and biomonitoring

06. December 2013

9^{00} –10^{00} **Plenary lecture**
Christine Achten
Polycyclic aromatic compounds (pac): sensitive analysis by gas chromatography – atmospheric pressure laser ionisation – time-of-flight – mass spectrometry (gc-apli-ms) and bioavailability from coals
Chair person Anne Marie Delort

10^{00}-10^{15} **Coffee break**

10^{15}-10^{30} **W. Schmidt, C. H. Redshaw**
Do non-steroidal anti-inflammatory drugs effect the germination, development and growth of higher plants?
Chair person Albert Lebedev

10^{30}-10^{45} **A. Wolfson, D. Tavor**
Organic synthesis in glycerol-based solvents

10^{45}-11^{00} **L A. Kartsova, E.A. Bessonova , A.V. Nikolaev, E.V. Obedkova**
New approaches for electrophoretic determination of biologically active compounds

11^{00}-11^{15} **J.M. Bonmatin, P.A. Marchand, D. Paradis & L.P. Belzunces**

	Insecticides analyzed at the ng/g level in pollen, nectar and in bees.
$11^{15}-11^{30}$	**J.M. Bonmatin, D. Paradis, G. Bérail & L.P. Belzunces** Three class of relevant pesticides analysed in honey by very sensitive methods (LC/GC-MS-MS) after a single QuEChERS-type extraction
$11^{30}-11^{45}$	**M. Alrhmoun, M. Casellas, C. Dagot** Removal of trace organic contaminants in conventional and membranes bioreactors systems
$11^{45}-12^{00}$	**M. Vemic, F. Bordas, G. Guibaud, P. N. L. Lens, E. D. van Hullebusch** Fractionation and leaching of metals from mineral sludge produced from a metal recycling plant
$12^{00}-12^{15}$	**MPflieger, M.Francese, P.Frisenda, M.Franko** Photodegradation and toxicity of ciprofloxacin used in aquaculture
$12^{15}-13^{30}$	**Lunch**
$13^{30}-17^{30}$	**Excursion /Old Town Kotor/**
$18^{00}-18^{15}$	**I. Spanik, M. Vojinović-Miloradov, B. Jovančićević, T. MuhićŠarac, B. Kukavica, G.Gajica, J.Radonić** Development of network for education and training of public environmental laboratories within the TEMPUS project Netrel *Chair person Josef Caslavsky*
$18^{15}-18^{30}$	**A. Vassiliu, S. Simon, V. Deluchat** Influence of aeration onto As trapping in ZVI/sand reactor
$18^{00}-19^{00}$	**Poster session:** Environmental and cultural heritage, Water and waste Streatment, Ecotoxicology and biomarkers
19^{00} -	**Board meeting/VIP Conference room-glass room**
21^{00} -	**Gala dinner**

07. December 2013

09^{00}-09^{15}	**H. Fallou, N. Cimetière, S. Giraudet, D. Wolbert, P. Le Cloirec** Adsorption of pharmaceuticals onto activated carbon cloths, Modeling and extrapolation of adsorption isotherms to low concentrations Chair person Isabel Villaescusa
09^{15}-09^{30}	**R. Žabar, P. Trebše, M. Sarakha** Photolytic and photocatalytic degradation of 3,5,6-trichloro-2-pyridinol in aqueous solution
09^{30}-09^{45}	**M. Vlahović, M. Mazaj, N. Zabukovec Logar, Ž. Jaćimović** Removal of heavy metals from aqueous solutions by natural and synthetic zeolites
09^{45}-10^{15}	**Closing ceremony**
10^{45}-15^{45}	**Optional excursion/Old Town Cetinje**

POSTER SESSION

Chemistry of water soil and atmosphere

C101	**Diffusive sampling of nitrogen dioxide in ambient air** S. Mico, A. Deda, A. Deliu, M. Alushllari
C102	**Monitoring of ambient air in Novi Sad – levels of benzene, toluene, ethylbenzene and xylenes** Lj. Torović, S. Bobić, B. Mihajlović, S. Bijelović
C103	**Quality evaluation of soils and sediments in Zeta plane using Danio rerio embrio toxicity test** A. Perović, D. Šuković, J. Vukić, B. Damjanović -Vratnica, P. Trebše, S. Perović
C104	**Microfluidic FIA coupled with thermal lens microscopy for rapid detection of pollutants by colorimetric reactions** M. Liu, M. Franko
C105	**The translocation ability of metals through organs of macrophytes** V.R. Kastratović, S.D. Krivokapić, M.R. Bigović, N.Z. Blagojević, D.D. Đurović
C106	**Microbiological and chemical properties of meat processing industry wastewater**

M. Stošić, D. Čučak, I. Mihajlović, S. Pap, M.Đogo, D. Radanović, J. Radonić

C107 **Benzene in motor vehicle exhaust**
D. Adamovic, M. Vojinovic Miloradov, J. Doric, J. Radonic, S.Adamovic, N. Raspopovic

C108 **Ethylcellulose and Lignin as Bearer Polymers in Controlled Release Formulations to Reduce Leaching of Metribuzin in a Calcareous Soil**
M. Fernández-Pérez, M. Villafranca-Sánchez, F. Flores-Céspedes & I. Daza-Fernández

C109 **Occurance of selected pharmaceuticals in municipial wastewater from city of Novi Sad**
S. Kovačević, M. V. Miloradov, A. Petković, J. Radonić, M. Sremački, D. Milovanović, M. Dimkić

C110 **Persistence and dissipation behavior of dicamba and bentazon herbicides in water under laboratory conditions**
S. Lazić, D. Šunjka, Na. Grahovac, Ne. Grahovac, V. Guzsvány

C111 **Toxicity evaluation of soil sampled in the vicinity of an aluminum smelter in Montenegro using the Ames, Bioluminescence and DR-LUC bioassays**
J. Vuki**ć**, A. Perovi**ć**, H.A. Leslie, J. Kamstra, P. Cenijn, E. Simon, T. Hamers

C112 **Use of biosorbents in controlled-release formulations of the botanical insecticide azadirachtin**
M. Fernández-Pérez, M. Villafranca-Sánchez, F. Flores-Céspedes, G. P. Martínez-Domínguez & I. Vila-Mompó

C113 **Contribution of aqueous and dietary exposuresin bioaccumulation of lead (Pb) in the amphipod *Gammarus pulex* and multi-pathway modeling**
R. Hadji, E. Uher, J.D. Lebrun

C114 **Optimization of methods for determination of organotin compounds and for evaluation of their ecotoxicity**
R. Sýkora, V. Rybová, J. Čáslavský, M. Vávrová, H. Zlámalová Gargošová

C115 **Investigation of polycyclic aromatic hydrocarbons in tissues of fish from the Tisza River (Serbia)**
G. Gajica, G. Grbović, S. Štrbac, A. Šajnović, K. Stojanović, P. Simonović, B. Jovančićević

C116 **Polybrominateddiphenylethers and polycyclicaromatichydrocarbons in soilsfromfireplaces**
M. Vávrová, M. Šubrt, J. Čáslavský, V. Kociánová

C117 **Gravimetric and Black Carbon Analysis, in PM2.5 samples, collected in the city of Patras, Greece, from January to June 2011**
M. Manousakas, H. Papaefthymiou

C118 **Environmental impact of agricultural activities in the region**

of Goriška, Slovenia
K. Kalister, T. Prebil, R. Žabar, A. Perović, P. Trebše

C119 **Determination of polycyclic aromatic hydrocarbons by gas chromatography- mass spectrometry in sediments of the river Danube through Serbia**
M. Stupavski, N. Šenk, M. Vojinović Miloradov, J. Radonić, I. Mihajlović

C120 **Biological Ice Nucleation Activity in Cloud Water**
M. Joly, P. Amato, L. Deguillaume, E. Attard, M. Monier, C. E. Morris, M. Sancelme, A.-M. Delort

C121 **Metabolomic study of the response to cold shock in *Pseudomonas syringae* isolated from clouds**
C. Dalle, C. Mendes, I. Canet, M. Sancelme, M. Lagrée, M. Traïkia, A.M. Delort C. Jousse, P. Amato

C122 **ANOVA and Nonparametric Alternatives: Influence of Statistical Nuisance Factors to the Analysis of the relations betweenthe Danube River and its Major Tributaries**
K. Ilijević, M. Obradović, V. Jevremović, I. Gržetić

C123 **Quality assessment of waters from South-East Serbia in respect to major dissolved elements**
Z. S. Stojanović,J.V. Švarc-Gajić, M. Ž. Đorđević, N. L. Grahovac

C124 **Dissolved gaseous mercury in natural waters – methodological aspects**
E. Begu, J. Kotnik, M. Horvat

Environmental and cultural heritage

E101 **Thymol as an alternative to pesticides: effect on olfactory memory and gene expression levels in the brain of the honeybee *Apis mellifera***
E. Bonnafé , J-L. Carayon , N. Téné , Lucie Hotier , C. Armengaud , M. Treilhou

E102 **The Pharma Transport Town - Understanding routes to sustainable pharmaceutical use: An Exercise in Interdisciplinary Study**
W. Stahl-Timmins, M. White, M. Depledge, L.E. Fleming, C. Redshaw

E103 **Development of a Validated Method for the Determination of Mercury Content in Seawater Matrices by ICP-MS: Preliminary Results**
R. Sánchez, G. Van Britsom, J. Snell, A. Held

E104 **Honeybees (*Apis mellifera* L.) as Bioindicators of Environmental Pollution: Concentrations of Metals in and around Belgrade area**
Nenad Zarić, Konstantin Ilijević, Branimir Jovančićević, Ljubiša Stanisavljević, Ivan Gržetić

E105 **A new approach for the production of a Certified Reference Material for biota monitoring**
I. Dosis, R. Lava, L. I. Majoros, M. Ricci, J. Charoud-Got, J. Seghers, H. Emteborg, A. Held, and H. Emons

E106 **Development of the way of steroid hormones and non-steroidal anti-inflammatory drugs determination in biological fluids by HPTLC**
E.V. Obedkova, L.A. Kartsova, L.I. Velikanova, D.O. Kirsanov

E107 **Early diagenetic processes in a geologically well-defined Krepoljin brown coal basin, Serbia**
G. Dević

E108 **Environmental and Public Health Aspects of Pharmaceutical Waste Management in Montenegro**
Ž. Bešović, M. Šahman –Zaimović, M. Drljević, R. Zejnilović

E109 **Kinetics of sorption of Cd(II) on bauxsol**
V.V. Grudić, N.Z. Blagojević, V.L. Vukašinović-Pešić, S.R. Vukanović

Water and waste treatment

W101 **Modelling natural and synthetic steroid estrogens from patient to river: A catchment level case study**
J.D. Heffley, S.D.W. Comber, B.W. Wheeler, C.H. Redshaw

W102 **Reuse of wastewater from meat processing plants after final filtration with activated carbon**
S. Pap, I. Mihajlović, M. Đogo, M. Stupavski, M. Turk Sekulić, M. Vojinović Miloradov, J. Radonić

W103 **Coagulation/flocculation and electrochemical oxidation using a anode BDD to the treatment nejayote from the corn industry**
T. Zayas, V. Tellez, L. Salgado

W104 **Investigation of the applicability of solar photocatalitic degradation in treatment of water containing high concentration of petroleum hydrocarbons**
M. Takić, B. Lalević, T. Šolević Knudsen, V. Raičević, M. Antić

W105 **Monitorization of estrogens rivers downstream outputs WWTP´sand impact onamphibians**
Ana Paula Fonseca,Salvador Massano Cardoso

W106 **Geopolymerization of fly ash as possible technology for immobilzation of electric arc furnace dust**
D. Djurović, I Nikolić, M. Tadić, B. Mugoša

W107 **Purification of wastewater in fur industry**
N. Avdić, F. Korać

W108 **Screening of pesticide residues in canal water in the northern Serbia**
S. Lazić, D. Šunjka, I. Milovanović, N. Grahovac

Biodegradation and bioremediation

B101 **Release of hydrophilic drugs and α-hydroxy acids from biocompatible copolymers**
J. Oborná, M. Vávrová, I. Chamradová, L. Vojtová

B102 **Polycyclic aromatic hydrocarbons in commercial barents sea fish species**
A.Yu. Zhilin, N.F. Plotitsyna, A.M. Litovskaya

Analytical methods for environmental science and biomonitoring

A101 **Derivative Spectrophotometry and Electron Spin Resonance (ESR) Spectroscopy for Ecological and Biological Questions**
Saakov V.S., Danilova I.GS

Ecotoxicology and biomarkers

E101 **Influence of newly synthesized Cu(II) complexes on the pyrazole based derivatives on inhibition of *Botryosphaeria dothide***
Ž. Jaćimović A. Radović, M. Kosović, N.Latinović

E102 **The influence of the environment on the quality of olive oil from different locations in Bar, Montenegro**.
M.Kosović, Ž. Jaćimović, M.Pekić, D.Šuković

E103 **A review of the contents of aflatoxins in animal feed samples in the Montenegrin market using ELISA and HPLC methods**
D. Šuković , J. Rešetar, V. Živković, Ž. Jaćimović

E104 **Occurence of aflatoxin M1 in milk samples on the market of Montenegro**
D. Šuković, V. Živkovic, J. Šekularac, Ž. Jaćimović

BOOK OF
ABSTRACTS

PLENARY LECTURES

INORGANIC NANOMATERIAL EFFECTS ON AQUATIC ORGANISMS

George P. Cobb[1,2], Emily Bigorgne[1], Leanne F. Baker[1], Shawna L. Nations[2] and Cole W. Matson[1]

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Lubbock, TX 79614 US

Inorganic nanomaterials (NMs) are widely used in our daily lives, serving as pigments, antimicrobials, catalysts and a many other useful products. Even so, relatively little has been done to evaluate inorganic nanomaterial toxicity throughout the developmental life stages of vertebrates. This is in large part due to the low acute toxicity of many NMs. However, standard acute toxicity evaluations do not present a complete picture of toxic effects that may manifest from chronic toxicant exposure or exposures during specific critical life stages.

Limited effects were observed during acute aqueous exposures of *Xenopus laevis* to several individual NMs: CuO, Fe_2O_3, TiO_2 and ZnO. At environmentally relevant concentrations CuO and ZnO NMs produced developmental effects, while Fe_2O_3, TiO_2 NMs did not affect development or survival. Chronic studies were then initiated for approximately 6 weeks to evaluate the dose response of developing *Xenopus* exposed to aqueous CuO and ZnO NMs. Studies encompassed all developmental stages, from embryo throughout metamorphosis. Observed toxicities included, mortality, altered growth, malformations, and failure to complete metamorphosis. As has been noted with several toxicants, a sharp increase in toxicity is observed for CuO and ZnO NMs after 4 days of exposure. The magnitude of this increase is greater than with the respective divalent cations. Chronic effects indicate that these nanomaterials are more toxic than a similar concentration of their respective divalent cations. There were also marginal improvements in survival and growth at very low concentrations of ZnO and CuO NMs.

Additional studies were employed to evaluate the influence of salinity on silver nanomaterial (Ag NM) toxicity, Gulf killifish (*Fundulus grandis*) embryos over a 48 hours interval. After 24 hours of exposure, a V-shaped toxicity pattern was observed with a high mortality in 0 ‰ artificial seawater (ASW) followed by a strong decrease in mortality at 0.1 and 0.5 ‰ ASW. At higher salinities (10 – 20 ‰ ASW), toxicity returned to between 60-80% mortality. After 48 hours, toxicity increased strongly only at 0.1‰ (USEPA water). Cysteine is a natural ligand for Ag+ and decreases silver ion toxicity. Counter to the pattern observed for $AgNO_3$, low salinity cysteine containing solutions revealed no decrease in Ag NM toxicity after 24 or 48 hours. Cysteine treatment significantly decreased toxicity at higher salinities. NM dissolution combined with subsequent silver speciation seems to explain 24 h toxicity, but not additional toxicity at 48 h in low salinities. A lack of cysteine rescue at low salinities and the differences between 24 and 48 h toxicity support the hypothesis that citrate-capped Ag NMs demonstrate at least partially nano-specific toxicity.

In a third line of inquiry, nanomaterial exposures in stream mesocosms were used to mimic emissions from wastewater treatment facilities (“press”-type exposures) and accidental spills (“pulse”-type exposures). Mesocosms were treated with either 1) a one-time addition (pulse) of acetate-coated cerium dioxide (CeO_2) NMs or 2) a 25-day continuous exposure (press) containing the same total amount of CeO_2 NMs in pulsed exposure. Mesocosms were lined with unglazed ceramic tiles and stocked with fish, invertebrate, plant and microbial species. Results suggest rapid precipitation of CeO_2 NMs in the pulsed dose with higher concentrations persisting in the press-dosed stream. Five days after completion of NM dosing in press mesocosms (day 30 of experiment), aqueous concentrations of Ce had declined but were still higher than any Ce concentration measured in the pulse-dosed stream. Consequently, the concentration of Ce in periphyton was lower in the press-dosed stream on day 30 than in the pulse-dosed stream. The press dose allowed longer-range transport of CeO_2 NMs, such that concentrations of Ce in the lower reaches of the press-dosed stream were nearly double those observed for the pulse-dosed stream, likely because of a reduced aggregation relative to the pulse addition. These results suggest that exposure scenarios may play a significant role in determining the environmental fate, transport, and bioavailability of stable metal oxide NMs.

Data from these studies provide clear evidence that future research is needed to better explain behaviors of metal oxide NMs in the environment and potential detrimental and beneficial effects of across this class of NMs.

POLYCYCLIC AROMATIC COMPOUNDS (PAC): SENSITIVE ANALYSIS BY GAS CHROMATOGRAPHY – ATMOSPHERIC PRESSURE LASER IONISATION – TIME-OF-FLIGHT – MASS SPECTROMETRY (GC-APLI-MS) AND BIOAVAILABILITY FROM COALS

Christine Achten
Institute of Geology and Palaeontology – Applied Geology, University of Münster, Münster, Germany

GC-APLI-MS is a highly sensitive and selective analytical technique for PAC which has recently been developed [Stader et al., 2013]. The method and first applications to environmental samples from different fields are presented. The limit of detection for 40 polycyclic aromatic hydrocarbons (PAH) in a standard mixture was 5 - 100 fg, demonstrating GC-APLI-MS to be a highly sensitive technique and more sensitive by a factor of 100 – 3,500 compared to GC-MS. Acenaphthylene and cyclopenta[cd]pyrene were not detectable < 2,500 fg per injection, probably due to not being ionized. A special sample preparation is necessary and ultra-sonic extraction proved to be suitable, if a thorough clean-up was performed and plastic materials avoided.

Amongst others, the method was used to study bioavailability of PAH from different types of coals (lignite, subbituminous coal, bituminous coals and anthracite of different origin and formation conditions) which showed PAH contents of up to 79 mg/kg EPA-PAH and 865 mg/kg total PAH. To study bioavailability, whole coal samples as well as extracts from the coals were investigated using the same organisms (*Caenorhabditis elegans, Danio rerio, Lumbriculus variegatus)* [Meyer et al., in press]. The results suggest that despite the high toxic potential of PAC present, their bioavailability from different coal types is very limited and independent of coal properties and native PAH content. Additionally, unknown toxic PAC were identified. Also, studies on microbial degradation [Achten et al., 2011] and oral bioaccessibility indicate limited bioavailability of PAH from coals.

Acknowledgements

C. Stader, W. Meyer, F. T. Beer and S. Kons, Institute of Geology and Palaeontology – Applied Geology, University of Münster; T.-B. Seiler, M. Reininghaus and H. Hollert, RWTH Aachen University, Institute for Environmental Research, Department of Ecosystem Analysis; J. Schwarzbauer, RWTH Aachen University, Institute of Geology and Geochemistry of Petroleum and Coal; W. Püttmann, J.W.-Goethe University Frankfurt am Main, Institute for Atmospheric and Environmental Sciences, Department of Analytical Environmental Chemistry; all Germany

References

Stader, C., F. T. Beer, Achten, C. (2013): Anal Bioanal Chem 405: 7041.
Meyer, W., Seiler, T.-B., Reininghaus, M., Schwarzbauer, J., Püttmann, W., Hollert, H., Achten, C. (in press): Environ Sci Technol
Achten, C., Cheng, S, Straub, K. L, Hofmann, T. (2011): Environ Pollut 159: 623.

ORAL PRESENTATIONS

ANALITICAL METHOD FOR ENVIRONMENTAL SCIENCE AND BIOMONITORING

Derivative Spectrophotometry and Electron Spin Resonance (ESR) Spectroscopy for Ecological and Biological Questions

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Derivative Spectrophotometry and Electron Spin Resonance (ESR) Spectroscopy for resolving Ecological questions and application of the PAM-fluorescence method allows to detect the functional status of photosynthesizing cells. The use of derivative spectrophotometry of 4-8 orders (HODPh) provides the structural state evaluation of cells and biologically-active substances. At the same time comparative researches carried out in equal time intervals under the influence of extremal environmental factors give the possibility to match structural changes of cells and corresponding failures of their functional reactions. For this purpose barley mutants lacking chlorophyll "b" and also Chlamydomonas and Scenedesmus algae mutants with different sensitivity to the light were used. Interpretation of derivative spectrophotometry data agreed with the analysis of PAM-fluorescence. Specialities of HODPh spectra are considered with discussion of the large factual material on Ca-ions interaction with ((benzylidene)amino)guanidine derivative substances containing electron-donating or electron-accepting substituents.

Also, evidence of polycomponency of the promising antitumor preparation «Ukrain» («NowickyFarma», Austria) is presented and the wide range of HODPh application in different biochemical researches is shown.

The summation of our materials is published in the monograph "Biological Questions" V. Saakov et al. Springer PH, 2012-2013, Wien, Heidelberg, ISBN 978-3-7091-1006-5 ; ISBN 978-3-7091-1007-2 (eBook)

BIDEGRADATION AND BIOREMEDIATION

Comparison of three macrophytes to remediate co-contaminated soils with Polycyclic Aromatic Hydrocarbons (PAHs) and Trace Elements (TEs), implications for green urban infrastructures.

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Many studies report successful phytoremediation using macrophytes to treat wastewater in constructed wetlands. However, little is known about their phytoremediation capabilities in urban green spaces as swales or biofilters where they are submitted to dry and flood periods.

