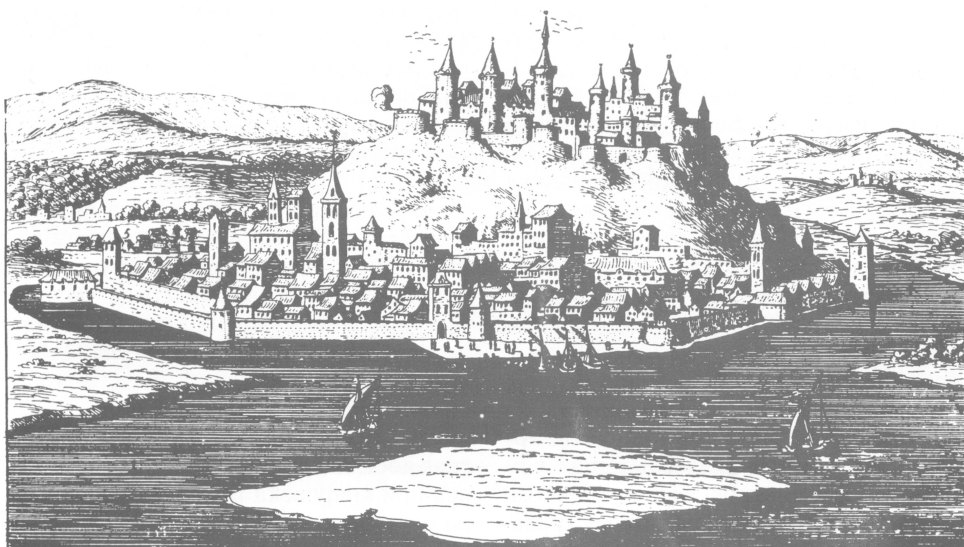


The Sixth European Meeting on Environmental Chemistry (EMEC6)

PROGRAMME AND THE BOOK OF ABSTRACTS



**Belgrade, Serbia and Montenegro
December 6-10, 2005**

**The Sixth European Meeting
on Environmental Chemistry (EMEC6)
Programme and The Book of Abstracts**

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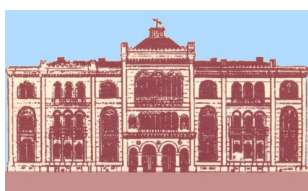
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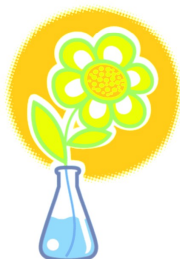
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**The European Association of Chemistry
and the Environment**

web: <http://www.research.plymouth.ac.uk/ace/>

Conference web-site:

<http://www.chem.bg.ac.yu/emec6/>

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emec6@chem.bg.ac.yu

The Conference will be held at:

Congress Hall of NIS Jugopetrol,
Milentija Popovića 1,
11070 Novi Beograd

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EMEC6 Programme

EMEC6 Programme (general)

Tuesday, December 6th

19:00-21:00 **Welcome reception**
*(Faculty of Chemistry, University of Belgrade,
Studentski trg 12-16, Belgrade)*

Wednesday, December 7th

08:00-09:15 **Registration**
(The registration desk will be opened during all period of the conference)

09:15-09:45 **Opening**

09:45-10:20 **Plenary lecture:** Paul Philp
THE EMERGENCE OF STABLE ISOTOPES IN ENVIRONMENTAL
AND FORENSIC GEOCHEMISTRY STUDIES
(Chairman: Dragomir Vitorović)

10:20-10:45 **Coffee break**

10:45-11:00 **Session lecture:** Nikos Katsaros
ENVIROMENTAL POLLUTANTS IN THE FOOD CHAIN

11:00-12:48 **Oral presentations**
(Chairmen: Nikos Katsaros and Petar Pfendt)

12:48-13:00 **Coffee break**

13:00-13:15 **Session lecture:** Biljana Škrbić
POLYCYCLIC AROMATIC HYDROCARBONS AND TRACE ELEMENT
DISTRIBUTION IN NOVI SAD

13:15-14:15 **Oral presentations**
(Chairmen: Biljana Škrbić and Mark Fitzsimons)

14:15-15:30 **Lunch**

15:30-16:05 **Plenary lecture:** Aleksandar Stamatović
RAPID DEVELOPMENT OF THE ANALYTICAL INSTRUMENTATION
AND ITS INFLUENCE ON THE ENVIRONMENTAL SCIENCE
(Chairman: Jan Schwarzbauer)