To access to the system behaviour under natural conditions, eight representative large-scale outdoor mesocosms were spiked with Cd, Pb, Zn, phenanthrene, pyrene and benzo[*a*]pyrene to reach 2, 100, 300, 10, 10, 10, mg.kg^{-1}soil dry weight, respectively. Three macrophytes species were tested for remediation: *Juncus effusus*, *Iris pseudacorus*, *Phalaris arundinacea* and compared to a graminaceae mix. PAHs were extracted from soils by microwave assisted extractions and analysed by GC-MS. Microwave-acid digestion was used to extract metals from plants, which were then analysed by ICP. TEs uptake varies considerably with plant species and the TE considered. Soil-plant transfer coefficients were calculated and allowed to identify the best accumulator. The transfer of TE to air parts is of best interest as shoots are cut once a year in urban green areas. The sequence of TEs availability to plant was determined. PAHs concentrations in soil were drastically reduced after six months and divided by 10 to 100 for low molecular weight PAHs and by 2 to 7 for benzo[a]pyrene depending on plant species. A special attention was paid to microbial community structure and function in the rhizosphere to emphasize our understanding of the soil-root interface. Investigations of total, fungal, and bacterial contents and enzymatic activities in soil and rhizosphere are in progress.

Macrophytes appeared to be of major interest compared to graminaceae for soil depollution. We suggest that introducing several macrophytes species in green urban infrastructures would be a best practice for soil remediation of TEs and PAHs. Two swales along the road, planted with graminaceae and macrophytes, were investigated. The first results show the same manure as in the experimental mesocosm.

POTENTIAL IMPACT OF MICROBIAL ACTIVITY ON THE OXIDANT CAPACITY AND THE ORGANIC CARBON BUDGET IN CLOUDS

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Within cloud water, microorganisms are metabolically active; so they are suspected to contribute to atmospheric chemistry. This paper is focused on the interactions between microorganisms and Reactive Oxygenated Species present in cloud water since these chemical compounds are driving the oxidant capacity of the cloud system[1]. For this, real cloud waters with contrasting features (marine, continental, urban) were sampled at the puy de Dôme mountain (France). They exhibit high microbial biodiversity and complex chemical composition. These media were incubated in the dark and subjected to UV-light radiation in specifically designed photo-bio-reactors. The concentrations of hydrogen peroxide (H_2O_2), organic compounds and the ATP/ADP ratio were monitored during the incubation period. Microorganisms remained metabolically active in the presence of hydroxyl radicals (•OH) photo-produced from H_2O_2. This oxidant and major carbon compounds (formaldehyde and carboxylic acids) were biodegraded by the endogenous microflora. This work suggests that microorganisms could play a double role in atmospheric chemistry: first, they could directly metabolize organic carbon species; second they could reduce the available source of radicals due to their oxidative metabolism. Consequently, molecules such as H_2O_2 would be no longer available for photochemical or other chemical reactions, decreasing the cloud oxidant capacity.

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CHEMISTRY OF WATER SOIL

The Emission and Pollution Level of Platinum, Palladium and Traffic-Related Elements in Road Dusts from Seoul, Korea

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The emission level and pollution characteristics of platinum (Pt) in dust, soils, and tree barks collected from Seoul, the capital of Korea, was published for the first time in Korea (1, 2). The total area of Seoul is about 605 km^2 and its population was about 10.45 million and the number of registered motor vehicles was 2.95 million in 2008. Road dust samples were collected from 31 sites of various traffic volumes in Seoul, and from 4 control suburb sites in satellite cities for comparison. The previous study confirmed that the important source of Pt in roadside environment is automobile catalytic converter, and that it indicates a tendency to increase Pt levels in road dusts along with traffic volume. The study also suggested that not only traffic volume but also driving style have a great influence on Pt levels in road dusts, for example 176 ng/g Pt in dust at the toll gate.

In this study previous dust samples and some new dusts collected from Seoul were reanalyzed to determine Pt, Pd and traffic-related trace elements by ICP-MS and ICP-OES. The concentration levels of Pt and Pd were in the range of 0 – 444 (median 76) ng/g and 172 – 1,215 (median 609) ng/g, respectively. Palladium also shows similar distribution trend with Pt, and remarkably high concentration of Pd and Pt in dust was found in the heavy traffic areas. The traffic-related elements such as Cr,Cu,Mo,Ni,Pb,Sb, and Zn were enriched in road dusts with high Pt level as compared with them from control suburb areas. Closely correlated elements with Pt and Pd in dust were Be, Cr, Cu, Fe, Mo, Ni, Au, Hg, and Bi (higher than $r = 0.50$).

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THE EFFECT OF THE ALIEN INVASIVE BIVALVE, *CORBICULA FLUMINEA*, IN NUTRIENT DYNAMICS UNDER CLIMATE CHANGE SCENARIO – A MESOCOSM EXPERIENCE.

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The main aim of this study was to evaluate the impact of the alien invasive bivalve *Corbicula fluminea* (Müller, 1774) in the ecosystem functioning of temperate estuarine systems (oligohaline areas) under climate change scenarios. The scenarios simulated climate changes, following salinity (0 or 5 PSU) and temperature (20 or 30°C) changes.

The effect of individual size (different size classes with same biomass) and density (same size class, various densities) on bioturbation associated nutrient dynamics was evaluated under a 18-day laboratory experimental setup. Experimental mesocosms (12*12*35 cm) were filled with 10 cm depth of sediment (1440cm^3) and 20 cm filtered water collected in situ (2880 cm^3 = 2.88l), adjusted to target salinity. Three *C. fluminea* size-classes were defined, small (< 1cm), medium (between 2-2.5cm) and large (> 3.5cm), and individuals were introduced adding up to the same total biomass, set in accordance to the average biomass per m^2 found in the field (the upstream Mondego river estuary, Portugal) (≈ 18.8 g wet weight per 0.0144m^{-2} mesocosm area), which corresponded to different density levels (13 small individuals, 2 medium-size individuals or 1 large *Corbicula*). Additionally, experimental mesocosms with 6, 12 and 24 small-size *Corbiculas* were used to evaluate the effect of density on the nutrient dynamics, for constant salinity (0) and temperature (20ºC). Water samples were collected at t_0, t_3, t_6, t_{12} and $t_{18\ days}$, and analysed for PO_4-P, NH_4-N and NO_x-N.

Results show that regardless the same total biomass in each mesocom, nutrient dynamics tend to be higher in the small and medium sized *Corbicula* mesocosms, probably as a result of increased surface sediment disturbance. Overall, we might conclude that the onset of climatic events such as drought periods and heat waves may have a significant impact on the nutrient dynamics in aquatic systems colonized by this alien invasive species.

CONTAMINATION OF WASTE WATERS BY SYNTHETIC FRAGRANCES

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This study deals with determination of synthetic fragrances (musk compounds) in waste waters. These compounds are used as fragrant ingredients of detergents, perfumes, cosmetics and other personal care products (PCPs). Wastewaters represent the main source of environmental contamination by these compounds, because these substances are not removed in sewage treatment plants and pass subsequently to aquatic ecosystems, where they bioaccumulate in water biota and this way they enter the food chain. Some of these compounds show potential toxic effects.

The presence of musk compounds was followed in industrial waste water from the Dermacol Company, Brno, producing cosmetics, further in waste water from the area of University of Veterinary and Pharmaceutical Sciences Brno where small waste water treatment plant operates, and in municipal waste water from the Brno area which are treated in large-scale waste water treatment plant in Brno-Modřice. Target compounds (14 musks) from the groups of nitromusks, polycyclic musks and linear musks were analyzed. Solid Phase Microextraction (SPME) was used for the isolation of analytes from the water matrix, gas chromatography with mass spectrometric detection (GC/MS) served as final analytical method.

The results show that the most important environmental contaminant in the studied locality is Galaxolide, whose concentrations in Brno waste water were in the range of $\mu g.l^{-1}$, followed by Tonalide in tenths of $\mu g.l^{-1}$. Musk ketone was on the third place showing levels of tens $ng.l^{-1}$. Linear musks were found in all untreated waste water samples in concentrations reaching $\mu g.l^{-1}$, but their importance as environmental contaminant was strongly reduced by their high removal efficiency in the waste water treatment process.

Acknowledgment

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SORPTION OF CU AND ZN IN 21 SOILS AS INFLUENCED BY SOIL Ph

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Copper and Zn, the most abundant of the anthropogenic trace metals, are being added to Southeast Mediterranean ecosystems in elevated concentrations through various human-induced pathways. Their sorption and desorption behaviour depends highly on soil pH, but the number of tested soils are usually low, thus the role of other soil properties within the group of acidic or alkaline soils has not been thoroughly examined. We conducted a batch sorption test with 21 low-organic C soils (12 alkaline and 9 acidic) from Central Greece with added metal concentrations of 0-100 mg L^{-1} at a 1-to-10 solid/solution ratio. We measured q_{100} (sorption at 100 mg L^{-1}), q_{max} (according to Langmuir), K_{d-50} (distribution coefficient at 50 mg L^{-1}, according to Freundlich), $DTPA_{100}$ (extraction of soils added with 100 mg L^{-1}), and desorption percentage of that sorbed at 100 mg L^{-1}. Copper K_{d-50} was higher than Zn (while q_{100} and q_{max} did not differ), but Zn desorption was faster than Cu (Table 1).

Table 1. Sorption parameters of Cu and Zn in all 21 tested soils.

	Cu	Zn	Significance
q_{100} (mg kg^{-1})^a	675	640	Non-significant
q_{max} (mg kg^{-1})^b	833	742	Non-significant
K_{d-50} (kg L^{-1})^c	1107	38.8	** (p=0.006)
$DTPA_{100}$ (mg kg^{-1})^d	19.2	53.0	** (p=0.002)
Desorption (%)^e	3.17	7.03	** (p=0.002)

When we differentiated sorption within acidic and alkaline soils, we found that sorption increased with pH (as rather expected), but we also found that desorption of both Cu and Zn was higher in alkaline than in the acidic soils (Table 2).

Table 2. Sorption parameters of Cu and Zn as differentiated between acidic (*n*=9) and alkaline (*n*=12) soils.

		q_{100}	q_{max}	K_{d-50}	DTPA$_{100}$	Desorption
		(mg kg^{-1})	(mg kg^{-1})	(kg L^{-1})	(mg kg^{-1})	(%)
Cu	Acidic	540 b	602 a	37 a	17.8 a	3.68 a
	Alkaline	775 c	1041 c	1910 d	20.2 a	2.79 a
Zn	Acidic	492 a	604 a	17 a	14.4 a	2.86 a
	Alkaline	751 c	846 b	55 c	82.0 b	10.16 a
	Significance	***	**	***	***	***
	p	$0.3x10^{-3}$	$2.4x10^{-3}$	$0.3x10^{-3}$	$0.6x10^{-3}$	$0.1x10^{-3}$
	LSD$_{0.05}$	38.51	79.49	382.4	8.14	0.92

We conclude that risks of elevated Cu and Zn mobility in low-organic matter soils are not minimized when the metals are introduced to high-pH value soils, because such soils tend to desorb these metals faster, and this behaviour may trigger environmental concerns over the years.

ORGANIC CONTAMINANT BURDEN IN WATER AND SEDIMENT FROM JAKARTA BAY, INDONESIA, AND ITS IMPLICATION FOR SEAFOOD CONSUMPTION

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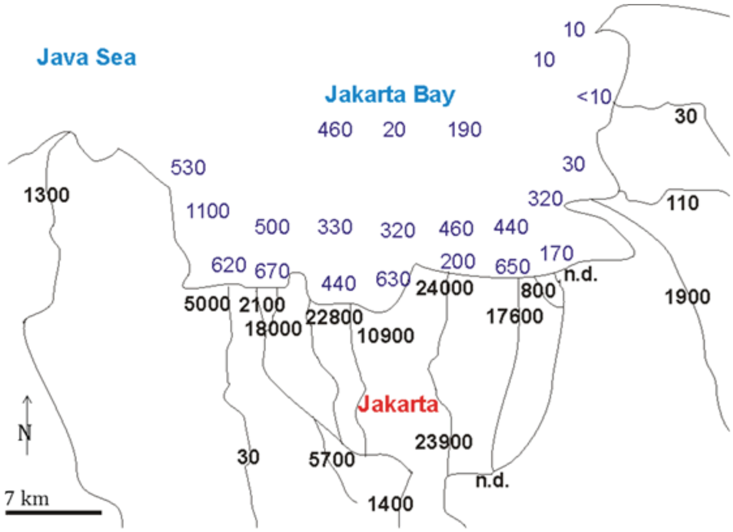
Seafood is the main protein source and an important income basis for many local communities in coastal areas of Indonesia. But seafood consumption is also an important route of human exposure to organic contaminants. Commercially important fish and benthic species from densely populated and industrialized coastal areas with inputs of untreated sewage such as Jakarta Bay may contain potentially harmful organic contaminants in levels which are exceeding international safety thresholds. This is probably posing a risk to human health, in particular with respect to bioaccumulating contaminants. It is therefore necessary to evaluate the quality of seafood from such Indonesian coastal systems in terms of contaminant burden. The aim of our ongoing project is based on a *source-to-cell* approach to state of pollution in Jakarta Bay and its implication for human food resources. It traces the implications of harmful substance loads from their primary emission sources via water and sediment pollution to the consumed seafood.

Riverine input is a major source of pollution in Jakarta Bay. First results show the presence of a broad organic contaminant spectrum in water and sediments from the rivers discharging into the bay, including rarely reported, emerging contaminants. Typical constituents of municipal sewage such as insect repellents, household pesticides, disinfectants, detergent residues and synthetic fragrances are detectable as well as compounds stemming from industrial inputs.

Figure 1



N,N-diethyltoluamide (DEET) is used in households as insect repellent. High DEET concentrations (up to 24,000 ng L^{-1}) in river water from Jakarta indicate a high usage rate in the city and the discharge of high DEET loads into Jakarta Bay. The compound was present in all water samples from the bay, illustrating the compounds` widespread distribution in the coastal system and indicating its stability in the aqueous phase.

PHOTOSENSITISED PROCESSES OF ATMOSPHERIC SIGNIFICANCE FOR THE FORMATION OF HUMIC-LIKE SUBSTANCES (HULIS) FROM PHENOLIC COMPOUNDS

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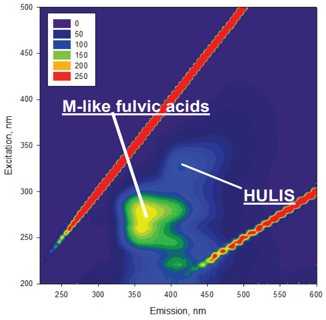
Humic-like substances (HULIS) have gained considerable interest in the field of atmospheric chemistry because they constitute an important fraction of the organic aerosol mass and affect the aerosol ability to absorb sunlight and nucleate water droplets [1–3]. Recent studies suggest that a possible pathway to HULIS formation involves phenolic compounds arising from biomass burning, in the presence of both photosensitisers and ozone [4]. Ozone is actually not necessary in the photosensitised transformation of phenols, as recently shown by us [5], which prompted the investigation of HULIS production by O_3-independent processes. We used 1-nitronaphthalene (1NN) as photosensitiser, which can play a potentially important role in the aerosol photochemistry [6]. The UVA irradiation of an aqueous solution of 1NN and phenol causes transformation of both compounds, with the triplet state of 1NN (^{3}1NN*) largely involved in phenol degradation. Laser flash photolysis experiments indicated that ^{3}1NN* reacts with phenol with second-order rate constant $k = (4.5\pm0.1)\times10^{9}$ M^{-1} s^{-1}, producing the phenoxy radical and 1NN radical anion. Phenoxyl undergoes dimerisation to dihydroxybiphenyls and phenoxyphenols, identified by GC-MS. Moreover, analysis of the irradiated system by fluorescence matrix spectroscopy (EEM) indicated the formation of species analogous to “M-like” fulvic acids and, at longer irradiation times, of material with HULIS properties (see figure below). The photoprocessed material also produced $^{1}O_2$ under irradiation, as shown by the degradation of furfuryl alcohol. These findings could shed new light on HULIS formation and on the photoactivity of organic material in atmospheric waters.



EEM (Emission-Excitation Matrix) fluorescence spectrum of an aqueous solution containing 0.1 mM 1-nitronaphthalene + 0.1 mM phenol, after 4 h of UVA irradiation. The two straight lines represent the Rayleigh scattering of water and its second harmonic.

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MODELING PB, CD AND NI BIOACCUMULATION IN *GAMMARUS PULEX*: APPLICATION TO REALISTIC ENVIRONMENTAL CONDITIONS AND IMPORTANCE OF WATER CHEMISTRY

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Bioaccumulation is an integrative indicator of the metal exposure in aquatic organisms and also enables to integrate the effect of water chemistry on metal bioavailability, fraction expected to be toxic for biota[1]. However, the link between water's contamination and accumulated metal in organisms is complex. Indeed, bioaccumulation depends on both physiological variables and various physicochemical parameters, such as water cationic composition which has often been pointed out as influencing metal uptake by competitive binding on biological surfaces. The development of bioaccumulation models as a tool for quantifying metal bioavailability constitutes promising approaches for understanding and predicting metal impacts on aquatic ecosystems[1].

The present study aims at evaluating the suitability of using conceptual models calibrated in the freshwater amphipod *Gammarus pulex* to predict the bioaccumulation of PB, CB and Ni in field conditions. Under laboratory controlled conditions, gammarids were exposed to dissolved PB, CB or Ni in order to determine the uptake and elimination rate constants (*ku* and *ke*) for each "metal/*G. pulex*" couple and required to modelling. Then, gammarids were exposed to constant concentrations of metal under various environmental concentrations of major ions (Ca^{2+}, Mg^{2+} and Na^{+}) in order to evaluate theirs effects on kinetic constants (*ku* and *ke*). Finally, model suitability was assessed through the comparison between predicted and measured bioaccumulation levels from gammarids transplanted on watersheds all different in terms of contamination and water chemistry (Rhône and Seine, France).

Experiments show that among the three ions tested, only Ca^{2+} has a significant competitive effect on PB, CB and Ni uptake which was integrated into models thanks to the expression of *ku* as a function of Ca^{2+} levels and a metal-dependent affinity constant $Ki_{(Ca2+)}$. Then, comparison between predicted and measured bioaccumulation from gammarids transplanted into the field reveals that both Pb, Cd and Ni models accurately predicted bioaccumulation. This suggests that the kinetic constants (*ku* and *ke*) determined in laboratory are applicable to the conditions encountered in environments. Furthermore, the consideration of Ca^{2+} influence into the models had permitted to improve the predictions for Pb, Cd and to a less extend for Ni. These results highlight the significance to consider the effect of water chemistry on metal bioavailability to understand metal bioaccumulation under field conditions.

To conclude, bioaccumulation models are potentially suitable to monitor freshwater quality and to improve the assessment of the impact of metal contamination on aquatic ecosystems.

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GC-TOF WITH SOFT IONIZATION AND HIGH RESOLUTION FOR ANALYSIS OF COMPLEX MIXTURES

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In spite of rapid evolution of mass spectrometric arsenal, the analysis of complex mixtures still remains a challenging task. We've chosen crude oils as a representative sample for developing analytical strategies. Major components could be analyzed with conventional GC-TOF and GCxGC-TOF with analysis capacity of 10,000 compounds. High resolution FTMS can idenify up to 50,000 compounds. However, R>300,000 mass resolution alone does not yet take care of structural and functional isomers, which requires additional chromatographic or ion mobility separation. Combination of high resolving MS with GC and GCxGC pushes boundaries, since most of high end instrument operate with slow scanning speed, measured in multiple seconds per scan. Besides, the mixture is diverse in nature and components vary from saturated alkenes to highly nonvolatile and polar compounds containing oxygen, nitrogen and sulfur. The latter complicates representative and quantitative analysis, since any known ionization method is discriminative between chemical classes. Finally, with major interest lying in high boilers, it makes challenging application of highly resolving gas chromatography (GC). The talk describes several recent developments which are directed for alleviating prior limitations.

For uniform ionization of crude oil components we developed two types of ion sources. To support fast separation in both GC and GCxGC modes the sources operate at controlled environment, with clean materials, with small reaction volume and at high temperature of 250-300C. A photo chemical ionization (PCI) source provides soft and uniform ionization of all major classes, but alkenes. A conditioned glow discharge (c-GD) source provides alkenes ionization, but adds some degree of analyte fragmentation.

To resolve isobars and isomers we developed an approach where gas chromatography is combined with Multi-reflecting TOF. The research grade MR-TOF provides 100, 000 resolution in full mass range, and about 160,000 in a so-called zoom mode providing analysis in the mass range Mmax / Mmin = 4:1, i.e. between 100 and 400 Th or between 200 and 800 Th. In those analyses we observed that most of close isobars appear to be separated in time by GC. This allows recording peak centroids with typical sub-ppm mass accuracy. The resultant mass spectrum, summed over the GC run is then presented by isobars centroids separated with effective resolution approaching million in dynamic range 1E+5 and integral dynamic range 1E+7. In such analyses we observe up to 30,000 various compounds accounting isomers.

Application of GC, however, is likely to discriminate against labile compounds, which may be degraded within the GC column. To characterize the effect we infused the same crude oils and ionized it with ESI source and analyzed on the same research grade MR-TOF. Spectra were compared with GC-MR-TOF while ionizing within the CI and EI sources, and with PCI and c-GD sources. Indeed, with ESI source we observed plenty of nitrogen containing compounds generating major signals, while those compounds provided low signals past GC, were presented by light fractions, and had very broad GC peaks indirectly indicating their decomposition within the GC column.

STABILITY AND RETENTION OF SULFAMETHOXAZOLE AND CIPROFLOXACIN IN SOILS

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A wide range of antibiotics are currently used for the therapy of infectious diseases in veterinary medicine. After consumption, these molecules are mainly released via excrements into the local environment, especially soils. As a result of leaching and surface runoff, soils can further act as a source of antibiotic contaminants for aqueous environments. In order to better comprehand the environmental fate of these compounds, it is necessary to assess their mobility in soil. This preliminary study reports on the retention in soil and stability of two very commonly used veterinary antibiotics – sulfamethoxazole and ciprofloxacin – belonging to sulphonamides and fluoroquinolones chemical groups, respectively. Due to their distinctive physicochemical characteristics, it is expected that they exhibit different behavior in the soil system. In the laboratory, we set up a column (40 cm long, 10 cm i.d.) experiment with two types of soil with different contents of organic matter, on which we applied known concentrations of both antibiotics. By simulated rainfall we collected leachate samples from the columns, which were filtered and analyzed by HPLC-FLD.

The obtained results showed that ciprofloxacin is poorly mobile and exhibits high affinity to both soils. On the other hand, sulfamethoxazole is characterized by high mobility in the soil system in both cases, related to short retention in soil. Sulfamethoxazole showed a slightly longer retention time in the soil with higher content of organic matter. However, by adding water equivalent to a precipitation of only 180 Lm^{-2}, sulfamethoxazole leached completely from the columns. On the contrary, ciprofloxacin was not detected in any of the samples even after a simulated precipitation of 530 Lm^{-2}. Our spectrophotometric measurements have also shown that both antibiotics are stable in solution and their concentration remained constant during the experiments. The results are consistent with our assumptions and data from the literature [1]. From the perspective of organic farming and the use of manure as fertilizer, sulfamethoxazole is less problematic than ciprofloxacin since it could be removed from soil with low amounts of precipitation. However, it has to be underlined that sulfamethoxazole, as well as compounds showing similar soil behavior, will further pose a threat to the aquatic environment.

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HEXABROMOCYCLODODECANE (HBCDD) - A HAZARDOUS BROMINATED FLAME RETARDANT USED IN POLYSTYRENE BUILDING PRODUCTS

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Hexabromocyclododecane (HBCDD or HBCD) is an emerging chemical with POP-properties used increasingly as a flame retardant in the increasingly used polystyrene-based building products (EPS/XPS). HBCDD is a lipophilic and persistent organic pollutant which has been detected in air, water, soil and sediments in many countries, and high levels of HBCDD is found in indoor air and dusts. HBCDD, especially of the most stable α-isomer, accumulates in natural organisms and magnifies through the food chain, leading to progressively increasing background levels in wildlife and in human tissues, including in human milk. Exposure to HBCDD can have wide-ranging and potentially severe effects – particularly endocrine disruption, thyroid effects and developmental toxicity. In 2008 The European Chemicals Agency identified HBCDD as 1 of 14 substances of "Very High Concern", and in September 2010 HBCDD was added to REACH's Authorization List. In February 2011 HBCDD was among 6 chemicals added to Annex XIV of the EU REACH Regulation selected to be phased out before August 2015. In May 2013 it was decided to list HBCDD in Annex A of the global Stockholm Convention as a persistent organic pollutant and has to be phased out globally.

WDXRF AND ICP-OES ANALYSIS: BIOMONITORING OF TOXIC METALS WITH DIFFERENT CONIFER SPECIES

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Conifer trees are favorable plants for biomonitoring, they can absorb toxic metals trough the pores in their leaves or collect toxic metal containing aerosol particles on the leaves surface. Conifers do not lose their leaves every year, therefore they can be used for biomonitoring for longer time periods.

Our research is based on the 3 conifer genera which are the most often present in the urban area of Belgrade City: *Pinus*, *Abies* and *Taxus*. Leave samples were taken in the spring in order to collect shoots and one year old needles from the same trees.

Samples were prepared and analyzed with 2 different methods WDXRF and ICP-OES. WDXRF was used for screening purposes. For some metals (Ni, Cr) WDXRF method had better detection limit than ICP-OES, because it was able to use larger sample masses for the analysis. Dry samples were first ashed at 450°C and then analyzed as a layer at the surface of boric acid pressed pellet. XRF analysis revealed all the elements which were later quantitatively determined by ICP-OES. WDXRF analysis was performed with Thermo Scientific UniQuant Software [1], also called standardless quantitative analysis. It gave us approximate concentrations of toxic metals and other elements, which significantly facilitated choice of analytical standards for ICP, spectroscopic lines and avoidance of spectral interferences. Prior to quantitative analysis with ICP-OES, dry samples were microwave digested with nitric acid and hydrogen peroxide.

Distribution of toxic metals between branches, needles and shoots was analyzed. *Abies* had tendency to concentrate Al, Ba, Cu, Fe, Ni, Pb and Zn in branches, *Pinuses* had elevated concentrations of Al, Cu, Fe, Ni, Pb and lower concentrations of K and Mn, while *Taxi* had the most similar concentrations of toxic metals in branches and needles (with the exception of Mn which was considerably elevated in the needles).

When the concentrations of metals in the shoots were compared to the concentrations in the needles, it was concluded that all 3 genera had significantly higher concentrations of Al, Ba, Ca, Fe, Li, Na, Pb, Sr in the needles, while K, Ni and Zn were more concentrated in the shoots. Additionally, *Taxi* had significantly elevated concentrations of Mn in the shoots, unlike the other analyzed species. The most of the toxic metals preferred to accumulate in some of the analyzed species (highest in *Taxus*, lowest in *Pinus*).

[1] UniQuant, 2012, Thermo Fisher Scientific Inc (http://www.uniquant.com/index.html)

FAST, CHEAP, SAFE AND RELIABLE GC/HRMS ANALYSIS OF PRIORITY POLLUTANTS IN WATER SAMPLES

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Sample preparation procedures for environmental applications of GC-MS analysis are often criticized for being rather time-consuming and laborious. Since the sensitivity of mass spectrometers have raised significantly, we have attempted to improve the method, making it cheaper, faster, more sensitive and reliable. As the first step polycyclic aromatic hydrocarbons were studied [1]. The present work deals with priority pollutants belonging to various classes. A novel simplified sample preparation method for quantitative analysis of priority pollutants in water samples by gas chromatography - mass spectrometry (GC-MS) was proposed. The method requires just 1 mL of water sample and 1 mL of dichloromethane and takes only 5-10 minutes. While applying accurate mass measurements the detection limits for all the analytes are about 1 µg L^{-1}, while the limits of quantification — 10 µg L^{-1}. These limits correspond to those for the standard 8270 method of the United States Environmental Protection Agency.

All experiments were performed with time-of-flight (TOF) high resolution mass-spectrometer GC-HRT (LECO Corporation, Saint-Josef, USA) with resolving power up to 50 000 with multiple reflecting geometry of mass analyzer (EI ion source temperature 300°C, electron energy 70 eV, mass range m/z 40 - 300). All results were processed with ChromaTOF-HRT 1.8 software of LECO Corporation (USA) that includes instrument control, spectra registration and data processing.

To establish recoveries and detection limits response factors (RF) for all analyzed priority pollutants were established by using 6 internal standards applied in the classic version of 8270 EPA method. RFs for individual compound were calculated to the nearest by retention time deuterated standard. The data show quite reasonable RF values and their statistical parameters for the majority of analytes. Ratios of the intensities of the two major characteristic peaks in the spectra of all the analytes (Q2/Q1 values) are also acceptable as 8270 EPA method allows 30% deviation for this value. Reproducibility of the results was quite high. For PAH, chlorobenzenes, halogens containing compounds and 10 miscellaneous analytes the results are in accordance with 8270 Method requirements, while RSD value does not exceed 1. The results for phenols look strange, as we were expecting lower values due to acidic nature of these compounds and low RF.

Thus the proposed method is definitely faster (more than 10 times), cheaper (100 times less reagents and simple glassware). Accurate mass measurements make the results more reliable than in EPA 8270

Method. Besides that all sample preparation may be carried on outside the laboratory in field conditions at sampling site. Besides, the method is safer for researchers since doesn't require any contact with large volumes of toxic organic solvents.

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INORGANIC NANOMATERIAL EFFECTS ON AQUATIC ORGANISMS

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Inorganic nanomaterials (NMs) are widely used in our daily lives, serving as pigments, antimicrobials, catalysts and a many other useful products. Even so, relatively little has been done to evaluate inorganic nanomaterial toxicity throughout the developmental life stages of vertebrates. This is in large part due to the low acute toxicity of many NMs. However, standard acute toxicity evaluations do not present a complete picture of toxic effects that may manifest from chronic toxicant exposure or exposures during specific critical life stages.

Limited effects were observed during acute aqueous exposures of *Xenopus laevis* to several individual NMs: CuO, Fe_2O_3, TiO_2 and ZnO. At environmentally relevant concentrations CuO and ZnO NMs produced developmental effects, while Fe_2O_3, TiO_2 NMs did not affect development or survival. Chronic studies were then initiated for approximately 6 weeks to evaluate the dose response of developing *Xenopus* exposed to aqueous CuO and ZnO NMs. Studies encompassed all developmental stages, from embryo throughout metamorphosis. Observed toxicities included, mortality, altered growth, malformations, and failure to complete metamorphosis. As has been noted with several toxicants, a sharp increase in toxicity is observed for CuO and ZnO NMs after 4 days of exposure. The magnitude of this increase is greater than with the respective divalent cations. Chronic effects indicate that these nanomaterials are more toxic than a similar concentration of their respective divalent cations. There were also marginal improvements in survival and growth at very low concentrations of ZnO and CuO NMs.

Additional studies were employed to evaluate the influence of salinity on silver nanomaterial (Ag NM) toxicity, Gulf killifish (*Fundulus grandis*) embryos over a 48 hours interval. After 24 hours of exposure, a V-shaped toxicity pattern was observed with a high mortality in 0 ‰ artificial seawater (ASW) followed by a strong decrease in mortality at 0.1 and 0.5 ‰ ASW. At higher salinities (10 – 20 ‰ ASW), toxicity returned to between 60-80% mortality. After 48 hours, toxicity increased strongly only at 0.1‰ (USEPA water). Cysteine is a natural ligand for Ag+ and decreases silver ion toxicity. Counter to the pattern observed for $AgNO_3$, low salinity cysteine containing solutions revealed no decrease in Ag NM toxicity after 24 or 48 hours. Cysteine treatment significantly decreased toxicity at higher salinities. NM dissolution combined with subsequent silver speciation seems to explain 24 h toxicity, but not additional toxicity at 48 h in low salinities. A lack of cysteine rescue at low salinities and the differences between 24 and 48 h toxicity support the hypothesis that citrate-capped Ag NMs demonstrate at least partially nano-specific toxicity.

In a third line of inquiry, nanomaterial exposures in stream mesocosms were used to mimic emissions from wastewater treatment facilities ("press"-type exposures) and accidental spills ("pulse"-type exposures). Mesocosms were treated with either 1) a one-time addition (pulse) of acetate-coated cerium dioxide (CeO_2) NMs or 2) a 25-day continuous exposure (press) containing the same total amount of CeO_2 NMs in pulsed exposure. Mesocosms were lined with unglazed ceramic tiles and stocked with fish, invertebrate, plant and microbial species. Results suggest rapid precipitation of CeO_2 NMs in the pulsed dose with higher concentrations persisting in the press-dosed stream. Five days after completion of NM dosing in press mesocosms (day 30 of experiment), aqueous concentrations of Ce had declined but were still higher than any Ce concentration measured in the pulse-dosed stream. Consequently, the concentration of Ce in periphyton was lower in the press-dosed stream on day 30 than in the pulse-dosed stream. The press dose allowed longer-range transport of CeO_2 NMs, such that concentrations of Ce in the lower reaches of the press-dosed stream were nearly double those observed for the pulse-dosed stream, likely because of a reduced aggregation relative to the pulse addition. These results suggest that exposure scenarios may play a significant role in determining the environmental fate, transport, and bioavailability of stable metal oxide NMs.

Data from these studies provide clear evidence that future research is needed to better explain behaviors of metal oxide NMs in the environment and potential detrimental and beneficial effects of across this class of NMs.

IRON-ORGANIC COMPLEXES PHOTOCHEMISTRY UNDER ATMOSPHERIC AQUEOUS PHASE CONDITIONS: FROM THE HYDROXYL RADICAL GENERATION UP TO THE FORMIC ACID TRANSFORMATION

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Iron represents one of the most important sources of hydroxyl radical ($^{\cdot}OH$) in clouds water, via dark (Fenton) and photochemical reactions (photo-Fenton). Strong organic complexing agents such as aminopolycarboxylic acids (APCAs) and siderophores (from bacteria) are naturally present in atmospheric aqueous phase and they can form complexes with iron modifying its speciation and photostability. In this work we used pyoverdine, a siderophore produced by bacteria isolated from cloud aqueous phase. Iron/siderophore complexes are expected to be present in atmospheric waters and their photoreactivity needs to be evaluated. Moreover it is well established that hydroxyl radical plays a significant role in cloud chemistry and on the oxidative capacity of the cloud aqueous phase. In a first step we have investigated the photoreactivity, of an iron-organic complex: Fe^{III}EDDS. EDDS (Ethylenediamine-*N*,*N'*-disuccinic acid) is an APCAs and can simulate the activity of naturally presents complexes. The photolysis quantum yield of Fe^{III}EDDS and the formation quantum yield of Fe^{II} were calculated under atmospheric relevant pHs. Fe^{II}, produced by Fe^{III}EDDS, can react with hydrogen peroxide increasing the hydroxyl radical steady-state concentration. The hydroxyl radical formation rate was measured for Fe^{III}EDDS/$h\nu$ and Fe^{III}EDDS/H_2O_2/$h\nu$ systems underlining the impact of such photochemical processes in the atmospheric aqueous phase. To evaluate the impact of such processes in real atmospheric conditions, the formic acid (one of the main carboxylic acids in the cloud water) transformation was also evaluated. Furthermore, we have studied the photochemistry and the impact on hydroxyl radical photogeneration of Fe^{III}-pyoverdine complex.

THE GEOCHEMISTRY, BIOAVAILABILITY AND TOXICITY OF THALLIUM IN THE AQUATIC ENVIRONMENT

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Thallium is a rare but highly toxic heavy metal that has been classified as a US EPA priority pollutant. Despite its toxicity, however, very little information exists on the environmental behaviour of Tl and, in particular, its mobilisation, distribution, impacts and fate in aquatic systems. This may, partly, be attributed to the relatively low economic value of the metal and, until recently, difficulty associated with its analysis at trace levels in natural samples. This presentation reports on measurements of Tl in the hydrosphere of south west England, performed by the latest generation of quadrupole ICP-MS. Specifically, concentrations of Tl in water, particulate matter, sediment and biota are given for fresh and brackish water environments. The results reveal that the principal sources of Tl to the region are from disturbed sulphidic metal deposits, where Tl occurs as discrete minerals or in conjunction with other minerals (e.g. chalcopyrite), and that concentrations are greatest (up to several ↘g L^{-1}) in systems affected by acid mine drainage. Since the principal species of the metal in aquatic systems (Tl^+) is a biogeochemical analogue of the potassium ion, interactions with sediment are relatively low. Moreover, chemical differences between Tl^+ and other, bivalent heavy metal ions means that conventional, industrial means of metal remediation (e.g. flocculation of hydroxides) are not applicable. The toxicity of Tl has been evaluated by determining its effect on the chlorophyll fluorescence quenching of the estuarine macroalga, *Ulva lactuca*. Toxicity is shown to be greater than equivalentconcentrations of Ag^+, widely regarded as the most toxic metal ion in brackish waters. It is suggested that Tl is able to pass through the cell membrane via Na-Cl-K porters but that K^+ itself has little impact in ameliorating the uptake and toxicity of Tl, at least in this alga. Implications for the monitoring and regulation of Tlin surface waters are discussed.

LINKING SURFACE-WATER PHOTOCHEMISTRY WITH CLIMATE CHANGE: A MODEL APPROACH

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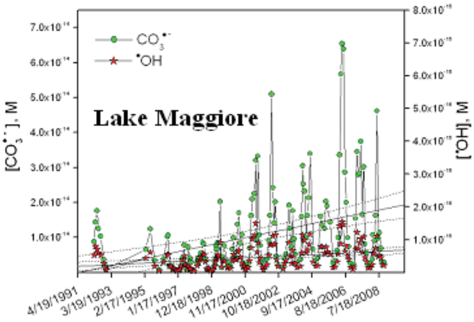
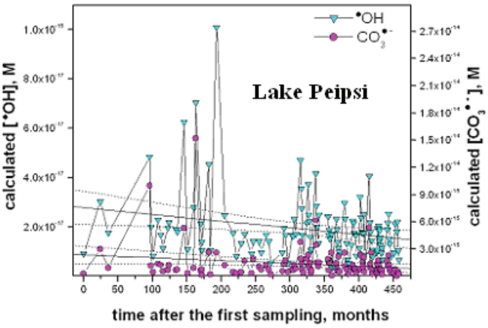
Photochemical processes in surface waters consist of direct photolysis, where pollutants are transformed upon absorption of sunlight, and indirect photochemistry. The latter is started by reactive transients ($^{\bullet}OH$, $CO_3^{-\bullet}$, $^1O_2$ and the triplet states of chromophoric dissolved organic matter, $^3CDOM^*$), produced by irradiation of nitrate, nitrite and CDOM [1]. Surface-water photochemistry is closely linked with irradiance, water chemistry and depth. The latter two parameters can be deeply affected by climate change [2], through enhanced solute leaching from soil (increasing the concentrations of ionic species and organic matter [3]) and because of water scarcity during the dry season, producing summer minima of the water depth [4]. However, the relationship between photochemistry and climate change was virtually unknown.

We have recently developed a model linking photochemistry with water parameters, validated by comparison with field data of pollutant photodegradation [5-7]. The model allows photochemistry to be linked with climate, notwithstanding the lack of long-term series of photochemical data. Sufficiently long time trends are fortunately available for photochemically relevant parameters: nitrate, nitrite, dissolved organic carbon (DOC), carbonate and bicarbonate, which enabled model application to Lake Maggiore (NW Italy) and Lake Peipsi (Estonia/Russia). The figure below reports as an example the time trends of the modelled [$^{\bullet}OH$] and [$CO_3^{-\bullet}$] for the two lakes. The significant increase of both transients for Lake Maggiore would be due to decreasing DOC (organic matter being a major scavenger of $^{\bullet}OH$ and $CO_3^{-\bullet}$), because of improving water quality from lower human impact, and to the climate-related increase of inorganic carbon (this only for [$CO_3^{-\bullet}$]). The opposite trend for Lake Peipsi is due to ongoing eutrophication caused by human activities and climate, despite the inorganic carbon increase. The consequence is an enhancement of the self-depollution potential of Lake Maggiore and a decrease of the same potential for Lake Peipsi.





Furthermore, model application to fluctuating water column depths in the dry season suggested that water loss by outflow would enhance reactions induced by $^{\bullet}OH$ and $CO_3^{-\bullet}$, while water evaporation with concentration of solutes would favour processes mediated by $^1O_2$ and $^3CDOM^*$.

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ENVIRONMENTAL AND CULTURAL HERITAGE

Do non-steroidal anti-inflammatory drugs effect the germination, development and growth of higher plants?

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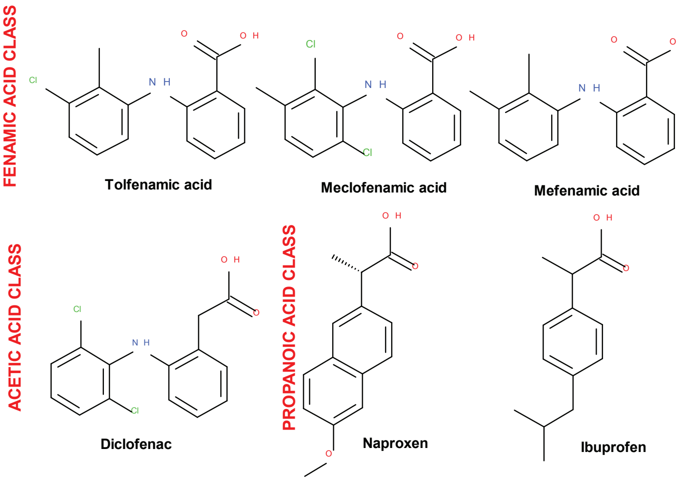
Recent years have seen a rising demand for pharmaceuticals, which is set to continue [1,2]. Consequently the presence of pharmaceuticals in the environment is now ubiquitous [3], which can have deleterious impacts upon organisms, and may enter the human food chain via various transport routes [4,5]. The recent inclusion of pharmaceuticals on a ‘watch list’ (Water Framework Directive) reflects growing concerns. One of the substances included in this legislation is from the non-steroidal anti-inflammatory drug (NSAID) class, which is one of the most importantly and heavily used medication groups worldwide [6].

Exploratory studies investigated the effects of NSAIDs on the germination, development and growth of higher plants, by exposing plants to six different but structurally related NSAIDs from the acetic acid (diclofenac), propanoic acid (naproxen, ibuprofen) and fenamic acid (meclofenamic acid, mefenamic acid and tolfenamic acid) classes (Figure 1).

The differential responses observed in different plant types to structurally related compounds indicate that elucidating the impact of pharmaceuticals upon plants is not straight forward. Utilising a group of structurally related NSAIDs allowed evaluation of the potential phytotoxicological roles of different chemical functional groups. Findings indicated that small structural differences resulted in widely differing effects on plants; ranging from enhancement to suppression of growth.

Figure 1: Chemical structures of select NSAIDs used in phytotoxicological assays



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INSECTICIDES ANALYZED AT THE NG/G LEVEL IN POLLEN, NECTAR AND IN BEES.

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Every year, a loss of about 30% of bee colonies occurs worldwide. This is called: Colony Collapse Disorder (CCD). The CCD affects deeply the survival of all pollinators, bumblebees, wild bees or honeybees. Where farming is intensive, new pesticides introduced in the mid-nineties are highly suspected to contribute to this disorder. Among them, nicotinoids and pyrazoles are systemic insecticides, often applied as seed-coating or for fruit-trees treatments. They have the highest toxicity so far known to bees.

To evaluate properly the risks in field's conditions, two main sets of data were required: the real exposure and the toxic effects. That is why analytical methods were built and validated to quantify these insecticides in pollen, nectar and bees, this at very low levels by using HPLC/MS/MS and GC/MS/MS. Limits of quantification are below 1 ng/g. As an application of these methods, fipronil (and its metabolites) were found in 49% of pollen samples (corn). Here, the mean level was established at 0.7 ng/g. Another example is given with thiamethoxam and its metabolite. They were found in 59% of pollen samples (corn and sunflower). Here the mean level was 0.6 ng/g. Measurements in dead bees, freshly collected, have permitted to detect such toxicants in their body.