16:05-18:25 **Oral presentations**
(Chairmen: Jan Schwarzbauer and Dragan Veselinović)

17:05-17:25 **Coffee break**

17:25-18:25 **Oral presentations**

18:25-19:30 **Announcement of poster presentations**

19:30-20:30 **Poster presentations**

Thursday, December 8th

- 09:00-09:35 **Plenary lecture:** Lorenz Schwark
ASSESSMENT OF AIR QUALITY IN THE COLOGNE CONURBATION
USING PINE NEEDLES AS A PASSIVE SAMPLER
(Chairman: Josef Caslavski)
- 09:35-09:50 **Session lecture:** Pietro Tundo
RECENT ASPECTS IN DIMETHYL CARBONATE CHEMISTRY
- 09:50-11:02 **Oral presentations**
(Chairmen: Pietro Tundo and Uuve Kirso)
- 11:02-11:30 **Coffee break**
- 11:30-11:45 **Session lecture:** Srećko Stopić
HYDROMETALLURGICAL TREATMENT OF SOLID WASTES AND
WASTEWATERS TOWARDS AN ENVIRONMENTAL PROTECTION
- 11:45-13:21 **Oral presentations**
(Chairmen: Srećko Stopić and Albert Lebedev)
- 13:21-14:15 **Announcement of poster presentations**
- 14:15-15:30 **Lunch**
- 15:30-16:18 **Oral presentations**
(Chairmen: Srđan Blagojević and Michele Aresta)
- 16:18-16:33 **Session lecture:** Marina Frontasyeva
TRACE ELEMENT CONTAMINATION AROUND A COPPER SMELTER
COMPLEX IN BOR REGION (SERBIA) STUDIED BY MOSS
BIOMONITORING
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(Chairmen: Marina Frontasyeva and Ivan Gržetić)
- 17:21-18:21 **Poster presentations**
- 19:00- **Reception at "Beli Dvor" (The White Palace)**
Conference dinner at "Milošev Konak"

Friday, December 9th

- 09:00-09:35 **Plenary lecture:** Sergio Rodriguez-Gonzalez
SOURCES AND FEATURES OF ATMOSPHERIC PARTICULATE
MATTER IN THE MEDITERRANEAN - CONSEQUENCES FOR THE
AIR QUALITY MONITORING
(Chairman: Isabel Villaescusa)
- 09:35-09:50 **Session lecture:** Panayotis Siskos
THE ROLE OF PRIMARY AND SECONDARY AIR POLLUTANTS IN
ATMOSPHERIC POLLUTION
- 09:50-11:02 **Oral presentations**
(Chairmen: Panayotis Siskos and Zorka Vukmirović)
- 11:02-11:30 **Coffee break**

- 11:30-11:45 **Session lecture:** Mila Laušević
QUADRUPOLE ION TRAP IN ENVIRONMENTAL ANALYSIS
- 11:45-12:57 **Oral presentations**
(Chairmen: Mila Laušević and Anatoly Golovko)
- 12:57-14:15 **Announcement of poster presentations**
- 14:15-15:30 **Lunch**
- 15:30-16:42 **Oral presentations**
(Chairmen: Mila Laušević and Anatoly Golovko)
- 16:42-17:00 **Coffee break**
- 17:00-18:00 **Poster presentations**
- 18:00-18:15 **Closing**

"Workshop of the Mediterranean Green Chemistry Network (MEGREC)"

will be organized on **Friday, December 9th** at **3:00 PM** at **Faculty of Technology and Metallurgy**
(Karnegijeva st. 4, Belgrade) in the Dean's Room.

Contact person: Prof. Teodor Ast, e-mail: ast@tmf.bg.ac.yu, phone: +381-64-1246103

Saturday, December 10th

- 11:00-14:00 **Belgrade city tour**
(optional)

EMEC6 Programme **(detailed)**

Tuesday, December 6th

19:00-21:00 **Welcome reception**
*(Faculty of Chemistry, University of Belgrade,
Studentski trg 12-16, Belgrade)*

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ENVIROMENTAL POLLUTANTS IN THE FOOD CHAIN

11:00-12:48 **Oral presentations**
(Chairmen: Nikos Katsaros and Petar Pfendt)

11:00-11:12 C. Ducoulombier-Crépineau, C. Feidt & G. Rychen
PALLADIUM AND PLATINUM TRANSFER TO MILK AND ORGANS OF
LACTATING GOATS

11:12-11:24 S. Jurjanž, S. Lutz, J. Mouriot & G. Rychen
EXTRACTION *in vitro* OF SOIL-BOUND PAHs IN THE RUMEN