Measurements indicate that these systemic insecticides were found below the acute LC50 values. Besides, toxicity of such insecticides was also measured in two steps: i) sublethal effects on bees after feeding with a contaminated syrup and, ii) mortality of bees after 10 days of repeated exposure by feeding. With a concentration identical to that found in fields, bees have stopped feeding after a 4 days. With concentrations even lower than that in fields, a significant mortality was induced after 10 days (+20 to 50%). Furthermore, synergies between these toxicants and pathogens (*nosema* species) have been demonstrated recently at low levels of toxicants. All these data permit a better understanding of CCD.

THREE CLASS OF RELEVANT PESTICIDES ANALYSED IN HONEY BY VERY SENSITIVE METHODS (LC/GC-MS-MS) AFTER A SINGLE QUECHERS-TYPE EXTRACTION.

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Honeybees play an essential role in pollination of plants. They are very sensitive to pesticides. They are also efficient bioindicators of agricultural pollution. New systemic pesticides are highly suspected to participate to the bee collapse worldwide, since a dozen years. Analytical methods are required to detect these relevant pesticides in hive products, with a high sensitivity (below the ng/g level).

We developed a single extraction process followed by two separation/detection methods depending on the pesticides of interest. This analytical protocol was tested with various types of honey (nectars and honey; mono-floral and multi-floral). These 2 methods were validated for 25 compounds belonging to 3 major classes of pesticides (nicotinoids, pyrethroids and pyrazoles).

The protocol started from 5g of honey. The best extraction was based on a QuEChERS EN 15662 method. Analyses were then performed by using GC-MS-MS for the pyrazoles and pyrethroids (2 µL injected), and by using LC-MS-MS for the nicotinoids (20 µL injected). Selectivity, linearity, reproducibility were statistically checked. Mean extraction yields were between 80% and 130%. The 2 methods were validated with a LOQ at 0.5 ng/g for the whole set of 25 pesticides.

These methods were used in routine to analyse honey sampled in France during 2 years, from 7 apiaries placed in diverse situations of agricultural impacts. Examples of results show that honey bees are exposed to several pesticides and that the duration of such exposure can be greater than several weeks.

ORGANIC SYNTHESIS IN GLYCEROL-BASED SOLVENTS

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In the past two decades a variety of green solvents have been proposed, including water, ionic liquids, fluorous solvents, and supercritical fluids. However, their implementation in industrial processes is still limited due to their tedious and non-sustainable synthesis, lack of experimental data and familiarity, as well as operational restrictions and high cost.

Several years ago we introduced glycerol, for the first time, as an alternative sustainable reaction medium in both catalytic and non-catalytic organic synthesis due to its renewable origin, beneficial physicochemical properties and reusability. Moreover, in many reactions, the presence of glycerol as a solvent has improved product yield and selectivity and enabled easy product separation and catalyst recycling. Furthermore, its high boiling point and polarity make glycerol the perfect candidate for non-conventional heating and mixing techniques such as ultrasound- and microwave-assisted reactions. Finally, glycerol has also been used simultaneously as both solvent and reactant in the catalytic transfer-hydrogenation of various unsaturated organic compounds and as acyl acceptor in the transesterification of ester and in the kinetic resolution of esters racemates.

However, despite glycerol's promise there are several drawbacks to its utilization that can be overcome by using of a glycerol-based family of solvents whose properties can be tuned and adjusted according to the requirement of each reaction and separation. It was found that glycerol-based solvents and their mixtures can be also successfully employed as green reaction mediums for various representative organic transformations. Both, reaction performance and product separation as well as catalyst recycling were found to be affected by the type and the polarity of the solvent in all reactions. It appeared that substrate solubility was the main determinant of reaction activity while the product solubility in the solvent determined the effectiveness of its extraction.

NEW APPROACHES FOR ELECTROPHORETIC DETERMINATION OF BIOLOGICALLY ACTIVE COMPOUNDS

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High-resolution separation technique such as capillary electrophoresis (CE) is very suitable for separating complex mixtures of natural objects. Our repot is focused on the development of new analytical approaches for electrophoretic determination of biologically active substances (neurotransmitters, antioxidants, such as polyphenols, proteins, steroid hormones) in natural objects with traditional capillary electrophoresis and developed microfluidic chip-analyzer using a combination of different variants of *on-line* preconcentration, modifiers the electrophoretic systems (ionic liquids, dendritic polymers, surfactants, cyclodextrins) and various preparation techniques of capillary columns on the basis of dendritic and methacrylate polymers.

The use of hypercrosslinked polystyrene as a sorption material in the preparation of biological samples (urine, blood serum) for analysis provided the decrease in detection limits for both hydrophobic and hydrophilic drugs. Application of water-soluble oligosaccharide derivatives hyperbranched polyethylenimin (PEI) as a covalent coating of silica fused capillary and combination of focusing principles of different variants *on-line* preconcentration (stacking with electrokinetic injection) for analysis of proteins resulted in a 1100-fold improvement in sensitivity.

Chemometric processing of the obtained characteristic profiles of biologically active analytes of blood serum and urine samples from healthy donors and patients with endocrine diseases proved to be informative as an additional diagnostic criteria. It was considered the possibility of chiral separation, including ligand exchange processes in electrophoretic conditions in combination with chiral agents.

This work was supported financially by grant of Russian foundation for basic research no. 11-03-91331-a.

WATER AND WASTE TREATMENT

REMOVAL OF TRACE ORGANIC CONTAMINANTS IN CONVENTIONAL AND MEMBRANES BIOREACTORS SYSTEMS

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The aim of this work is to study the efficiency of micropollutant elimination in raw hospital wastewater that comprises a complex matrix with micropollutant concentrations ranging from low ng/L to low mg/L and to evaluate the influence of filter balls suspended in AG-MBR system, on the removal of the pharmaceutics composes and its principal metabolites on microbial behaviour and compared it to that of SG-MBR.

Tow pilot-scale attached growth (AG) and suspended growth (SG) membrane bioreactors (MBRs) were installed and operated for 65 days. It was fed an influent directly from the hospital's sanitary collection system. LC/ MS-MS methods used to evaluated the concentration more of 40 pharmaceuticals (antibiotics, antiviral, anti-inflammatory, cytostatics, diuretics, beta blockers, anaesthetics, analgesics, antiepileptic, antidepressants, and others in addition of 11 metabolites. The MBR influent contained the majority of those target analysts. The micropollutant elimination efficiency was assessed through sampling of the MBR influent and sampling of the MBR effluent in the beginning and the finished of this experience.

Results showed that the performance of AG-MBR was demonstrated to be more stable than SG-MBR. A comparison between the two reactors was made for total and volatile suspended solids (TSS and VSS), COD and Nitrogen removal rates (Tableau 1and 2). This comparison was intended to check whether the attached growth treatment of effluent hospitalises could increasing performance the MBR in removal the organic pollutants and the micropolluants. Tramadol Sulfamétoxazole,Trimethoprim, Triclosan, metoprolol, Sotalol, Losartan, carboxy ibuprofen, 2-hydroxy ibuprofen , Epoxy carbamazepine , 4 androstène-3,17-dione, loméprol could be completed removed by AG-MBR, while any removal by SG-MBR was found for them. Nevertheless, no difference removal efficiency was found for Ketoprofen, Naproxen, Paracétamol, Ibuprofen, Caféine, Metronidazole, Pravastatin, Atenolol in both BRMs. This finding confirmed that the filter balls, with conditions this study, played a major role in increasing of efficiency the membrane bioreactor to arrive for ideal technology in treatment the hospital effluent and in lower cost.

Tableau 1: Stabilised COD, N and SS removal efficiencies for AG-MBR and SG-MBR

Efficiency of removal %	**TSS**	**VSS**	**CODt**	**CODs**	**Nt**	**Ns**
SG-MBR	93,57	87,82	80,45	71,63	78,00	85,36
AG-MBR	99,00	97,67	94,21	90,77	84,91	84,33

Tableau 2: Nutrient removal performances of the two AG and SG-MBR (fed with hospital effluents)

	[TSS] effluent (g/L)	Total NTK removal (%)	[NO_3-] effluent	[NH_4+] effluent
			(mg N/L)	(mg N/L)
AG-BRM	0.0018	84	10.58±0.3	20.2±0.3
SG-BRM	0.0119	78	17.8±0.9	8.3±0.4

FRACTIONATION AND LEACHING OF METALS FROM MINERAL SLUDGE PRODUCED FROM A METAL RECYCLING PLANT

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The presence of heavy metals in mineral-rich sludge, even at low concentrations, can cause detrimental effects on the ecosystem due to their accumulative behavior and phyto-toxicity effects. A prior quantification and assessment of the metal composition, their concentration levels, chemical form (speciation) and leaching properties will help practicing engineers to adopt suitable sludge treatment techniques and metal recovery approaches that will prevent further environmental damage. In this study, mineral sludge sample collected from a collection basin of a catalyst, metallic oxide and battery recycling plant (France) was tested, wherein Mo, Ni, Co, Cr and Zn leaching contents and yields were quantified. The collection basin sample showed pH value of 8.4 and organic matter contents of 8.5%. The total metal content results of the collection basin sample have been compared with the regulatory limits used to determine maximum allowable metal concentrations in industrial waste or sludge. With respect to sludge regulations, our sample exceeds allowable limits for Mo, Ni and Cr (with metal concentrations of 11.9, 17.5 and 11.2 mg/g, respectively), which suggests that the sample might present an environmental hazard if left untreated. On the other hand, zinc concentrations (7.2 mg/g) are on the border to exceed allowable limits, while cobalt concentrations (2.9 mg/g) do not surpass the regulatory limits. The results from sequential extractions indicated that, Mo is bound mainly to the oxidizable and residual fractions, while, Ni, Cr and Co were bound to the residual fraction and Zn to the soluble acid fraction. Anew, from statistical analysis, it was observed that, a strong correlation existed between Mo and Co, between Ni, Zn and Cr, respectively.

After determining mineral sludge characterization, sample leaching properties were examined. Different leaching reagents were tested under different operational parameters (type of leachant, solid–liquid ratio, leaching time and temperature), in order to test their leaching properties and appoint the leaching reagent with the highest metal leaching yields. The tested leaching reagents were different single acids (sulfuric, nitric, hydrochloric, citric, formic, acetic, ascorbic and oxalic), acid mixtures (aqua regia, nitric + sulfuric (1:1), nitric + sulfuric + hydrochloric (2:1:1)), then sodium carbonate, ammonium acetate, sodium hydroxide and hydroxylamine hydrochloride. After performing a set of different experiments, sulfuric acid (H_2SO_4) was found to be the leachant with the highest metal leaching potential for the mineral sludge studied. The optimal leaching conditions were found to be at temperature of 60°C, leaching time were of 2 h and S/L ratio of 0.25 g/L. Under these conditions, the first stage leaching recovery yields reached 32, 16, 58, 6 and 38 % for the target metals of Mo, Ni, Co, Cr and Zn, respectively.

Keywords: Mineral sludge, Metal recovery, Molybdenum, Sequential extraction, Chemical leaching.

REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTIONS BY NATURAL AND SYNTHETIC ZEOLITES

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Disposal of heavy metals, into the environment poses a great threat to our health. Waste-waters of metallurgical and galvanization plants, electronic industry and agriculture are mostly polluted with copper, manganese and iron cations.[1] We have studied the performance of natural zeolite clinoptiolite from Brus, deposit in Serbia, and synthetic zeolite 4A for the removal of Cu^{2+} , Mn^{2+} and Fe^{3+} species from the aqueus solution. By a detailed sorption study of Cu^{2+} , Mn^{2+} and Fe^{3+} cations from aqueous solutions on the natural and pretreated zeolite tuff we wanted to determine optimum sorption conditions and concentrations in waste-waters that can be after treatment disposed to river or municipal plant. The focus was on the influence of time, metals concentration and zeolite pre-treatment with Na^+ ions on sorption. We have also made a parallel study of sorption on synthetic zeolite 4A produced in Slovenia, Kidričevo by Silkem d.o.o. The efficiency of both zeolites for metal immobilisation was demonstrated for concentrations up to 5 mg of metal / 1 g of zeolite. Samples of both zeolites were structurally studied using X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), elemental analysis (EDX), and thermogravimetry (TG) analysis for zeolite tuff characterisation. The metals concentration in the solution after sorption was determined by atomic emission spectroscopy with inductively coupled plasma (ICP-AES). The results suggest that the studied zeolite tuff could successfully be used.

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PHOTODEGRADATION AND TOXICITY OF CIPROFLOXACIN USED IN AQUACULTURE

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As the depletion of wild fish stocks constantly increases and the demand for seafood increasingly rises, aquaculture production has rapidly developed over the past decade to address the shortages in capture fisheries. It is the fastest growing food-producing sector, accounting nowadays for about 50% of the food fish worldwide[1]. For the first time this year, the production of farmed fish has outstripped the one of farmed beef. However, intensive culture practices, with heavy input of formulated feeds or agrochemicals and deficient waste management, have negative impacts on local environments. For instance, up to 75% of the administrated antibiotics are lost in the surroundings of the fish farms, hence a special attention should be given to these chemicals. It is currently recognized that the improvement of the practices to protect water is essential for the sustainability of the aquaculture activities.

The INNOVAQUA[2] project is a network dedicated to the development of optimal environmental conditions, appropriate animal feeding and effective prevention of diseases in aquaculture. This investigation, being a part of this European project, focuses on i) the aqueous fate of antibiotics used in aquaculture and, ii) the development of photocatalytic water treatments adapted to the need of fish farming. The results presented deal with the fluoroquinolone antibiotic ciprofloxacin (CPF) dissolved in artificial freshwater (pH 7.3). In a first step, CPF solutions were exposed to simulated sunlight in a Suntest XLS+ apparatus. The obtained halflives ranged from 20 to 70 min for irradiation intensities of 750 and 250 W m^{-2}, respectively. Although CPF undergoes a relatively fast photolysis, no mineralisation and the formation of toxic by-products were observed. In a second step, the aqueous solutions of CPF were exposed to UV-A light (150 W m^{-2}; λ_{max}=355nm) and/or to TiO_2 thin films in a circular photoreactor. The presence of TiO_2 photocatalyst resulted in up to 10-fold enhancement of the removal of CPF. The complete elimination of CPF in less than 30 min and the abatement of 95% of initial TOC in 3h were achieved. The elimination of the initial and residual toxicity was observed by applying different toxicity tests (*Vibrio fischeri*, *Pseudokirchneriella subcapitata* and *Lepidium sativum*). As a result, photocatalysis with immobilized nano-TiO_2 provides a fast and efficient methodology for the removal of CPF and its toxic by-products from the water of the fish farms. Further studies will focus on the identification of the degradation products and the evaluation of their individual toxicity.

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DEVELOPMENT OF NETWORK FOR EDUCATION AND TRAINING OF PUBLIC ENVIRONMENTAL LABORATORIES WITHIN THE TEMPUS PROJECT NETREL

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In the countries of Western Balkan region, the surface water is often contaminated by different pollution sources (discharging of untreated municipal and industrial waste waters, leakage of liquid manure from cultivated fields, improperly designed septic tanks). In Serbia and Bosnia & Herzegovina like in the other Western Balkan countries, no systematic and detailed monitoring programme for the screening of river pollutants is performed. The major reasons for absence of monitoring programmes performed by the public laboratories are lack of accredited methods for environmental analysis, insufficient experience and skills and up-to-date knowledge in sampling, sample treatment and analytical methodology. Withnin the TEMPUS Project-Network for education and training for public environmental laboratories-NETREL, the catchment of the Danube and Sava/Vrbas River and its tributaries is of the particular interest as an important source of drinking water in Europe and, especially, Western Balkan region. An overall objective of NETREL is to establish a network of academics and other experts in Serbia and Bosnia & Herzegovina in the area of environmental monitoring of priority, hazardous priority and emerging substances.

NETREL project is based on a core-network of academic research institutes from EU countries (Slovak Republik, Czech Republik and United Kingdom) dealing with analytical chemistry, environmental sampling and monitoring and universities and public laboratories from Serbia and Bosnia & Herzegovina with experience in the environmental field. Within the Project, up-to-date knowledge gathered during development of EU environmental policies will be shared with academia experts from partner WBC and further be transferred to the staff of public laboratories. The proposed NETREL training programme is designed as a well-balanced mixture of different training elements - sampling, training in analytical methodologies, data handling and QA/QC. This main objective requires active cooperation between academia, public authorities and decision makers in WBC with possibility to open it to private companies and other stakeholders in the environmental sector. After the completion of the Project, already developed courses will be presented to major stakeholders, private laboratories, companies and others.

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INFLUENCE OF AERATION ONTO AS TRAPPING IN ZVI/ SAND REACTOR

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Arsenic toxicity and occurrence in the environment lead to the research of easy to handle and cheap water treatment process. Zero Valent Iron (ZVI) supports meet these requirements. ZVI trapping capacity is due to iron by-products, such as green rusts, lepidocrocite… According to physico-chemical conditions applied, the nature of by-products changes and arsenic trapping capacity is highly impacted. The aim of this work concerns the influence of aeration onto arsenic trapping in ZVI/sand columns.

Four up-flow reactors filled with a ZVI/sand mixture were fed with synthetic water spiked with As^{V}. Two columns were aerated by air diffusers placed at the bottom while the two others were not aerated. Arsenic concentrations were monitored for three months in order to characterize arsenic sorption capacity of both configurations.

A nearly complete removal was observed during the first five days into aerated system, whereas arsenic removal was stable, close to 50% during the first 20 days for the non aerated units. After this period an inversion of arsenic trapping capacity was observed, the non-aerated columns showed a higher arsenic removal than the aerated ones. Finally, when all columns reach their saturation, highest As trapping capacities were obtained in the non-aerated systems. According to arsenic monitoring, these retention capacities were estimated at 220 and 140 mg(As)/g(Fe) for non-aerated and aerated columns respectively.

Solid support samples were collected along the reactor and four different layers were distinguished. After acid mineralization, analysis of total arsenic highlighted different repartitions inside the reactors: a homogeneous concentration in the non-aerated systems and a decreasing concentration form inlet to outlet for the aerated pilot units.

In order to characterize As sorption into ZVI/sand columns, breakthrough curves were modelized using Thomas model. The determined K_{Th} constants were different for aerated and non-aerated columns, which confirmed that the affinity of arsenic for solid support was different in the two systems.

Oxygen measurement showed that synthetic water was close to saturation for aerated systems while it increased from 0.5 to 8 within 70 days in the non-aerated units. According to iron corrosion mechanisms, aeration induced a fast ZVI iron by-products generation, and thus a higher arsenic trapping capacity at the beginning of the experiment. Arsenic sorption into non-aerated reactors was lower but lasted longer, due to the regular ZVI-by-products generation. The lower trapping capacity of aerated systems could be due to a conversion over time of the early-created byproducts to less reactive forms.

ADSORPTION OF PHARMACEUTICALS ONTO ACTIVATED CARBON CLOTHS MODELING AND EXTRAPOLATION OF ADSORPTION ISOTHERMS TO LOW CONCENTRATIONS

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Nowadays, many authors have shown that waters are contaminated by micropollutants. Drugs concentrations can reach some µg/L in waste waters. After their ingestion, drugs are metabolized and rejected in waste waters and eventually in surface waters. In waste waters, Diclofenac, a nonsteroidal anti-inflammatory, is found at a level of 4 µg/L at the entry of waste water treatment plant. After treatments, the concentration is about 2 µg/L [1]. In surface waters, concentrations can reach 1 µg/L in some rivers [2].

The adsorption onto activated carbons is one of the most used techniques to remove pesticides and pharmaceuticals in these waters. Activated carbon clothes have many advantages in water treatment. Their specific surface and adsorption capacity are important [3]. At high concentration, large amounts of the targeted compounds were adsorbed (for a residual concentration of diclofenac of 1 mg/L, adsorption capacity is about 130 mg/g).

The adsorption capacity of the activated carbon is predicted from equilibrium sorption isotherms. Most if the isotherm studies are achieved at high concentrations (mg/L). However, experimental studies at low concentrations are more difficult and expensive. It could be interesting to be able to extrapolate results from high to low concentrations. This useful methodology allows an easy determination of adsorption capacity and does not require sophisticated analytical system and procedures. However, adsorption capacities determine could not be easily transposable to realistic conditions.

The aim of this study was to estimate the reliability of the usual adsorption isotherm models, (such as Freundlich, Langmuir, Langmuir-Freundlich, etc.) when the model is extrapolated from high (mg.L^{-1}) to low concentrations (ng.L^{-1}). Numerous error models were tested in combination with ten different isotherm models. These forecasts were compared considering their accuracy at low concentrations. The presence of natural organic matters in surface waters was also studied and although no impact was observed at high concentrations, the influence of the competition for the adsorption sites at low concentrations was significant.

PHOTOLYTIC AND PHOTOCATALYTIC DEGRADATION OF 3, 5, 6-TRICHLORO-2-PYRIDINOL IN AQUEOUS SOLUTION

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Synthetic pesticides have been used for more than six decades and their consumption increases constantly. A lot of information is available on the stability and fate of parent pesticides and not so many on their transformation products. In this study we focused on 3,5,6-trichloro-2-pyridinol (TCP) a degradation product of organophosphorus insecticide chlorpyrifos. Photolytic and TiO_2 photocatalytic degradation processes under different simulated sunlight conditions were evaluated in terms of disappearance rate, mineralisation rate and identification of degradation products.

The efficient photodegradation of TCP was first studied by using monochromatic light at 300 nm and 334 nm. The disappearance quantum yield was evaluated to 0.070 in aerated conditions and was found to slightly higher in oxygen free solution (0.090) demonstrating a partial inhibition effect of molecular oxygen. Under our experimental conditions, the total disappearance of TCP was observed within 120 minutes irradiation time. From the analytical point of view, LC/MS studies revealed the formation of various byproducts mainly arising from chlorine substitution by hydroxyl groups. We clearly showed that the concentration of chloride increased with irradiation time demonstrating the almost total substitution process.

TiO_2 photocatalytic experiments were performed for 120 min in photoreactor equipped with polychromatic low-pressure mercury lamps (365 nm) and immobilised TiO_2 glass slides fastened around the spinning basket inside the cell. TCP aqueous solution was irradiated for fixed periods of time and analysed with HPLC-DAD, LC-MS, UV-Vis spectrophotometer, TOC analyser, and ion chromatography. The photocatalytic degradation of the TCP aqueous solution with immobilised TiO_2 after 120 min resulted in first-order degradation reaction. The observed rate constant was $k = 0.024 \pm 0.001$ min^{-1} with a half-life time of $t_{½} = 28.5 \pm 1.3$ min^{-1} and the concentration of TCP after 120 min reached 4.5 ± 0.6 % of the initial concentration. The TOC measurements revealed high mineralisation rate, i.e. 53.6 ± 1.9 % and the ion chromatography measurements showed almost quantitative transformation of chlorine into chloride. Additionally, the UV-Vis spectra indicated a transformation of TCP into other compounds, which were later proposed by the LC/MS analyses.

On the basis of gathered data, we can assume that TCP acts like photosensitive chemical, which rapidly transforms into several other compounds, depending on the light source used.

POSTER SESSION 1

CHEMISTRY OF WATER SOIL

C101

DIFFUSIVE SAMPLING OF NITROGEN DIOXIDE IN AMBIENT AIR

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Diffusive sampling has been used so far quite extensively to estimate average concentrations of nitrogen dioxide. It is simple and cost-effective method for large scale monitoring to characterize the spatial distribution of NO_2 concentrations. In this study we aim to present the use of diffusive sampling to estimate traffic-related NO_2 concentrations. During the period from 20 February 2013 to 4 March 2013, a total of 30 diffusive tubes were exposed in different positions along and perpendicularly on each side of the Kavaja Street in Tirana, which has two sided building facades. Collected samples were analyzed by Saltzman method using a spectrophotometer at 540 nm.

Key words: diffusive sampling, nitrogen dioxide concentrations, vehicle emissions

MONITORING OF AMBIENT AIR IN NOVI SAD – LEVELS OF BENZENE, TOLUENE, ETHYLBENZENE AND XYLENES

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Volatile aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes (BTEX), may significantly affect ambient air quality if present in elevated concentrations. The main source of BTEX in urban areas is traffic. Benzene is listed in the IARC Group 1 as human carcinogen. City of Novi Sad has established air monitoring network, with BTEX compounds included.

Four sites monitored in 2012 were charasterized as following: A and C – urban background, B – industrial, D – urban traffic. Samples were collected during 24 hours, on the same ten consecutive days of a month on all monitoring sites. Concentrations of BTEX were determined by gas chromatography mass spectrometry after solvent desorption from charchoal sorbent tubes, as described by reference method EN 14662-2. Temporal and spatial distribution of benzene are illustrated on Figure 1 (A), as comparison of mean monthly concentrations over calendar year and between four monitoring sites, respectively. Annual average concentrations of BTEX for all four monitoring sites are presented on Figure 1 (B).

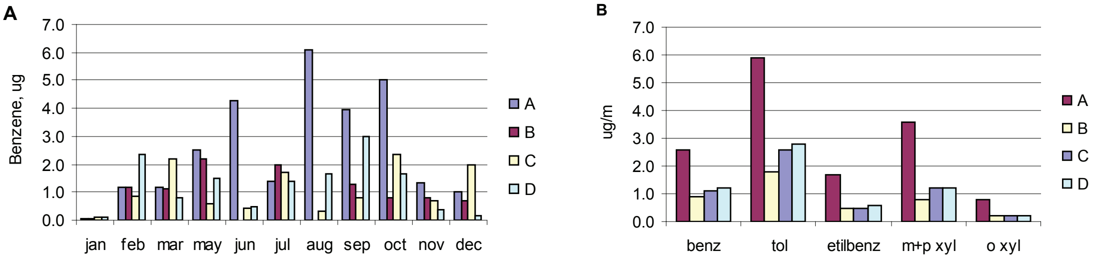

Figure 1. (A)- Monthly average concentrations of benzene (ug/m^3); (B)- Annual average concentrations of BTEX (ug/m^3) (sites A, B, C and D, in 2012)

Monthly averages of both benzene and toluene showed highest values during summer season when monitoring sites A and B were investigated, while on sites C and D there was no obvious temporal trend. Analysis of spatial distribution showed that site A was characterized with highest BTEX levels. Regarding annual averages, highest value of each of BTEX compounds was registered on site A, followed by site D. Importantly, level of benzene did not exceed limit value of 5ug/m^3 for calendar year (Directive 2008/50/EC). It should be noted that recorded levels of BTX were generally higher in comparison with monitoring data from 2011.

In conclusion, 2012 annual average level of benzene in ambient air of Novi Sad was below the lower assessment threshold (2ug/m^3) on monitoring sites B, C and D, while on site A this level was above the lower but below the upper assessment treshold (3.5ug/m^3). In order to gather data for assessment of human health risk, monitoring of BTEX compounds in ambient air has to be continued.

QUALITY EVALUATION OF SOILS AND SEDIMENTS IN ZETA PLANE USING DANIO RERIO EMBRIO TOXICITY TEST.

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This study was conducted in 2013 as part of the national project that deals with possible applications of bioassays to test cause-effect relationship between environmental pollutants and the level of toxicity of soil in the case of the Zeta plain and sediments of Lake Skadar.

This area is of great importance for food production and is located close to the capital city Podgorica. A large part of the fruits and vegetables grown in this valley ends at the green markets of the city.

However Zeta plain, Moraca river (main tributary of Lake Skadar) and Skadar Lake are strongly influenced by the factors of pollution originating from the Aluminum Plant (KAP) and the pools of red sludge, municipal Wastewaters of the City Podgorica and sometimes quantitative improperly used pesticides in agriculture.

Moreower, this area is often flooded having a significant impact on the transfer of pollutants.

The aim of this study was to assess the sensitivity of Danio rerio embryo toxicity test on organic pollution and compare the sensitivity of the tests that have been applied earlier, such as Ames, Bioluminescence and DR-LUC bioassays.

Eight soil and two sediment samples were taken at different distances downwind from the KAP. Potential organic contaminants were extracted from freeze-dried soil and sediments samples by soxterm extraction with organic solvents. The extracts were transferred to DMSO, a solvent compatible with the bioassays and applied in diferent concetrations in test system..

Sensitivity was measured by comparing the level of mortality of embryos Danio rerio LC50 after 24, 48 and 72 hours, with the level of pollutants measured by chemical analytical methods. Tipe of taratogenic efects (malformations of embryo) were also recorded in subletal concentrations of samples.

Danio rerio embryo toxicity test showed significant sensitivity to organic pollution in the sampling points near the aluminum plant, where are land parcels with cultivated vegetables and showed good correlation with measured levels of PAHs, which have been above and below the allowable values mostly dependent on the distance from KAP.

MICROFLUIDIC FIA COUPLED WITH THERMAL LENS MICROSCOPY FOR RAPID DETECTION OF POLLUTANTS BY COLORIMETRIC REACTIONS

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Thermal lens microscope (TLM) is one of recent promising developments of thermal lens spectrometry (TLS) towards miniaturization. Advantages of TLM, such as high sensitivity, high temporal (~ ms) and spatial resolution (~ µm), enable fast and small-volume detection of a variety of compounds when it is coupled to lab-on-chip chemistry. In microfluidic chips, the microchannels provide short diffusion distances and large specific interface areas, contributing to considerable reduction of analysis time. This was however not yet exploited for rapid determination of analytes in microfluidic flow injection analysis (µFIA) mode.

A new µFIA-TLM system was developed in laboratory for detection of on-line generated colored compounds. Compared to conventional FIA-TLS, 100 times lower sample/reagent consumption and 10 times shorter analysis time for one sample injection were obtained in this system. As an example, hexavalent chromium [Cr(VI)] in aqueous solution was detected following the colorimetric reaction with diphenylcarbazide (DPC). Analytical signals for twelve sample injections in one minute (Fig. 1) were recorded on this setup. Besides, the influence of the excitation power density and flow rate on the photodegradation of the analyte was investigated. It was found that for about 4000 absorbed photons by a single Cr-DPC complex, the Cr-DPC complex is slightly photodegraded. For high power excitations, increasing the flow rate (e.g. from 20 to 50 µL/min) can alleviate photodegradation of the complex to some extent (about 10%). Limits of detection corresponding to an absorbance of 9×10^{-6} AU were achieved in a 50-µm deep microchannel at excitation power of 60 mW. The presented µFIA-TLM setup offers possibilities for high throughput detection of pollutants in micro space.

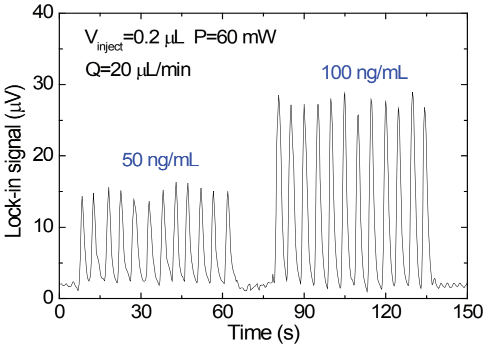

Fig. 1. µFIA-TLM signals of Cr-DPC complex for twelve consecutive injections of Cr (VI) standard solutions at 50 and 100 ng/mL. The detection position is 6 cm away from the microchannel junction.

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THE TRANSLOCATION ABILITY OF METALS THROUGH ORGANS OF MACROPHYTES

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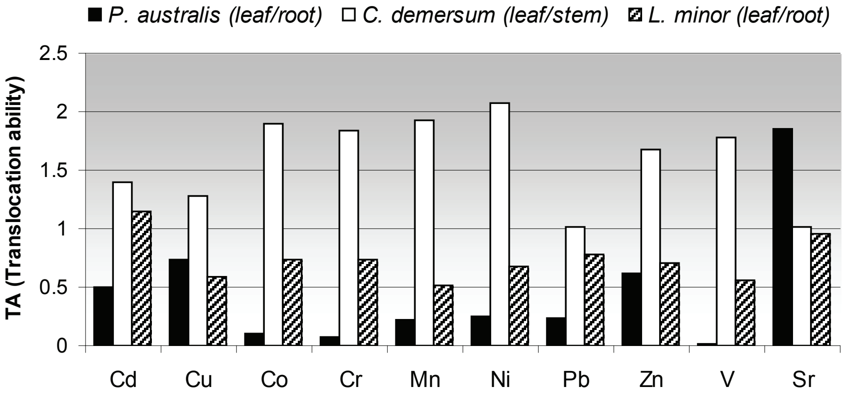
Aquatic macrophytes differ both in their capacity to take up metals in root tissues and in the proportion of metals transferred to above-ground parts. A variety of trace metals translocation from roots to shoots depending with plant species, high levels of element in the sediment, location and testing season [1].

The possibility of plants to transport metals from the roots (stems) to the above-ground organs (leaf) was estimated using the translocation ability (TA). The value of the translocation ability was calculated [2] as the ratio of the concentrations of metals in leaves and a part of the plant (root or stem for rootless macrophytes): $TA = [Metal]_{leaf}/[Metal]_{part\ of\ the\ plant}$. A higher TA means a higher translocation ability.

In this study, the translocation ability of heavy metals (Cd, Cu, Co, Cr, Mn, Ni, Pb, Zn, Sr and V) in different organs in macrophytes plants: *Phragmites australis* (emergent), *Ceratophyllum demersum* (rootless submerged) and *Lemna minor* (free-floating) were investigated. Plants were collected from six sites locality of Skadar Lake, Montenegro, during the different seasons of the year 2011.

The concentrations of heavy metals were determined using the ICP-OES technique on a Spectro Arcos instrument. The analytical accuracy was determined using certified reference materials for plants, Tea Leaves (INCT-TL-1). The recoveries were within 10 % of the certified values.

Mobility tested metals through tissues of macrophytes following descending order: *C. demersum* > *L. minor* > *P. australis* except for Cu (*C. demersum* > *P. australis* > *L. minor*) and Sr (*P. australis* > *C. demersum* > *L. minor*). A higher ratio of leaf / root or leaf / stem might be an expected of submerged and free floating macrophytes in relation to emergent macrophytes. Metals are present in the leaf next to the translocation from stem or roots, and due to the accumulation from water. The highest mobility in all three macrophytes showed Sr and the lowest Pb.



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MICROBIOLOGICAL AND CHEMICAL PROPERTIES OF MEAT PROCESSING INDSTRY WASTEWATER

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Meat processing and abattoir operations produce highly organic, highly nitrogenous, biologically degradable waste water which is directly discharged without any treatment into sewer. This large amount of wastewater could be reused after adequate treatment for irrigation, fish farming or other purposes, otherwise meat indstry wastewater could cause pollution of surface receiving water.

The aim of this study was to determine physical, chemical and microbiological characteristics of the wastewater discharged from meat processing industry in order to get deeper insight into meat industry wastewater pollution and to suggest possible treatment methods allowing water reuse. In two sampling campaigns, in spring and summer period in 2013, wastewater was collected from four meat processing plants in the Province of Vojvodina, Republic of Serbia.

The pH values were measured in range from 7.09 to 10.03. An average COD and BOD concentrations in spring sampling campaign were 1994 mg/L (range: 1380 - 3460 mg/L) and 1524 mg/L (range: 876 - 2620 mg/L), while in summer sampling campaign values for two meat processing plants were much higher indicating higher average values of 6065 mg/L (range: 840 – 14160 mg/L) and 3470 (range: 610 – 6960 mg/L), respectively. Electrical conductivity was measured in similar ranges in both sampling campaigns; the variations were observed between the large scale and the small scale meat industry plants and were measured from 1024 to 3910 µS/cm. Ammonium ion concentrations also varied greatly and in two meat processing plants were above the limit value of 10 mg/L according to Regulations of the Republic of Serbia, No. 67/2011 and 48/2012.

Microbiological and biochemical analysis included monitoring of seven parameters: number of aerobic mesophile bacteria, total coliforms, faecal coliforms, *E. coli* and faecal streptococci, presence of *Salmonella sp*. as well as determining the phoshatase activity index which is used as a biochemical indicator of heterotrophic activity of aquatic microorganisms. All monitored parameters varied in a very wide range, and most often none of them met the criteria prescribed by Regulations of the Republic of Serbia, No. 67/2011 and 48/2012. In many cases, counts were above $1x10^6$ CFU/ml.

None of the studied samples, except sample 4, is treated before being discharged to receiving waters. Samples 3 and 4 are inlet and outlet water from the same monitored site, and their analysis showed a significant decline in the value of all monitored microbiological parameters. Decrease in parameter values was from 98.69 to 99.99% in the spring campaign, and from 97.86 to 99.99% in the summer campaign. Presented results indicated high biological and chemical pollution effect of meat processing industry wastewater especially for the large scale meat industry plants where wastewater should be pre-treated before its discharge in the sewer.

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BENZENE IN MOTOR VEHICLE EXHAUST

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Motor vehicle exhaust is a complex mixture, the composition of which depends on the fuel, type and operating condition of the engine, and the use of any emission control device. Pollutants and their metabolites can cause adverse health effects by interacting with, and impairing, molecules crucial to the biochemical or physiological processes of the human body. Three factors condition the risk of toxic injury from these substances: their chemical and physical properties, the dose of the material that reaches critical tissue sites, and the responsiveness of these sites to the substance.

Benzene is a constituent of crude oil, and in Europe is present in petrol in a proportion of around 5%, occasionally up to 16%, while in the U.S.A. the benzene of gasoline does not exceed 1.5 to 2%. The major source of benzene is emissions from motor vehicles and evaporation losses during handling, distribution and storage. Benzene concentration in ambient air of residential areas generally ranges from 3-30 $\mu g/m^3$ (0.001-0.01 ppm) depending on the traffic. Due to its high liposolubility, benzene is distributed mainly to the fat rich tissues such as adipose tissue and bone marrow.

This paper presents the results of research in the field of benzene concentration in the exhaust gases of spark ignition engine at different operating conditions. Aim of the paper is to obtain a clearer insight into the impact of different engine working parameters on the concentration of benzene. Experimental investigation was performed on SCHENCK 230W test stand with the controlled SI engine. Benzene have been sampled directly at tailpipe and analyzed in exhaust air samples by Perkin Elmer Photovac Voyager-mobile GC. For this article was examined impact of air-fuel ratio, speed, load and fuel on concentration of benzene. For engine load of 10% benzene concentrations were in range from 10.1 to 41.4 ppm, 10.9 to 47 ppm, 12.1 to 49.9 ppm and 14.2 to 56.9 ppm for 2000, 2500, 3000 and 3500 rpm of experimental engine, respectively.
The analysis showed that there was a close correlation between benzene emission and air-fuel ratio. Furthermore, the correlation became more significant when using ordinary unleaded fuel, also results showed a

very close relation of benzene concentration and engine speed, load and quality of unleaded fuel.

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ETHYLCELLULOSE AND LIGNIN AS BEARER POLYMERS IN CONTROLLED RELEASE FORMULATIONS TO REDUCE LEACHING OF METRIBUZIN IN A CALCAREOUS SOIL

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The leaching of herbicides through soil can be minimized using controlled release formulations (CRFs). In this research, polymeric materials like ethylcellulose and lignin have been used to improve the application of the herbicide metribuzin. The lignin-based formulations prepared were coated in a Wurster-type fluidized-bed equipment using ethylcellulose and dibutylsebacate. These CRFs have been evaluated in water and soil.

Metribuzin has been successfully trapped, with encapsulation efficiency (EE) higher than 85 % in all cases. FT-IR and DSC studies indicate the compatibility between polymers and metribuzin in lignin based CRFs. SEM studies show a homogeneous film in ethylcellulose coated CRFs. Using experimental equations, the time taken for 50% of the active ingredient to be released into water (T_{50}) was calculated. From the analysis of the T_{50} values, it can be deduced that the release rate of metribuzin can be controlled by changing the thickness of the coating film and modifying its surface properties adding a plasticizer for ethylcellulose coated CRFs. Mobility experiments carried out in a calcareous soil have shown that the use of CRFs reduces the presence of the herbicide metribuzin in the leachate compared to the technical and commercial products of metribuzin.

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OCCURANCE OF SELECTED PHARMACEUTICALS IN MUNICIPIAL WASTEWATER FROM CITY OF NOVI SAD

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In Europe, around 4,000 different pharmaceutical active compounds, used as human and veterinary drugs, are susceptible to reach every environmental medium [1]. Since most of the pharmaceutical residues and metabolites are not completely removed during conventional wastewater treatment [2], especially in the Republic of Serbia where only 15% of wastewater is treated [3], significant amount of compounds belonging to this group reaches the surface water. In Serbia, wastewaters are mainly mixed type and include domestic and industrial effluents, as well as runoff [4]. Due to the rather poor wastewater management practice, with less than 5% of all being biologically treated, most of the contaminants present in wastewaters may represent a significant environmental concern [4]. This fact is crucial, and represents the basis for one of the first attempts to identify and determine concentration levels of selected pharmaceuticals in municipal wastewater from the city of Novi Sad. The sampling site was municipal wastewater discharge GC2. This site was selected as representative, due to the fact that the city of Novi Sad has three clinical Centres connected to the sewerage system and, discharging wastewater without any treatment. On the field site 24h composite sample was taken and flow in the collector of wastewater was simultaneously measured. A total number of the 20 pharmaceuticals were analysed using the method of liquid chromatography coupled with tandem mass spectrometry (HPLC-MS^2). The results of analysis have showed the presence of 9 pharmaceuticals (Trimethoprim, Sulfamethoxazole, Erythromycin, Carbamazepine, Metamizole metabolites 4 AAA and 4 FAA, Enalapril, Atrovastatin, Metoprolol, Bisoprolol) at significant concentrations. The results confirmed a widespread occurrence of selected pharmaceuticals in municipal wastewaters of the Novi Sad city.

This research was supported by the Ministry of Science and Technological Development of the Republic of Serbia (project TR 37014 and project III 46009).

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PERSISTENCE AND DISSIPATION BEHAVIOR OF DICAMBA AND BENTAZON HERBICIDES IN WATER UNDER LABORATORY CONDITIONS

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The characteristics of water used in a spray mix influence the effectiveness of pesticides. It is important to know the pH of water used with a pesticide and the susceptibility of the pesticide to hydrolysis. In order to investigate the persistence, dissipation and degradation kinetics of bentazone and dicamba, laboratory study was conducted in deionized water (pH 7.0) at 25±2ºC (T1) and 4±2ºC (T2). Herbicides were dissolved at rate of 0.05 mg/ml. Concentration of analytes was monitoried 0 (1 h), 2, 4, 7, 10, 14, 18, 24 and 28 days after treatment and analysing as triplicate samples. Samples were analyzed by high pressure liquid chromatography (HPLC/DAD). The chromatographic separation was carried out with Zorbax Eclipse XDB-C_{18} (50 mm × 4.6 mm × 1.8 µm) analytical column, using reverse phase column with gradient conditions of mobile phase consist of water (with 0.05% H_3PO_4) and acetonitrile. In T1 the dissipation were 1.3, 5.1, 7.5, 7.9, 8.1, 15.3, 24.1, 26.9% for dicamba and 11.5, 33.3, 44.6, 46.9,48.8, 49.6, 50.1, 51.8% for bentazone in 2, 4, 7, 10, 14, 18, 24, and 28 days. Corresponding dissipation in T2 experiment were 2.0, 2.7, 3.9, 5.0, 6.1, 6.9, 6.8, 8.0% for dicamba and 7.7, 15.2, 26.7, 29.4, 30.3, 30.6, 31.4, 31.9% for bentazone, respectively. The dissipation data in water showed the DT_{50} and DT_{90} values 57.3 and 114.9 days for dicamba and 17.1 and 125.9 days for bentazone herbicide. Several simulation models were used to evaluate the experimental data, such as Exponential and Mittag-Leffler function. The dissipation of analized herbicides residues over the time in water were described by the Mittag-Leffler function, with the best-fit model for dicamba and bentazone [1]. The dissipation of dicamba and bentazone residues on 25±2ºC and 4±2ºC over the time in deinoized water were described by function a*Eα,β (-bt). Coefficients a, b, α, β were obtained from the experimental data by using fitting procedure. We got for dicamba and bentazone herbicides on 25±2ºC coefficients α=0.8, β=3.71, a=159.11, b=12.79 and α=2.17, β=4.56, a=1387.45, b=1.96 for 4±2 ºC α=0.8, β=4.11, a=82.53, b=7.0 and α=0.99, β=3.15, a=205.81, b=0.117, respectively. The hydrolysis study indicated that the dicamba and bentazone pesticides hydrolysed faster at 25±2°C. These findings can be useful in the prediction of the dissipation behavior of this pesticides in the spray tank immediately before application. The dissipation rates of dicamba and bentazone pesticides depended on the temperature and pH of water to be used.