11:24-11:36 A. D. Tappin, M. Fitzsimons & G. E. Millward
NATURAL ESTUARINE PARTICLES AND THEIR UPTAKE OF NITROGEN
IN ESTUARIES (NEPTUNE)

11:36-11:48 U. Kirso, G. Urb, N. Irha, J. Reinik & M. Laja
LEACHING BEHAVIOR OF A SOLID WASTE IN LABORATORY TESTS
AND LANDFILL

11:48-12:00 P. Trebše, M. Blažić & D. Drobne
A RELATION BETWEEN PHYSIOLOGICAL, BIOCHEMICAL AND
ENERGETIC RESPONSES IN TERRESTRIAL ISOPODS *Porcellio scaber*
AFTER EXPOSURE TO DIFFERENT PESTICIDES

12:00-12:12 S. Pejcinovska-Andonova & D. Chamovska
SET OF CORE INDICATORS FOR WATER DURING THE PREPARATION
OF LOCAL ENVIRONMENTAL ACTION PLANS IN MACEDONIA

- 12:12-12:24 J. Adamov, M. Vojinović-Miloradov & J. Hlpka
DIETARY EXPOSURE OF THE VOJVODINA POPULATION TO PERSISTENT ORGANIC POLLUTANTS IN THE DANUBE FRESHWATER FISH
- 12:24-12:36 A. Tsakirakis, E. Kapetanakis, M. Jovašević-Stojanović, M. Mojašević, S. Vitorović & K. Machera
ESTIMATION OF POTENTIAL DERMAL AND INHALATION OPERATOR EXPOSURE TO MALATHION IN REPRESENTATIVE FIELD CONDITIONS
- 12:36-12:48 M. Turk, J. Jakšić, M. Vojinović-Miloradov & J. Klanova
DETERMINATION OF POPs IN GASEOUS PHASE BY ACTIVE AND PASSIVE SAMPLING METHODS
- 12:48-13:00 **Coffee break**
- 13:00-13:15 **Session lecture:** Biljana Škrbić
POLYCYCLIC AROMATIC HYDROCARBONS AND TRACE ELEMENT DISTRIBUTION IN NOVI SAD
- 13:15-14:15 **Oral presentations**
(Chairmen: Biljana Škrbić and Mark Fitzsimons)
- 13:15-13:27 H. Mestankova, J. Jirkovsky, J. Krysa, M. Bolte & G. Mailhot
DEGRADATION OF POLLUTANTS IN AQUEOUS SOLUTION BY A POWERFUL COMBINED PHOTOCATALYTIC SYSTEM (IRON-TiO₂)
- 13:27-13:39 O. Lanitou, D. Dimotikali, K. Agiamarnioti, T. Triantis, K. Papadopoulos & R. Saičić
ASYMMETRIC SYNTHESIS OF α -AMINO ACIDS USING NOVEL CHIRAL FUNCTIONALIZED INORGANIC CATALYSTS
- 13:39-13:51 A. K. Golovko
OPTIMIZATION OF PETROLEUM RAW MATERIAL TO OBTAIN ECOLOGICALLY PURE PETROLEUM PRODUCTS
- 13:51-14:03 S. Raccanelli, S. Libralato, M. Favotto & S. Guerzoni
FATE OF POPs IN THE VENICE LAGOON: INSIGHTS FROM AN OVERVIEW OF ENVIRONMENTAL, BIOLOGICAL AND HUMAN MILK CONCENTRATIONS
- 14:03-14:15 P. Pato, M. Válega, J. Dias, E. Pereira & A. Duarte
VARIABILITY OF MERCURY FLUXES BETWEEN A TIDAL ESTUARY AND THE SEA
- 14:15-15:30 **Lunch**
- 15:30-16:05 **Plenary lecture:** Aleksandar Stamatović
RAPID DEVELOPMENT OF THE ANALYTICAL INSTRUMENTATION AND ITS INFLUENCE ON THE ENVIRONMENTAL SCIENCE
(Chairman: Jan Schwarzbauer)
- 16:05-18:25 **Oral presentations**
(Chairmen: Jan Schwarzbauer and Dragan Veselinović)
- 16:05-16:17 M. Koutny, M. Sancelme, J. Lemaire & A. M. Delort
ARE POLYETHYLENE FILMS WITH PROOXIDANTS BIODEGRADABLE?
- 16:17-16:29 A. Wishkerman, M. Petri & H. Biester
DISTRIBUTION AND SPECIATION OF IODINE AND BROMINE IN TWO FOREST SOILS