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TOXICITY EVALUATION OF SOIL SAMPLED IN THE VICINITY OF AN ALUMINUM SMELTER IN MONTENEGRO USING THE AMES, BIOLUMINESCENCE AND DR-LUC BIOASSAYS

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Keywords: Soil, pollution, toxicity, bioassay, Ames, Bioluminescence, DR-LUC

The purpose of this study was to test the general toxicity and genotoxicity of soil in an area where emissions may be expected of various environmental contaminants (e.g. PAHs, dioxins, PCBs, heavy metals, perfluorinated chemicals, pesticides, etc.), including some that could be genotoxic (e.g PAHs and some metals). Six soil samples were taken from the Zeta Plain in Montenegro at different distances downwind from the KAP aluminum smelter (n=5) and one upwind from the industrial site. Potential organic contaminants were extracted from freeze-dried soil samples by pressurized liquid extraction (PLE) with organic solvents. The extracts were transferred to DMSO, a solvent compatible with the bioassays. Genotoxicity induced by the soil extracts was measured with the Ames assay in two strains of *Salmonella typhimurium* (TA98 and TA100). In order to evaluate the toxic effect of soil extracts two additional bioassays were performed on cells with vastly different taxonomies: a bioluminescence assay on prokaryotic cells of *Vibrio fischeri* for general toxicity and the DR-LUC assay using eukaryotic, rat hematoma cells for dioxin-like toxicity. In addition to PLE extracts, bioavailable metals extracted from soils with $CaCl_2$ were tested for toxicity in the bioluminescence assay. Both bacterial strains in Ames test reacted to toxicants in the soil extracts and particularly TA98 (specific for frameshift mutations) showed high levels of mutagenicity in all samples compared to controls. The bioluminescence assay showed no toxic activity in any of the soil extracts including extracts of the bioavailable metal fraction. DR-LUC, on the other hand, indicated the presence of dioxin-like activity in cells exposed to PLE soil extracts even after purification of non-stable compounds from the raw extract (results indicated between 50 and 5000 pg DR-LUC TEQ/g dry weight of soil was present in the six samples). Since toxic and genotoxic effects of the soil samples were recorded in this study we suggest further chemical analytical work on the samples to provide additional information on potential toxic agents in Zeta Plain soil and provide insight into other tests that could be performed.

USE OF BIOSORBENTS IN CONTROLLED-RELEASE FORMULATIONS OF THE BOTANICAL INSECTICIDE AZADIRACHTIN

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The interest for biopesticides as crop protection-agents has increased in the last decades not only due to their low environmental impact and their low toxicity in mammal, but also due to the increasing resistance that show the pests by the synthetic pesticides. The Neem seed oil (Azadirachtin), is a natural plant-derived substance which possess a high insecticide capacity, quick action, low residual power, and they are practically no toxic. Nevertheless, they suffer environmental degradation quickly, which limits their use in agriculture. Controlled release formulations (CRFs) can be used to facilitate a gradual and controlled discharge of the azadirachtin, providing a higher stability and therefore improving its effectiveness.

In this research the botanical insecticide azadirachtin was incorporated in alginate-based granules to obtain CR properties. The basic formulation [sodium alginate (1.47%) – azadirachtin (0.28%) – water] was modified by the addition of biosorbents. The effect on azadirachtin release rate caused by the incorporation of lignin, humic acid and olive pomace in alginate formulation was studied by immersion of the granules in water under static conditions. The time taken for 50% of the active ingredient to be released into water, T_{50}, was calculated for the comparison of the formulations. The lowest value of T_{50} corresponds to the azadirachtin-alginate formulation, which means that this CRF produces the fastest azadirachtin release in water. The addition of the biosorbents to the basic alginate formulation reduces the rate of release, being the lignin-based formulation that produces a slower release. Taking into account the variation shown for T_{50} values by the different formulations prepared, this study might be useful for selecting the most appropriate formulation, depending on the environmental factors that affect azadirachtin use in agronomic practices.

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CONTRIBUTION OF AQUEOUS AND DIETARY EXPOSURES IN BIOACCUMULATION OF LEAD (Pb) IN THE AMPHIPOD *GAMMARUS PULEX* AND MULTI-PATHWAY MODELING

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Because of their important roles in the functioning of aquatic ecosystems, their wide distribution in Europe and their resistance to metals, the invertebrates of the genus *Gammarus* are candidates commonly used as tools for biomonitoring of the bioavailable fraction of metals in freshwaters [1]. However, the interpretation of bioaccumulation data depends on the knowledge of the behavior of these organisms against contamination: what exposure route? what ability to regulate the contaminant according to the exposure route? Aquatic bioaccumulation studies have long focused on the uptake of metals freely dissolved in water that accumulate in organisms through direct contact [2]. However, the contamination of animals can also be due to the ingestion of contaminated particles. To date, the importance of this exposure route in the contamination of gammarids remains to be assessed, especially in the case of metals known to bind to organic matter including food resources, such as Pb.

This study aims at characterizing different uptake routes of Pb in *Gammarus pulex* and modeling the processes involved in its bioaccumulation.

Leaves of hornbeam or poplar were enclosed in netting (150 µm-pore nylon) and immersed in aquatic microcosms contaminated by Pb at environmental concentrations (0.5 à 10 µg/L) until reaching the equilibrium of metal exchanges between the encaging systems of leaves and exposure media. To distinguish the aqueous and dietary uptakes, gammarids were introduced in the contaminated microcosms for a week with the encaging systems, remained intact or opened. In the last case, the organisms thus fed the contaminated leaves. Finally, gammarids were transferred in uncontaminated microcosms to assess their ability to eliminate Pb according to the exposure route.

Results show that water was the dominant exposure route of gammarids to Pb. Nevertheless, we determined significant contributions of dietary route in the contamination of animals, which depended on the type of food, i.e. 21% for hornbeam and 37% for poplar. Ingestion rates of leaves by animals increased with exposure levels, suggesting that gammarids need a surplus of metabolic energy to meet to metal stress. Determining aqueous and dietary uptake and elimination constants allowed the construction of a model integrating the two exposure routes to describe Pb bioaccumulation in *G. pulex*. Further studies will aims at assessing the prediction of this multipathway bioaccumulation model from in situ data.

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OPTIMIZATION OF METHODS FOR DETERMINATION OF ORGANOTIN COMPOUNDS AND FOR EVALUATION OF THEIR ECOTOXICITY

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Abstract

Organotin compounds are a group of environmental contaminants which enters the environment exclusively as the result of anthropogenic activities. In industrial and commercial applications tin in these compounds is most often substituted with methyl-, butyl-, octyl-, cyclohexyl- or phenyl- groups with number of substituents ranging from 1 to 4. Tetrasubstituted compounds are mainly used for the industrial production of lower-substituted compound; trisubstituted organotins are contained in pesticide formulations, fertilizers, wood preservatives and special paints; disubstituted compounds serve as stabilizers in production of PVC and for the treatment of glass. Many of these compounds exhibit neurotoxic, immunotoxic and mutagenic effects [1,2].

The most widely used separation technique for the determination of organotin compounds is gas chromatography (GC) due to its high separation efficiency and the possibility of using different types of detectors. Usually, organotins are extracted from the sample and subsequently derivatized in order to improve volatility. Flame photometric detector (FPD), atomic emission detector (AED) and mass spectrometer are most suitable for their detection [3].

For the evaluation of ecotoxicological effects of the organotin compounds the following aquatic organisms seem to be the most suitable: crustaceans *Thamnocephalus platyurus* and *Daphnia magna* from the group of aquatic invertebrates, *Lemna minor* (Duckweed lesser) from the group of monocotyledonus plants. A set of alternative tests Thamnotoxkit F™ and Daphtoxkit F™ could be also used as an alternative.

Acknowledgment

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INVESTIGATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN TISSUES OF FISH FROM THE TISZA RIVER (SERBIA)

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Polycyclic aromatic hydrocarbons (PAHs) in tissues of fish from the Tisza River in Serbia were investigated, since it was found that oil pollution is present in the sediments of Tisza River.[1] Samples of fish were taken during September 2010 from the local fishermen.

The fish samples were immediately and individually frozen in plastic bags containing river water until permanent storage and further processing. Afterwards, the specimens were dissected, appropriately labeled and frozen until analysis. Presence of PAHs was investigated in liver tissue of four fish species (*Cyprinus carpio* L., *Acipenser ruthenus* L., *Brama brama* L. i *Esox lucius* L.). Liver tissues were homogenized with activated anhydrous sodium sulfate and Soxhlet extracted with *n*-hexane-dichlormethane (4:1, *v/v*) for 20 h. The extracts were fractionated by column chromatography. Polycyclic aromatic hydrocarbon fraction was collected using *n*-hexane-dichlormethane (1:2, *v/v*) and analysed by gas chromatography - mass spectrometry (GC-MS). The mass spectra and retention times of PAHs in river fish were compared with retention times of PAHs in standard mixture.

In all cases, the PAH distributions are dominated by phenanthrene followed by its methyl derivatives, while in samples of *Esox lucius* L. and *Cyprinus carpio* L. pyrene was also identified. Since phenantrene and its derivatives belong to the petrogenic type of PAHs, their dominant abundance confirms the presence of petroleum-type of pollutants in the Tisza River. Other PAHs, belonging to pyrogenic type, except pyrene, were not identified. This could be the consequence of their high molecular mass i.e. lower solubility, and/or the absence of any combustion process in the vicinity.

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POLYBROMINATEDDIPHENYLETHERS AND POLYCYCLICAROMATICHYDROCARBONS IN SOILS FROM FIREPLACES

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Abstract

The attached study is focused on detection concentrations of PBDEs and substitution derivatives of PAHs in soil samples collected from the scene of the fire. Both of these classes of pollutants are persistent organic pollutants (POPs) and they are long-term monitored.

PBDEs belong to group of brominated flame retardants. Many products of daily use content PBDEs, such as televisions, carpets, mattresses and others. The basic characteristics of PBDE are their persistence, lipophilicity and high potential to long-range transport.

PAHs are important environmental pollutants. Sources of contamination are not only of anthropogenic but also of natural origin, such as volcanic dust, wildfires and biochemical reactions. The ratio of anthropogenic and natural pollutants has considerably changed in the last 50 years as the result of increase in burning of fossil fuels. Negative environmental characteristics of PAHs and substituted PAHs are practically identical with the PBDEs, especially with regard to lipophilicity and ability of accumulation in environmental media. Furthermore, they exhibit carcinogenicity and mutagenicity.

Pressurised solvent extraction of PBDEs and PAHs was selected as the isolation method. For the determination of PBDEs, gas chromatography with electron capture detector was chosen, for the analysis of PAHs and their derivatives, gas chromatography with mass spectrometry was used.

Our study was focused on monitoring contamination levels of PBDEs, PAHs and alkyl derivatives of selected polycyclic aromatic hydrocarbons in samples taken at the fireplace. The concentrations of targeted organic pollutants were as follows: PBDE concentrations ranged from below detection limit up to a concentration of 337 $\mu g \cdot kg^{-1}$, for alkylderivatives of PAH concentrations ranged from below limit of quantification up to a concentration of 228.7 $\mu g \cdot kg^{-1}$.

Acknowledgment

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GRAVIMETRIC AND BLACK CARBON ANALYSIS, IN PM2.5 SAMPLES, COLLECTED IN THE CITY OF PATRAS, GREECE, FROM JANUARY TO JUNE 2011

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Several PM2.5 samples were obtained in the city of Patras for the first half of the year 2011 (January to June 2011). Gravimetric and Black Carbon, (BC), analysis of the samples were performed in order to investigate the air quality of the area. Patras is medium sized city (about 150000 citizens) located in north Peloponnese peninsula. Patras has low industrial activity and can be considered as an urban background area. The PM2.5 sampler (Partisol FRM model 2000) was installed in the city center, on the roof of a public building (about 20 m from ground level). All PM2.5 samples were collected onto Teflon membrane filters (47 mm in diameter, 1μm pore size).For black carbon analysis a model 43 smoke stain reflectrometer (Diffusion Systems) was used. The mean PM2.5 concentration for the sampling period was 21.04 μg/m^3, and the mean B.C. concentration 2.1 μg/m^3. Figure 1 shows PM and BC concentrations for each month of the study. PM concentration for the colder months of the study was higher compared with PM concentration of the hotter months. BC followed almost the same trend as PM concentration.

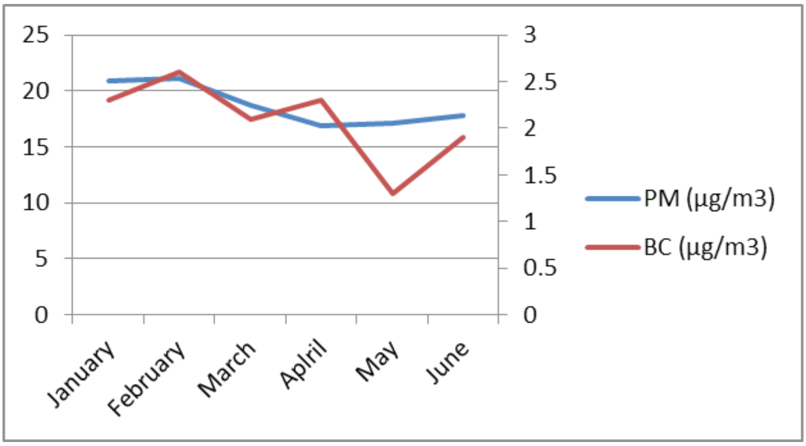

Figure 1. PM (primary axis) and BC (secondary axis) concentration for the months of the study

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ENVIRONMENTAL IMPACT OF AGRICULTURAL ACTIVITIES IN THE REGION OF GORIŠKA, SLOVENIA

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Goriška region is situated in south-west part of Slovenia. It has favorable agricultural position, where intensive agriculture with the existing infrastructure (e.g. irrigation systems) is present. Agricultural area in Goriška Slovenia, is located between two major rivers (Vipava, Soča). For agricultural areas it is required to ensure sufficient degree of caution in the use of different nutrients (regarding the variety of agricultural activities) since of the possibility of introduction various pollutans in water ecosystems.

Six sampling points on stream Vrtojbica and stream Koren on Slovenian and Italian side of the border were defined. Samplings were performed in different seasons of the year in order to estimate the influence of different nutrients on water bodies. The first sampling was carried out in July 2012, the second in February 2013 and the last in June 2013.

Different chemical analyses were performed direct on sampling site; such as pH, temperature and dissolved oxygen. Other chemical analyses were performed in laboratory - ion chromatography, total organic carbon and total nitrogen. Moreover, the toxicity was determined with luminescent bacteria *Vibrio fischeri* in all samples, according to the ISO standard.

In case of stream Vrtojbica, the analyses revealed higher values of TOC/TN and ion chromatography results downstream sampling points. There is also observed impact of seasons fluctuations on values of TOC/TN. Toxicity testing with marine bacteria *Vibrio fischeri* has shown the increased toxicity downstream sampling points, however during the summer, the influence of hospital's wastewaters was observed.

In case of stream Koren, the testing showed higher values of ion chromatography analyses and TOC/TN downstream. Seasonal fluctuations revealed higher values for all analyses for summer time. Meanwhile, for toxicity testing with *Vibrio fischeri* showed no seasonal fluctuations, but only the downstream increasing of luminescence inhibition.

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DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS BY GAS CHROMATOGRAPHY- MASS SPECTROMETRY IN SEDIMENTS OF THE RIVER DANUBE THROUGH SERBIA

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Bed sediment can often act as a sink for nonpolar organic pollutants released into the aquatic environment. When sources of contamination disappear or when emissions are strongly reduced, sediments could become a secondary source of contaminants to the surrounding environment. As a result of the difficulties encountered when attempting to predict contaminant bioavailability and mobility, assessing the risk posed by these contaminated sediments remains challenging. Strong sorption of nonpolar organic compounds to certain types of organic matter in sediments tends to reduce their accessibility to benthic organisms and their concentration in sediment pore waters thereby limiting their potential for biodegradation.

Sediment contaminated with hydrophobic organic compounds (HOCs) like polycyclic aromatic hydrocarbons (PAHs) are widespread, and assessing the hazard they pose is problematic since the mobility and bioavailability of the HOCs are so uncertain. Polycyclic aromatic hydrocarbons are of considerable interest, primarily due to their toxic, carcinogenic and mutagenic potential.

Concentrations of 16 EPA PAHs in the Danube bank sediment sample were measured by gas chromatography- mass spectrometry. The sampling sites were chosen in order to cover the whole Danube area through Serbia and the results correspond to a network of ten representative sampling sites. The total content of PAHs ranged from 99.48 to 520.48 ng/g with arithmetic mean value of 271.86 ng/g and median of 235.37 ng/g dw represented PAHs level in the Danube sediment. Value of total PAHs content obtained in bank sediment sample along the Danube River through Serbia was 2718.59 ng/g.

The results of this study add new data to the international database of the river Danube producing comparable and reliable information of sediment and water quality.

Keywords: polycyclic aromatic hydrocarbons, PAHs, sediment, Danube, GC-MS, monitoring

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BIOLOGICAL ICE NUCLEATION ACTIVITY IN CLOUD WATER

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Ice nucleation active (INA) biological particles, in particular microorganisms, were studied in cloud water. Twelve cloud samples were collected over a period of 16 months from the puy de Dôme summit (1465 m, France) using sterile cloud droplet impactors. The samples were characterized through biological (cultures, cell counts) and physico-chemical measurements (pH, ion concentrations, carbon content…), and biological ice nuclei were investigated by droplet-freezing assays from -3°C to -13°C. The concentration of total INA particles within this temperature range typically varied from ~1 to ~100 per mL of cloud water; the concentrations of biological IN were several orders of magnitude higher than the values previously reported for precipitations. At -12°C, at least 76% of the IN were biological in origin, i.e. they were inactivated by heating at 95°C, and at temperatures above -8°C only biological material could induce ice. By culture, 44 Pseudomonas-like strains of bacteria were isolated from cloud water samples; 16% of them were found INA at the temperature of -8°C and they were identified as *Pseudomonas syringae*, *Xanthomonas sp*. and *Pseudoxanthomonas sp*. Two strains induced freezing at as warm as -2°C, positioning them among the most active ice nucleators described so far[1,2]. We estimated that, in average, 0.18% and more than 1%.of the bacterial cells present in clouds (~104 mL-1) are INA at the temperatures of -8°C and -12°C, respectively.

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METABOLOMIC STUDY OF THE RESPONSE TO COLD SHOCK IN *PSEUDOMONAS SYRINGAE* ISOLATED FROM CLOUDS

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The environmental conditions in cloud droplets can vary dramatically within very short time frames, exposing the living organisms they carry to stressful conditions and shocks. In order to better understand the metabolic functioning of the bacteria that survive in clouds, we are developing metabolomics approaches, which is very promising but highly challenging. One of our main model microorganism, the ice nucleation active bacterium *Pseudomonas syringae* strain PDD-32b-74 isolated from cloud water collected from the summit of the puy de Dôme Moutain, was investigated for its response to brutal temperature shift from 17°C to 4°C. Cells cultured at 17°C on agar medium were resuspended in water at a concentration of~10^{10} cells mL^{-1} and incubated at 4°C for *c.a.* 15 hours; suspensions maintained at 17°C were used as controls. The intrametabolome of cells was extracted by methanol/ acetonitrile/ water treatment, and analyzed using a metabolic profiler platform, which couples HPLC-MS and ^{1}H-NMR. The metabolic signatures of cells incubated at each temperature were compared by principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA). Metabolites such as glutathione and trehalose were found relatively more abundant at 4°C than at 17°C, as expected, which suggests rapid physiological adaptations related to the temperature downshift. Data are still under investigation for establishing a more complete description of the metabolic changes induced by such cold shock in this strain, and these will be presented.

ANOVA AND NONPARAMETRIC ALTERNATIVES: INFLUENCE OF STATISTICAL NUISANCE FACTORS TO THE ANALYSIS OF THE RELATIONS BETWEEN THE DANUBE RIVER AND ITS MAJOR TRIBUTARIES

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One-way ANOVA, nonparametric Kruskal-Wallis and Mann-Whitney tests were used to explore influence of the major tributaries (the Rivers Tisa, Sava and Velika Morava) to the eco-chemical status of the Danube. Various nuisance factors (outliers, departures from normality, seasonality, heteroscedasticity) affect objectivity these tests, therefore it was important to estimate their robustness, but also to apply proper procedures to detect presence of nuisance factors and mitigate their influence.

The analysis of selected eco-chemical parameters: BOD-5, COD, UV extinction at 254nm, DO, Oxygen saturation, TDS, Electrical conductivity, Suspended matter, Total P, Phosphates, Nitrates, Ammonia, pH, Tot. alkalinity, m-2p alkalinity, CO_2 and Temperature was performed for 15 years period. Because many eco-chemical parameters are subjected to changes over the time, relations determined during one year may not be the identical after 5 years or a decade. Advantage a large data base is that enables us to expand analysis to longer time periods and cover cyclic or linear variations of parameters which expand to longer periods of time than one year.

We investigated applicability of ANOVA, post-hoc and related nonparametric tests (Kruskal-Wallis and Mann-Whitney test) combined with statistical tests developed to detect presence of various nuisance factors (Grubbs' test for identification of outliers, Kolmogorov-Smirnov test for departures from normality, turning point test, Wald–Wolfowitz runs test and pairwise rank test for seasonality, Bartlett's test for heteroscedasticity) and tested their performance, especially when they are combined with data transformations (e.g. Box-Cox transformations) whose role was to mitigate the effect of nuisance factors.

ANOVA is generally robust enough to resist violations of required preconditions by various levels of the nuisance factors found in the environmental data sets collected from analyzed rivers, which suggests that these statistical methods are suitable for evaluating the influence of the tributaries in any other similar river system. Influence of the most of the nuisance factors can be reduced or avoided by using nonparametric methods and data transformations. The most severe negative influence resulted from the lack of independence related to the pronounced seasonality.

The River Tisa was the most polluted tributary, but its pollution load was not substantial enough to exceed the Danube self-purification potential. The Belgrade city was also identified as serious pollution source.

QUALITY ASSESSMENT OF WATERS FROM SOUTH-EAST SERBIA IN RESPECT TO MAJOR DISSOLVED ELEMENTS

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According to the density of water resources and the diversity of physico-chemical properties of mineral waters, the territory of Serbia belongs to the one of the most resourceful areas of the European continent. Due to poor data on the quality, only a small fraction of these waters is used as drinking and bottled water. Since safe and minerally-rich drinking water is one of the preconditions of good health and one of the basic health indicators of any country, the aim of this work was to evaluate the quality of spring, ground and some river waters from South-East Serbia region. The study area included the territory between the valley of the South Morava down river flow in the West, Balkan mountain range in the East, the mountains Bukovik and Rtanj in the north, and the mountains Vrdenik and Čemernik in the south. The technique of inductively coupled plasma-atomic emission spectrometry was used for mineral characterisation of natural waters from South-East Serbia. The analysis included determination of aluminium, arsenic, calcium, cadmium, cobalt, chromium, cooper, iron, potassium, magnesium, manganese, sodium, nickel, lead and zinc in spring, ground and river waters. Calculated contents were compared with Serbian regulations on the quality of water for human use, and directive of World Health Organization for maximum acceptable concentrations of chemical substances.

Some spring and ground water samples contained high concentrations of macro-elements Ca, Mg and K. Those waters can be classified as mineral water in accordance with Serbian regulation for natural mineral water, spring water and bottled drinking water. Concentrations up to 84.2 μg/L, 8.10 μg/L and 14.9 μg/L of iron, manganese and copper, respectively, were recorded in some water samples and were within the permissible limits. Other heavy metals were not detected in analysed samples.

Based on the derived results, it can be concluded that tested ground and spring water samples have a significant potential to be used as sources for the production of bottled water. Good quality of the river water samples qualifies these alluvial deposits as good sources of water supply to many communities close to this river. Although results are promising, further investigations are necessary. In the meantime, precautionary measures should be immediately taken to protect and preserve these water resources. The preservation of water resources should be performed in economically, socially, and environmentally sustainable manner.

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DISSOLVED GASEOUS MERCURY IN NATURAL WATERS – METHODOLOGICAL ASPECTS

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The most important mercury forms in the aquatic environment are reactive Hg (RHg), dissolved gaseous mercury (DGM) and methylmercury (MeHg). DGM consists mainly of elemental mercury (about 95 %) and dimethylmercury (<5%). Surface waters are supersaturated with Hg (0) relative to the atmosphere. Recent studies suggest that the evasion of Hg (0) from oceanic waters to the global atmosphere plays an important role in the global mercury cycle. The production of DGM is a function of abiotic and biotic processes. Photochemical reactions, bacterial activity (especially in deep waters), and tectonic activity are the main contributors to mercury losses/production from/to fresh and marine ecosystems. The levels of total Hg in non contaminated surface waters are in the range between 0.2 to 5 ng/L, while the percentages of DGM varies between 1 to 30%.

Common analytical protocols for DGM are based on purging of aqueous solutions and pre-concentration of DGM onto gold traps followed by detection using cold vapour atomic fluorescence spectrophotometry (CV AFS). Manual and automated protocols are available and comparability of the results have been demonstrated. The main sources of errors in these protocols are related to sampling and calibration of the instruments. DGM species are not stable in aqueous media therefore timing of analysis after sampling is very important. On-site measurements are recommended but not always achievable. Careful checking of DGM stability in surface water samples showed that DGM in sea water is less stable (4 hours) than in fresh water samples (8 hours). In addition, no significant effects of exposure to light and various temperatures during storage were observed.

Calibration is the second most critical step as it provides the evidence of traceability and comparability in time and space. In this work different calibration methods were tested and compared: calibration with Hg (0) from an automated system, Hg (0) from the reduction of Hg(II) and calibration with Hg(0) formed in the headspace between the liquid phase and the gaseous phase. Almost no differences were found between the first and the second method, while the third one cannot be used for low level DGM measurements, due to poor and irreproducible results.

The method validated and optimized for total DGM measurements is very sensitive. With a 250 mL of water samples, the LOD is 0.002 ng/L with a method uncertainty of 5 %. As such it is applicable for surface waters with lowest DGM values reported in the literature.

POSTER SESSION 2

ENVIRONMENTAL AND CULTURAL HERITAGE

E101

THYMOL AS AN ALTERNATIVE TO PESTICIDES: EFFECT ON OLFACTORY MEMORY AND GENE EXPRESSION LEVELS IN THE BRAIN OF THE HONEYBEE *APIS MELLIFERA*

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The problems of hive weakening and depopulation encountered by beekeepers over the last 10 years have driven the development of much research. A part of this has focused on the fight against the Varroa destructor ectoparasite, which is regarded as an important scourge of bees. Initial treatments were based on synthetic pesticides such as coumaphos, fluvalinate, or amitraz. However, the development of resistance caused by some synthetic molecules and/or the undesired transfer to the honey, as well as the increasing demand for organic agricultural products, has lead beekeepers to abandon these active substances in favor of natural products such as essential oils.

Thymol, a phenolic compound from *Thymus vulgaris*, is an effective acaricide, especially concerning the Varroa ectoparasite [1], and it has been shown that this monoterpene can kill Varroa without noticeable loss of bees [1]. It has been used for several years in the form of evaporating tablets (Apilife Var®) or gel boxes (Apiguard®) that beekeepers can place in hives after honey harvest. Nonetheless, in spite of the success obtained using thymol against Varroa, few studies have covered its sublethal effects on bees [1,2]. We present here the results of the “BeeThym” research program where the side effects of thymol on bees’ behaviour have been assessed. Initial studies under laboratory conditions demonstrated an impairment of phototaxis in bees after exposure to sublethal doses of thymol or Apilife Var® [3,5]. In a second part, its effects on olfactory memory were explored plus gene expression in the brain of honeybees from treated hives. The octopamine receptor OA1, Rdl (coding for a GABA receptor subunit) and trpl genes’ expression were assessed after exposure to sublethal doses. Data indicated that the genes coding for the cellular targets of thymol could be rapidly regulated after exposure [4]. Thymol levels in the brain, the body and the beeswaxes of bees have been monitored throughout the study [5]. However, memory and sensory processes should be investigated in bees after chronic exposure in the hive to thymol-based preparations.

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THE PHARMA TRANSPORT TOWN - UNDERSTANDING ROUTES TO SUSTAINABLE PHARMACEUTICAL USE: AN EXERCISE IN INTERDISCIPLINARY STUDY

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Over recent years the value of using interdisciplinary approaches in tackling complex environmental issues has been recognised; with interdisciplinary research described as the mantra of science policy [1], alongside calls for its application to "become the standard rather than the exception" [2: 343]. The obstacles and challenges that interdisciplinary work poses for mixed discipline research teams stem from the often opposing paradigms that researchers of different scientific disciplines identify with [3]. This can led to different conceptual frameworks and even approaches to scientific study. Before such teams can begin to tackle potential conflicts due to differing epistemologies [4], they must first identify their common ground and take necessary steps to ensure effective communication; overcoming discipline specific language nuances.

The award winning Pharma Transport Town [5] (which has been further developed since its publication in Science), illustrates an exercise in interdisciplinary study which utilised information graphics as a means to break down communication barriers. This visual approach allowed researchers from a range of disparate disciplines (including analytical chemistry, ecotoxicology, psychology, epidemiology, and graphic design), to express their knowledge and viewpoints around a particular topic: the environmental transport, fate and sustainable use of pharmaceuticals. This particular graphic was designed to provide interactive education and communication with those not familiar with the many issues associated with pharmaceuticals, and was placed in the context of an environment to which everyone can relate (a town), to ensure maximum impact of its key message: that everyone (including pharmaceutical companies, medical practitioners, water treatment companies, and individuals) all have a role to play in ensuring safe sustainable use of pharmaceuticals. As these disparate individuals interacted with the Pharma Town graphic, the content of the graphic evolved and expanded as did their shared understanding of the complexity and extent of the issue.

The team involved in the development and production of this graphic, advocate the use of such an approach to break down barriers in interdisciplinary study, thus providing insights into different disciplinary perspectives and opening up new avenues for interdisciplinary research.

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E103

DEVELOPMENT OF A VALIDATED METHOD FOR THE DETERMINATION OF MERCURY CONTENT IN SEAWATER MATRICES BY ICP-MS: PRELIMINARY RESULTS

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The Water Framework Directive (WFD) 2000/60/EC [1] established a protection of the aquatic environment and constitutes a strategy against the chemical pollution of water bodies.

The WFD provided a list of priority substances that present a risk for the good chemical status of the aquatic environment defined in terms of compliance with all the environmental quality standards (EQS) established in the daughter Directive 2013/39/EU [2]. According to both directives, mercury concentration must be monitored to assess the chemical status of the aquatic environment. The EQS for mercury expressed as a maximum allowable concentration is 0.07 μg/L. The low EQS value introduces a challenge for analytical techniques. This situation becomes more complicate due to the strict performance criteria (limit of quantification, uncertainty) for the methods of analysis imposed by the Directive 2009/90/EC [3].

In response to the European directives, a certified reference material (CRM) for the determination of mercury in seawater is under development at the Institute for Reference Materials and Measurements (IRMM), with the aim of producing a suitable quality assurance standard for trace mercury analysis. To evaluate the homogeneity and stability of the CRM produced, a method for mercury determination based on the combination of the cold vapour generation and inductively coupled plasma mass spectrometry (ICP-MS) was developed. Among the elemental analysis techniques, ICP-MS could be considered as the most sensitive technique for the determination of trace metals in natural waters [4]. However, the direct analysis of seawater by ICP-MS is difficult due to high salinity content of the sample. Cold vapour (CV) generation techniques have been widely used to separate the analyte from the sample matrix. CV generation offers several advantages over conventional sample introduction systems such as the improvement of analyte transport efficiency and removal of the matrix to minimize non-spectral interferences [5]. The work focuses on the optimization of parameters affecting the measurement such as choice of reductant agent and its concentration, mixing time, gas flow rate and sample liquid flow rate. Moreover, the work summarises the in-house validation of the method in accordance with ISO/IEC 17025.

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E104

HONEYBEES (*APIS MELLIFERA* L.) AS BIOINDICATORS OF ENVIRONMENTAL POLLUTION: CONCENTRATIONS OF METALS IN AND AROUND BELGRADE AREA

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The use of bioindicators for monitoring of the environment pollution has increased in the past decades. One of the species that is increasingly being used as a bioindicator is the honeybee (*Apis mellifera*). Honeybees are a good biological indicator because they can be used to monitor the level of soil, water, plant, and air pollution in areas of several square kimoleters. Since 1970, bees have increasingly been used to monitor heavy metal environmental pollution [1].

The aim of this study was to determine levels of Cu, Pb, Zn and Mn in bodies of forager bees. The study was conducted at six locations in Serbia. Two locatons were in urban zones (Belgrade), two were near an industrial zone (Pančevo), one was in a small town with no heavy industry (Vršac) and one was in a mainly agricultural area (Mesić). Samples were mineralized using microwave digestion. Quantitative analysis was done using atomic absorbtion spectrometry (AAS).

Of the analyzed metals the highest concentration in bees has Zn, next were Mn and Cu. Pb had the lowest concentrations. It was found that Pb content was highest in urban areas, while lowest in agricultural area. For the other three metals (Zn, Cu and Mn) there were no significant differencies depending on the location, exept for two cases. Zn levels were lower in one urban location compared to all the others, and Mn had the lowest concentrations in the agricultural area compared to the other locations in this study. The results in this study are comparable to the results in other studies [2] [3]

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A NEW APPROACH FOR THE PRODUCTION OF A CERTIFIED REFERENCE MATERIAL FOR BIOTA MONITORING

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Certified Reference Materials (CRMs) are homogeneous and stable materials with a metrologically established property value and its uncertainty. These materials are used to assure comparable and reliable analytical measurement results between laboratories worldwide and to guarantee a traceability of these results. The aim of this study is to produce a novel biota matrix CRM to support EU Member States in the assessment of the quality of European water bodies (rivers, lakes, ground and coastal waters), as required by the EU Water Framework Directive 2000/60/EC (WFD) [1]. The subsequent daughter Directive 2008/105/EC set Environmental Quality Standards (EQSs) for priority substances [2]; two of those are the target priority substances of the CRM, namely hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD), with EQSs in biota at 10 and 55 μg kg^{-1} wet weight, respectively. The recently released Directive 2013/39/EU [3] setting biota EQSs in several priority substances for achieving cost-effective water monitoring, confirms the need of biota matrix CRMs. The novel approach of this study consists of producing a fresh-like biota matrix CRM. The challenge is to achieve a homogeneous and stable “wet” CRM, more commutable to environmental samples, in contrast to the already existing reference materials that are usually freeze-dried or powder-like. This will lead to the benefit of circumventing the conversion of dry to wet basis and the need for including correction factors in data calculations. Naturally contaminated catfish (*Silurus glanis*) was chosen as the starting material for the CRM production. The fish, procured from the Ebro river basin in NE Spain was cut in fillet cubes, cryo-milled and homogenized. Thereafter, the material was heated at 92°C, transferred into glass jars and autoclaved to achieve sterilization. A critical point in the processing was the mixing steps of the individual fish samples to reach the desired mass fractions of the two analytes. The final material is prepared as a fresh-like fish paste material, without the use of any additives or stabilizers. Currently, the project runs in the final phase of stability assessment and certification. The material will be released in the near future.

A. Oostra, H. Leys, P. Conneely and M.-F. Tumba-Tshilumba of the RM

Processing group (IRMM) are acknowledged for their invaluable contribution to the production of the final material.

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DEVELOPMENT OF THE WAY OF STEROID HORMONES AND NON-STEROIDAL ANTI-INFLAMMATORY DRUGS DETERMINATION IN BIOLOGICAL FLUIDS BY HPTLC

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Control of steroid hormones level in human organism is an important analytical task. Variations of its concentrations, presence or absence of some substances enables to find the causes of steroidogenesis derangements. Synthetic steroidal and non-steroidal anti-inflammatory drugs (NSAIDs) is used to its recovery. In case of NSAIDs it is known that some of them are supplied to pharmaceutical market as recemic mixture. In fact, only one of enantiomers has a positive effect.

In this investigation we offer the way of steroid hormones and its synthetic analogs determination in biological fluids (urine, serum) by thin-layer chromatography (HPTLC) with densitometric detection. We investigated an influence of chromatographic system modifiers (sodium dodecyl sulfate, cetyl trimethylammonium bromide, β-cyclodextrine) at separation selectivity of analytes under determination. The procedure of biological sample preparation for determination of steroids is recommended. It involves use of RP-C18 sorbent for the serum and hyper-crosslinked polysterene – for the urine.

The opportunities of NSAIDs enantiomers separation by HPTLC (modification of stationary or mobile phase by *L*-aminoacids, β-cyclodextrine) and ligand-exchange HPTLC (modification of phases by complex of Cu(II) with *L*-proline/*L*-hydroxyproline) were detected.

In accordance with proposal scheme charachteristic HPTLC-patterns (as well as HPLC and MEKC) of corticosteroids in urine samples of healthy donors and patients with Cushing's syndrome were obtained. Steroidal patterns were processed by principal component analysis (PCA) and soft independent modeling of class analogy (SIMCA). The possibility of use of characteristic steroidal profiles as additional diagnostic criteria was estimated.

E107

EARLY DIAGENETIC PROCESSES IN A GEOLOGICALLY WELL-DEFINED KREPOLJIN BROWN COAL BASIN, SERBIA

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The Krepoljin brown coal is situated in the Homolje mountains, Eastern Serbia. The sediments of the coal-bearing series of Krepoljin basin were formed in complex structural-tectonic conditions of freshwater bogs during the Lower Miocene. Older stratigraphic elements which form the base, i.e. underlayer for Tertiary products, can be divided into two distinct structural complexes: (i) the complex which is the base and underlayer for Tertiary coal-bearing sediments and (ii) the synchronous Mesosoic complex laid over coal beds (Ercegovac *et al.,* 2006).

The characteristics of early diagenetic processes which influenced the composition of the organic matter of coals from the Krepoljin coal basin from Serbia, Miocene age, was assessed by statistical correlation analysis and multivariate principal component analysis (PCA). The principal component which are defining the coals and promoting individual early diagenetic processes were the precursor materials and environmental factor respectively, representd by higher plants, algae and molds; expressed by the relative contents of the Cs_{29}-, Cs_{28}-, Cs_{27}-steranes, respectively, and the content of organic sulphur-Sorg, average content 166±101μmole/g. The main and highly interrelated effects of the higher plant material were the followings: (i) increase of the sulphur content of coal orgaic matter, (ii) promoter of sulphate reducing conditions, and (iii) establishment of the H/C- and N/C-ratios of organic matter. Pyrite formed by the participation of Sorg. Within the geological sequence of bogs in which the coals were formed differing degree of reductivity of the aquatic environment existed. According to the degree of pyritization of coal samples, in four bogs were euxinic, i.e. highly reductive conditions occuring ($DOP_{Fe}>0.7$), whereas in the other four bogs prevailed a oxigenated or suboxic water column (DOP_{Fe} = 0.40—0.67).

Key words: Brown coal, diagenetic processes, precursor materials, sulphur species, statistical analysis.

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ENVIRONMENTAL AND PUBLIC HEALTH ASPECTS OF PHARMACEUTICAL WASTE MANAGEMENT IN MONTENEGRO

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Waste is a result of every human activity including health care activities. Not only may improper management of waste in health care facilities endanger health workers and service users, but it may also endanger the environment.

A significant part of the process of the disposal of waste is medicinal waste, and within this category – pharmaceutical waste. Pharmaceutical waste, as a constituent part of medicinal waste, requires a special treatment in terms of control, selection, categorizing, packaging and destruction. In European Union it is classified in compliance with Directive 75/442/EEC, as well as with Basel Convention, i.e. with its Annex 1. Most commonly used technique of this type of waste disposal is high temperature destruction - incineration.

EU countries are obliged to apply so-called Take Back Scheme (TBS) – system of taking medicines back (collection, disposal and destruction of unused and outdated medicines) in which pharmacy has a central role. According to research of European Institute for Water, surface waters across Europe are getting more and more polluted by pharmaceutical waste (steroids, hormones from the contraceptive pills, residues of antibiotics, antidepressants, tranquilizers and medicines to treat cancer).

Currently, there is no adequate research or relevant data on size and manner of disposal of pharmaceutical waste in Montenegro. The legislative framework is provided by the Law on Waste Management (*Official Gazette of the Republic of Montenegro*, no. 80/2005 and Official Gazette of Montenegro, no.73/2008) and by the National Strategy for Medicinal Waste Management from 2008.

A regulated system of management of pharmaceutical and hazardous waste should be established in Montenegro, along with the implementation of legislation in the whole process of waste management, from the waste producer to the processing of waste and its final disposal.

KEY WORDS: pharmaceutical waste, ecology, health impact

E109

KINETICS OF SORPTION OF Cd(II) ON BAUXSOL

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Analysis of the kinetic parameters of the sorption process is important because it can provide information about the velocity of the investigation process and the dominant mechanism of mass transfer.

To explain the kinetics of the sorption Cd(II) following models were used: pseudo(I) order, pseudo(II) order and pore diffusion model. It is shown that the model of pseudo (II) order the better description investigated sorption process than the model of pseudo(I) order and calculated sorption capacities are close to the experimentally obtained values. These facts indicate that the sorption of Cd(II) on bauxsol is controlled by chemical reaction.

Applying the pore diffusion model is shown that the overall sorption process is controlled not only by the diffusion inside the particles, but also the diffusion in the film of fluids is a significant limiting stage of the process [1].

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POSTER SESSION 3

WATER AND WASTE TREATMENT

W101

MODELLING NATURAL AND SYNTHETIC STEROID ESTROGENS FROM PATIENT TO RIVER: A CATCHMENT LEVEL CASE STUDY

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Concerns over the presence and potential effects [1] of pharmaceuticals in the environment, along with growing demand [2], have recently led to changes in European level legislation; for the first time pharmaceuticals have been named in a watch list (as part of the water framework directive [3]), and include 17-♌-ethinylestradiol (EE2) and 17-♌-estradiol (E2). Although Environmental Quality standards (EQS) have not yet been set, it has been estimated that the compliance cost for the UK water industry to achieve the initial proposed EQS for EE2 alone would likely be in the region of £20 billion [4]. It will therefore be necessary and pertinent to focus limited financial resources within 'pollution hotspots'. One means by which to identify such hotspots is predictive modelling at a small geographical scale.

To this end a new model has been developed which uses newly available localised prescription data (National Health Service, England) to calculate *actual usage* (as opposed to predicted) of prescription medications, in *small geographical locations* (down to individual sewage treatment works; STWs). This model can be applied to *any human pharmaceutical* in *any location* (provided data is available). For illustrative purposes of the model's function this has been applied to a case study: the steroid estrogens, estrone, 17β-estradiol, and 17α-ethinylestradiol in a selected catchment.

As steroid estrogens also have a natural source, this must be accounted for in risk assessment exercises. To estimate naturally excreted estrogenic compounds the popular population group approach developed by Johnson and Williams [5] was used as a foundation, but updated to increase its accuracy by bringing it in-line with current socio-economic and cultural conditions.

Outputs from these two approaches were refined using local census data, along with local statistics which reflect cultural conditions, to obtain accurate predictions of excretion. Additionally, the recent publication of measured pharmaceutical concentrations in influent

/ effluent for a number of UK STWs allowed appropriate validation of this model with 'real' data (as opposed to predicted concentrations often previously used for validation), inclusive of exercises to optimise transformation and removal rates for sewer transport and within the STWs; thus providing predicted influent and effluent data. Validation work demonstrated that values predicted by this model were in good agreement with measured values, and have made advances to the accuracy of prediction when compared to previous modelling approaches (particularly for EE2). Models such as this allow limited resources to be focused upon localities which pose the greatest risk, thus functioning as an environmental management tool.