- 16:29-16:41 D. Fangueiro, J. L. Pereira, J. Coutinho, N. Moreira & H. Trindade
EFFECT OF DAIRY EFFLUENTS PRE-TREATMENT ON N₂O EMISSIONS
AND N-ORGANIC DEGRADATION AFTER SOIL APPLICATION
- 16:41-16:53 E. Lichtfouse, V. Sappin-Didier, L. Denaix, G. Caria, L. Metzger & J. Schmidt
A 25-YEAR RECORD OF POLYCYCLIC AROMATIC HYDROCARBONS IN
SOILS AMENDED WITH SEWAGE SLUDGES
- 16:53-17:05 S. Beduschi, A. Cafissi, B. Sacchi & S. P. Trasatti
CHEMICAL DECHLORINATION OF POLYCHLORINATED BIPHENYL
(PCB) IN DIELECTRIC OILS ENHANCED BY ULTRASOUND
- 17:05-17:25 **Coffee break**
- 17:25-17:37 M. Maata & S. Singh
HEAVY METAL POLLUTION IN SUVA HARBOR SEDIMENTS, FIJI
- 17:37-17:49 L. Jean, F. Bordas, J. C. Bollinger, A. Hitmi, P. Vernay & C. Gauthier
EFFECT OF CHELATES ON CHROMIUM AND NICKEL MOBILITY AND
ON THEIR UPTAKE BY *Datura innoxia* FROM AN INDUSTRIAL SOIL
- 17:49-18:01 S. Chiron & D. Vione
PHOTOTRANSFORMATION OF CARBAMAZEPINE IN ESTUARINE
WATERS
- 18:01-18:13 M. O. Jedrysek & A. Gryczko
CARBON, OXYGEN AND SULPHUR ISOTOPIC PICTURE OF MICROBIAL
BIODEGRADATION OF CONTAMINANT HYDROCARBONS
- 18:13-18:25 J. Čáslavský, M. Vavrova, L. Vojtova, J. Jancar & L. Nova
CHARACTERIZATION OF BIOCOMPATIBLE HYDROGELS:
DEGRADATION AND ENVIRONMENTAL IMPACT OF THE PRODUCTS
- 18:25-19:30 **Announcement of poster presentations**
- 19:30-20:30 **Poster presentations**

Thursday, December 8th

- 09:00-09:35 **Plenary lecture:** Lorenz Schwark
ASSESSMENT OF AIR QUALITY IN THE COLOGNE CONURBATION
USING PINE NEEDLES AS A PASSIVE SAMPLER
(Chairman: Josef Caslavski)
- 09:35-09:50 **Session lecture:** Pietro Tundo
RECENT ASPECTS IN DIMETHYL CARBONATE CHEMISTRY
- 09:50-11:02 **Oral presentations**
(Chairmen: Pietro Tundo and Uuve Kirso)
- 09:50-10:02 D. Drobne, V. Lešer, M. Milani, N. Nolde & S. Drobne
EFFECTS OF CHEMICAL POLLUTANTS ON DIGESTIVE GLANDS
INVESTIGATED BY MICROSCOPY TECHNIQUES
- 10:02-10:14 J. Schwarzbauer, A. Kronimus, S. Heim & G. Grannemann
NON-TARGET SCREENING ANALYSES OF ORGANIC POLLUTANTS
IN RIVERINE SYSTEMS
- 10:14-10:26 A. Đ. Duborija & S. Blagojević
DISTRIBUTION OF HEAVY METALS IN THE SKADAR LAKE
SEDIMENTS