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W102

REUSE OF WASTEWATER FROM MEAT PROCESSING PLANTS AFTER FINAL FILTRATION WITH ACTIVATED CARBON

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The meat processing industry generates a large amount of wastewater which represents a serious problem due to its high levels of organic matter and need for effective and high cost treatments. Meat-processing wastewaters contain high concentration levels of nitrogen, phosphorus and suspended solids, which could cause serious problems to surface water pollution, since, in developing countries, they are usually discharged without any treatment.

Wastewater treatment of meat processing industry can be divided into three steps: 1) *Primary treatment* (equalization of waste flows, the separation of large materials, removal of suspended solids, fats and oils, standardization of composition and flow rate); 2) *Secondary treatment* (biodegradable organic matter is eliminated by biological processes); 3) *Tertiary or advanced treatment* (filtration, removal of ammonia and other specific pollutants, disinfection, sterilization, advanced oxidation processes and adsorption).

Within the research, we have analyzed raw wastewater and water after tertiary treatment (denitrification and disinfection) from the selected meat industry pilot plant in the Province of Vojvodina, Republic of Serbia (Table 1).

Table 1. Pollutants concentrations in raw wastewater and purified water before adsorption

Pollution indicators	Concentration of pollutants [mg/L]	
	Raw wastewater	Purified water
COD	1255	48
BOD_5	876	42
Total Kjeldahl nitrogen	28.8	7.7
Total phosphate	27.05	6.61
Total suspended solids	318	80
Permanganate index	84.2	8.7

The results showed that the adsorption with commercial activated carbon can be applied as the final treatment of the analyzed wastewater. Additional treatment with adsorption enables it to be reused in the production cycle. The further studies should be focused on final filtration with different commercial activated carbons, as well as with the alternative adsorbents obtained from biomass (apricot stones, plum stones, cherry stones).

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W103

COAGULATION/FLOCCULATION AND ELECTROCHEMICAL OXIDATION USING A ANODE BDD TO THE TREATMENT NEJAYOTE FROM THE CORN INDUSTRY

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The manufacturing processes of tortilla, corn chips, tortilla chips, and related products yield a liquid waste called "*nejayote*" [1]. The nejayote contains lots of organic matter equivalent to COD values greater than 20000 mg/L; BOD of the order of 7000 to 10000 mg/L and alkaline pH (10-12) [2]. The tortilla industry in Mexico produces large amounts of nejayote, for a ton of corn will produce about 3 tons of nejayote, which represents a serious environmental pollution problem. In this work we report the study nejayote treatment by coagulation/flocculation integrated with electroxidation and exclusively electroxidation using a BDD (Boron-Doped Diamond) anode. The processes were evaluated coupled manner and independently on nejayote treatment. The effectiveness of natural coagulant (chitosan) and flocculant (terrana; commercial natural bentonite) was studied. It was determined the dose of coagulant/flocculant and the influence of pH. The nejayote treated by chemical coagulation/floculation process was subjected to electroxidation. Electroxidation effectiveness was studied as a function of pH and electrolysis time. The control variables were the potential difference (9V) and concentration of NaCl (8.3 g/L) as supporting electrolyte with constant stirring. Analysis of the quality of nejayote treated was performed by measured of color, turbidity, COD and UV-vis spectroscopy. The results of the coagulation/floculation process show that at pH 5.2 a ratio chitosan:terrana, 2:1, was enable to removal color 87.2%, turbidity 95.5% and COD 8.4%. The main contribution of integrated electroxidation process was 99.0% of removal of COD with 180 minutes electrolysis. The nejayote treated exclusively by electroxidation process was studied as a function of pH and time of electrolysis with a constant difference potential (9 V) and NaCl (8.3 g/L). At pH 12 and electrolisis time of 120 min, the removal values of color, turbidity and COD were 99.4 %, 99.6 % and 99.9 %, respectively.

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INVESTIGATION OF THE APPLICABILITY OF SOLAR PHOTOCATALITIC DEGRADATION IN TREATMENT OF WATER CONTAINING HIGH CONCENTRATION OF PETROLEUM HYDROCARBONS

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Methods based on photolysis and chemical catalysis are useful and attractive alternative in wastewater treatment, especially for wastewaters containing small amounts of refractory organic substances [1]. In treatment of waters containing low amount of petroleum pollutants, the solar light/TiO_2 slurry system was proven to be able to remove up to 70 % of benzene, toluene, ethylbenzene and xylenes (BTEX) and total petroleum hydrocarbons TPH during 4 h [2].

In the present research we investigated the efficiency of the solar light/TiO_2 slurry system for treatment of water containing high concentration of petroleum hydrocarbons.

Mixture of commercial desulfurized diesel fuel, water and TiO_2 was solar irradiated for five hours. Simultaneously, comparative samples of mixture of diesel fuel and TiO_2 were solar irradiated. Diesel fuel was treated under the same conditions in the dark to evaluate the evaporation loss. At the end of the experiment, organic phase was separated from water and/or the catalyst, diluted with *n*-hexane and analyzed by gas chromatography – mass spectrometry (GC-MS) technique. Detailed GC-MS analysis comprised following compounds: *n*-alkanes, *iso*-alkanes and isoprenoids, alkyl-cyclopentanes, alkyl-cyclohexanes and alkyl-benzenes.

After 5 h of aqueous solar irradiation, significant loss of hydrocarbons was noticed only in the fraction of hydrocarbons having less than 15 carbon atoms. Additionally, among *n*-alkanes, *iso*-alkanes and isoprenoids, preferential removal of higher homologues was noticed as well. However, at the end of the experiment, the majority of the pollutant remained nondegraded.

These results show that the efficiency of solar light/TiO_2 slurry system in treatment of waters containing petroleum pollutants is highly dependent on the amount of the contaminant. In the case of water containing high concentration of petroleum hydrocarbons, solar photocatalitic degradation was shown to be of limited usage and, accordingly, much less efficient comparing to other known remediation techniques.

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W105

MONITORIZATION OF ESTROGENS RIVERS DOWNSTREAM OUTPUTS WWTP´S AND IMPACT ON AMPHIBIANS

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During the last years, great attention was laid to the environmental diffusion of natural and synthetic estrogens, and to their harmful effects on human and wildlife health, such as increasing of the incidence of cancer and the decreasing reproductive fitness of humans and responsible for disruption of reproduction and development in some wildlife populations, altering blood hormone levels, reducing fertility and fecundity, masculinisation of females and feminization of males[1].

A precise monitorization of natural and synthetic estrogens in Waste Waters Treatment Plants (WWTPs), waters for human consumption, rivers, lakes, etc., is essential for a risk assessment regarding endocrine disrupting effects in the public health and aquatic environment.

Estrone, 17b-estradiol, 17a-ethinylestradiol and estriol were identified and quantified using an HPLC procedure with UV detection, under optimized conditions, preceded by a solid phase extraction (SPE) as a pre-concentration method. The occurrence of these compounds was studied in four rivers downstream outputs WWTP´s, located in Portugal Central Region. Were also investigated the concentrations of estrone and 17β-estradiol in *Rana/Pelophylax perezi* male comparing to two control groups living in a non-contaminated water environment, using the radioimmunoassay method in blood/serum fraction of these amphibians.

The use of SPE-HPLC method allows limits of detection of 0.089 µg L^{-1} for estrone, 0.25 µg L^{-1} for estradiol, 0,45 µg L^{-1} for estriol and 0.11 µg L^{-1} for ethinylestradiol.

The concentrations obtained in the four downstream outputs WWTP´s were in the range of 0.15-0.72 µg L^{-1} for estrone, 0.10-0.51 µg L^{-1} for estradiol, and 0.11-0.23 µg L^{-1} for ethinylestradiol. Concentrations between 53-101 pg/ml were founded for estrone, and 37-149 pg/ml for estradiol in *Rana/Pelophylax perezi* male. However, the information of impacts of estrogenicity on wildlife populations is still limited to a few species of animals [2], so these results demonstrated that a great concern should be addressed to the potential risk of the presence of estrogens in the aquatic environment.

Keywords: Estrone; 17b-Estradiol; 17a-Estradiol; Estriol; SPE; HPLC; WWTPs analysis; RIA, Amphibians

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GEOPOLYMERIZATION OF FLY ASH AS POSSIBLE TECHNOLOGY FOR IMMOBILZATION OF ELECTRIC ARC FURNACE DUST

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Electric arc furnace dust (EAFD) is by product generated during remelting of old iron and steel scrap in the electric arc furnace which is considered as hazardous waste due to the content of heavy metals and possible dangerous impact on the environment.

There are several methods for its recycling but the most promising and cost effective is its stabilization into the construction materials through innovative method for waste stabilization – geopolymerization, [1,2].Geopolymerization process involves the chemical reaction of alumino-silicate oxides with highly alkaline activator yielding the new material with amorphous or semi-amorphous structure, called geopolymer. Immobilization of toxic materials may occur by chemical bonding, adsorption, as well as physical encapsulation but the mechanism by which heavy metal cations are incorporated into the polymer network is not yet fully understood.

The aim of this research was to investigate the effectiveness of immobilization of heavy metals from electric arc furnace dust in the fly ash based geopolymers, depending of alkaline dosage.

Fly ash is activated by alkaline solution prepared by mixing sodium silicate and NaOH solutions in a mass ratio of 1.5. Concentration of NaOH was 7, 10 and 13 $\text{mol}\times\text{dm}^{-3}$. EAFD was added in quantity of 10 % of total solid phase.Immobilization efficacy of heavy metals from EAFD was evaluated using leaching tests TCLP Method No. 1311, EN 12457-2 for granular waste for monolithic materials, which can be used as a criterion for defining hazardous and non-hazardous wastes for the purpose of disposal.

The result of TCLP and EN 12457-2 testsevaluate the chemical immobilization of heavy metals into the geopolymer matrix and the results indicate that increase of NaOH concentration used for geopolymer synthesis favour the immobilization of heavy metals from EAFD. On the other side, the results of monolithic test indicate that the immobilization efficiency increase with decrease of NaOH concentration.

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W107

PURIFICATION OF WASTEWATER IN FUR INDUSTRY

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Depending on the capacity and type of processing, wastewater in fur industry can be more or less loaded with various components which are isolated in this wastewater during the production process. In this review, we will primarily pay attention to the wastewater obtained in the manufacturing process of small companies which are located in the area of former Yugoslavia and involved in this activity and are very flexible in terms of processing of different types and amounts of fur. In order to provide opportunities for manufacturers and designers to select the appropriate technological process of purification, we will use the information about the quality of wastewater obtained in the company called „DoniaTrade“ which is located in Bugojno and on the basis of this information suggest a solution on purification of this and similar wastewater.

SCREENING OF PESTICIDE RESIDUES IN CANAL WATER IN THE NORTHERN SERBIA

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Non-point-source contamination of surface water has emerged as an important environmental problem during the last decades. This is particularly obvious in areas with intensive pesticide application. Considering importance of water and soil quality, pesticide residues in our environment need to be more effectively documented. This study has focused on determination of pesticide residues in drainage water. Monitoring of pesticide residues were conducted at different locations in the northern part of Serbia, the main agricultural area of the country. The sampling was performed during spring and summer 2012 on twelve potential risk sites. The extraction of pesticides from water was carried out with ENVI™ C18 DSK 47 mm (Supelco 5-7171, Bellafonte, PA). Prior to extraction disc was conditioned with 5 ml of methanol and 5 ml of ultrapure water. Afterward, water sample was filtered through the disc under vacuum and disc was dried for 1 h at 25 °C. Pesticides were eluted from the disc with 5 ml of mixture dichloromethane/n-hexane (40/60, v/v) and evaporated to dryness. The extract was reconstituted in 1 ml of methanol, ultrasonically homogenized and analyzed. Analyses were performed on Agilent Technologies GC-MS Model 7890 A Series gas chromatograph coupled to 5975 C mass selective detector. A HP5MS (30 m × 0.25 mm i.d.) fused silica capillary column was used. Helium was used as the carrier gas at a constant pressure. Injection volume was 2.0 µl, in splitless mode at 280 °C. The total run time was 41.86 min. The interface was kept at 250 °C, the quadropole at 150 °C and the mass spectra were obtained at electron energy of 70 eV. After validation and measurement uncertainty evaluation steps, results obtained showed that the method can be applied to efficiently for monitoring of pesticide residues in water samples. In analyzed samples 22 pesticides were detected - 8 fungicides, 9 herbicides and 5 insecticides. Herbicides were most frequently detected (in 41% of the samples), followed by fungicides (36%) and insecticides (23%).

ACKNOWLEDGEMENT
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POSTER SESSION 4

BIODEGRADATION AND BIREMEDIATION

RELEASE OF HYDROPHILIC DRUGS AND A-HYDROXY ACIDS FROM BIOCOMPATIBLE COPOLYMERS.

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This study is focused on the release of paracetamol, glycolic and lactic acids from biocompatible copolymers. Paracetamol is classified as a Non-Steroidal Anti-Inflammatory Drug (NSAID). Acetaminophen is ranked among aniline derivatives and it was chosen like model drugs due to its structure and good water solubility. Currently, acetaminophen is one of the most widely used analgesics and antipyretics [1]. Therefore, the new methods of administration of drugs are being developed. The main aim is the gradual release of the drug during several days. The gradual release of a drug should be a more efficient therapy and also more friendly to the organism.

Copolymers based on poly(lactic-co-glycolic) acid and poly(ethylene glycol) PLGA-PEG-PLGA were studied. Applications of PLGA-PEG-PLGA based polymers in delivery of therapeutics and tissue engineering are employed. This group of copolymers is considered as the stimuli-responsive polymers. These polymers or "smart" polymers react on a small change in external environmental conditions by dramatic changing of their physical and chemical properties. Copolymers based on PLGA-PEG-PLGA are sorted into groups of temperature-sensitive polymers. With increasing temperature the sol copolymer changes to hydrogel copolymer and vice versa [2].

Release of paracetamol and α-hydroxy acids occurred at 37 °C in MilliQ-water and phosphate buffer with pH 7.4. High performance liquid chromatography with UV-VIS detection of diode-array type was used for quantitative determination of paracetamol, lactic and glycolic acids as the final degradation products of copolymer PLGA-PEG-PLGA.

Acknowledgment
This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic, specific research, project No. FCH-S-13-2087.

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POLYCYCLIC AROMATIC HYDROCARBONS IN COMMERCIAL BARENTS SEA FISH SPECIES

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Being a major component of the aquatic food web and a main food resource for humans, fish have received special attention with respect to ecotoxicological analysis. Polycyclic aromatic hydrocarbons are important widespread environmental pollutants, which are formed and released into environment through natural and anthropogenic sources. They are toxic; some of them carcinogenic, persistent and bioaccumulative compounds. Recently, interest has grown in research on the organ-specific distributions of PAHs in aquatic organisms, but the patterns of bioaccumulation of PAHs in fish tissues remain unknown. Concentrations of 16 polycyclic aromatic hydrocarbons (PAH) from the list of the US EPA were determined in fish tissues from the Barents Sea. 41 samples of 7 species of fishes were collected in ten fishing areas of the Barents Sea in February 2013. Biological samples were selected, prepared and analyzed in compliance with methodical guidelines of the International Council for the Exploration of the Sea (ICES). PAHs tended to concentrate more in the liver than in the muscle tissues. This pattern was repeated in the fish species studied here and probably reflects the distinct composition of lipids in the tissues is known to influence the distribution of toxicants in marine species. The range of total average PAH concentrations in individual organs were: 0,36-4,11 (muscle tissue) and 55,5-267 (liver) in ng/g of wet weight. Naphthalene and phenanthrene were predominant PAH present in samples. The highest total concentrations of PAH in the muscle were found in spotted wolffish and halibut. Higher contaminant concentrations were found in the livers of haddock. Feeding habits and migration patterns are likely explanations for this observed inter-species variation. The PAH levels in the fish of Barents Sea not may be of toxicological concern to both the other trophic components of the marine ecosystem, and to human health at present.

POSTER SESSION 5

ANALYTICAL METHODS FOR ENVIRONMENTAL SCIENCE AND BIOMONITORING

A101

DERIVATIVE SPECTROPHOTOMETRY AND ELECTRON SPIN RESONANCE (ESR) SPECTROSCOPY FOR ECOLOGICAL AND BIOLOGICAL QUESTIONS

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Derivative Spectrophotometry and Electron Spin Resonance (ESR) Spectroscopy for resolving Ecological questions and application of the PAM-fluorescence method allows to detect the functional status of photosynthesizing cells. The use of derivative spectrophotometry of 4-8 orders (HODPh) provides the structural state evaluation of cells and biologically-active substances. At the same time comparative researches carried out in equal time intervals under the influence of extremal environmental factors give the possibility to match structural changes of cells and corresponding failures of their functional reactions. For this purpose barley mutants lacking chlorophyll "b" and also Chlamydomonas and Scenedesmus algae mutants with different sensitivity to the light were used. Interpretation of derivative spectrophotometry data agreed with the analysis of PAM-fluorescence. Specialities of HODPh spectra are considered with discussion of the large factual material on Ca-ions interaction with ((benzylidene)amino)guanidine derivative substances containing electron-donating or electron-accepting substituents.

Also, evidence of polycomponency of the promising antitumor preparation «Ukrain» («NowickyFarma», Austria) is presented and the wide range of HODPh application in different biochemical researches is shown.

The summation of our materials is published in the monograph "Biological Questions" V. Saakov et al. Springer PH, 2012-2013, Wien, Heidelberg, ISBN 978-3-7091-1006-5 ; ISBN 978-3-7091-1007-2 (eBook)

POSTER SESSION 6

ECOTOXICOLOGY AND BIOMARKERS

E101

INFLUENCE OF NEWLY SYNTHESIZED Cu(II) COMPLEXES ON THE PYRAZOLE BASED DERIVATIVES ON INHIBITION OF *BOTRYOSPHAERIA DOTHIDE*

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Widely spread disease of olives caused by Botryosphaeria dothidea fungi has provoked initiation of multidisciplinary research in Montenegro. Based on the fact that the pyrazoles, as fungicide active ingredient, have shown practical application in the protection of fruit trees and taking into account available data on the biochemical role of copper in the ecosystems, the synthesis of copper (II) acetate with selected pyrazole derivative , then its structural characterization and finally determination of the biological effects of Cu(II)complex and Cabrio top on *Botryosphaeria dothidea* has been performed.

In order to determine the biological effect of newly synthesized Cu (II) complex five samples of fungicide Cabrio top (whose active ingredient pyraclostrobin belongs to pyrazole derivatives) with the range of concentrations ($1.45 \cdot 10^{-3}$mol/dm^3 – $0.09 \cdot 10^{-3}$mol/dm^3) and also five samples of newly synthesized complex $CuC_{12}H_{20}N_4O_6$ with concentration range ($5.66 \cdot 10^{-3}$mol/dm^3 - $0.35 \cdot 10^{-3}$mol/dm^3) have been prepared. By analysing statistical results obtained from biological testing (LSD (0,01) = 0.107 and LSD (0,01) = 0.129) it is noted that all concentrations of Cabrio top and $CuC_{12}H_{20}N_4O_6$complex in above mantioned ranges showed a significant inhibitory effect comparing to the control sample.

THE INFLUENCE OF THE ENVIRONMENT ON THE QUALITY OF OLIVE OIL FROM DIFFERENTLOCATIONS IN BAR, MONTENEGRO

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In this paper we tested the soil and the local (home maid) olive oil from two different locations in the city of Bar,Montenegro. For the soil that contains investigated olives we have determined pH, metal content(Pb,Cd,Hg,As,Cr,Ni,Cu,B,Mo,Co and Zn)and fluorine. Except these we also determined the content of polycyclic aromatic hydrocarbons (PAH) and PCB congeners. Based on the results of tested soil it can be concluded that at the first selected location we have a greater presence of As 20.84%, Cr 157.26%,Ni 171.83% than maximum allowed quantities.

The contents of heavy metals and pesticides are determined in the olive oil. The contents of heavy metals and pesticides are below maximum allowed quantities.

E103

A REVIEW OF THE CONTENTS OF AFLATOXINS IN ANIMAL FEED SAMPLES IN THE MONTENEGRIN MARKET USING ELISA AND HPLC METHODS

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Aflatoxins are naturally occuring mycotoxins produced by many species of *Aspergillus fungi* ,i.e. molds, that grow on grains, of which the most important are *Aspergillus flavus* and *Aspergillus parasiticus* .[1] The main aflatoxins are aflatoxin B1 , B2 , G1 and G2 . Aflatoxin B1 is in a group of carcinogenic substances , ie . belongs to a group 1according to a classification by IARC (International Agency for Research on Cancer).[2]

In the period from January till October of 2013, total of 1467 of samples of animal feed, intended for consumption of different types of domestic animals, were analyzed using a screening ELISA (Enzyme Linked Immuno Sorbent Assay) and the confirmation method of liquid chromatography with fluorescence detection

. In this paper we summarize the results of comparative analysis of animal feed obtained by screening and confirmation method.

It is also given a comparison of the results with acceptable levels of EU / national legislation

.

Keywords: aflatoxin B1 , B2 , G1 , G2 , animal feed , HPLC , RF detector

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OCCURENCE OF AFLATOXIN M1 IN MILK SAMPLES ON THE MARKET OF MONTENEGRO

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Aflatoxin M1 is a mycotoxin that can often be found in milk and dairy products. It represents a metabolite of Aflatoxin B1 and its presence in milk is the result of the metabolism of animals that consumed feed contaminated with aflatoxin B1.

There is sufficiency evidence that aflatoxin M1 is genotoxic carcinogen , its carcinogenic potential is estimated to be about 10 times smaller than of aflatoxin B1.

However, taking into account that the intake of dairy products in humans is considerable, especially in infants and children, therefore is a significant risk of exposure to aflatoxins, in this paper is given the overview of aflatoxin M1 content in samples of raw milk and heat-treated milk intended for placing on the market of Montenegro, partly from domestic production and from import.

In period January-October 2013. have been analyzed total of 134 samples of raw milk and 1420 of heat treated milk samples.

All milk samples were analyzed using screening method ELISA (Enzyme Linked Immuno Sorbent Assay) and confirmation method-triple quadrupole liquid chromatography - mass spectrometry with electrospray - positive ionization technique
(LCMSMS) [1]..

Keywords: Aflatoxin;Aflatoxin occurence; Method of analysis

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