- 10:26-10:38 C. Nebot, R. Falcon, K. G. Boyd, Sh. Lu & S. W. Gibb
HUMAN PHARMACEUTICALS IN SCOTTISH WASTEWATER EFFLUENTS
- 10:38-10:50 M. DellaGreca, M. R. Iesce, M. Brigante, M. Isidori, A. Nardelli, L. Previtera, M. Rubino & F. Temussi
ENVIRONMENTAL FATE OF LANSOPRAZOLE, OMEPRAZOLE AND AMOXICILLIN
- 10:50-11:02 J. P. Coelho, M. Rosa, M. E. Pereira, M. A. Pardal & A. Duarte
Scrobicularia plana ANNUAL BIOACCUMULATION RATES IN A HUMAN INDUCED MERCURY GRADIENT (RIA DE AVEIRO, PORTUGAL)
- 11:02-11:30 **Coffee break**
- 11:30-11:45 **Session lecture:** Srećko Stopić
HYDROMETALLURGICAL TREATMENT OF SOLID WASTES AND WASTEWATERS TOWARDS AN ENVIRONMENTAL PROTECTION
- 11:45-13:21 **Oral presentations**
(Chairmen: Srećko Stopić and Albert Lebedev)
- 11:45-11:57 A. Lebedev, O. Polyakova, E. Polyakova & Z. Zholdakova
POSSIBLE PATHWAYS OF TRANSFORMATION OF NEW DISINFECTION AGENT ALKYLDIMETHYLBENZYLAMMONIUM CHLORIDE IN CONDITIONS OF DRINKING WATER PREPARATION
- 11:57-12:09 D. Vione, V. Maurino, M. Lucchiari & C. Minero
Fe(III)-ENHANCED SONOCHEMICAL DEGRADATION OF METHYLENE BLUE IN AQUEOUS SOLUTION
- 12:09-12:21 E. Polyakova, Z. Zholdakova, L. Sycheva, V. Zhurkov & A. Lebedev
PERSPECTIVES OF WATER DISINFECTION IN MUNICIPAL WATER-SUPPLY TAKING INTO ACCOUNT PRODUCTS OF TRANSFORMATION
- 12:21-12:33 A. Houas, L. Elsellami, H. Lachheb & J. Ph. Nogier
PHOTOCATALYTIC ACTIVITY OF DOPED TiO₂ IN DEGRADATION OF METHYLENE BLUE AND MALIC ACID IN WATER UNDER VISIBLE OR UV LIGHT
- 12:33-12:45 M. Jitaru, A. Savall, M. Stan, M. Lang, K.-G. Serano & E. Weiss
ELECTROCHEMICAL BEHAVIOR OF AZO BOND ON DIFFERENT ELECTRODE MATERIALS. FUNDAMENTS FOR COLOR REMOVAL IN WASTE WATERS
- 12:45-12:57 M. Daković, M. Živić & D. Đikanović
URANIUM UPTAKE BY FRESHWATER ALGA *Chara globularis*: POSSIBLE APPLICATIONS IN CONTAMINATED WATER TREATMENT
- 12:57-13:09 M. Ortueta, M. A. Celaya, F. Mijangos & D. N. Muraviev
ION EXCHANGE ISOTHERMAL SUPERSATURATION (IXISS) OF MAGNESIUM-AMMONIUM PHOSPHATE (STRUVITE) SOLUTIONS IN COLUMNS
- 13:09-13:21 L. Méité, P. Mazellier & J. De Laat
PHOTOCHEMICAL TRANSFORMATION OF EMERGING

POLLUTANTS: EXAMPLE OF ETHINYLESTRADIOL AND
DICLOFENAC

13:21-14:15 **Announcement of poster presentations**

14:15-15:30 **Lunch**

15:30-16:18 **Oral presentations**

(Chairmen: Srđan Blagojević and Michele Aresta)

15:30-15:42 S. Zuehlke, A. Ligon, M. Spiteller & H. Fahlenkamp
INVESTIGATIONS OF OCCURRENCE AND ELIMINATION OF
HAZARDOUS COMPOUNDS IN WASTE WATER TREATMENT
PLANTS

15:42-15:54 L. Perelomov & S. Yoshida
EFFECT OF MICROORGANISMS ON THE SORPTION OF
LANTHANIDES BY QUARTZ AND GOETHITE AT THE DIFFERENT
pH VALUES

15:54-16:06 I. Landa & Z. Wittlingerová
APPLICATION OF REGIONAL HYDROCHEMICAL IN-SITU
BARRIERS IN SIGNIFICANT GROUNDWATER RESERVOIRS

16:06-16:18 C. Escudero, N. Fiol & I. Villaescusa
COMPETITIVE ADSORPTION OF TRIVALENT AND HEXAVALENT
CHROMIUM ON GRAPE STALKS ENCAPSULATED IN CALCIUM
ALGINATE GEL BEADS: KINETICS STUDY

16:18-16:33 **Session lecture:** Marina Frontasyeva
TRACE ELEMENT CONTAMINATION AROUND A COPPER SMELTER
COMPLEX IN BOR REGION (SERBIA) STUDIED BY MOSS
BIOMONITORING

16:33-17:21 **Oral presentations**

(Chairmen: Marina Frontasyeva and Ivan Gržetić)

16:33-16:45 G. Postole, M. Caldararu, A. Auroux & B. Bonnetot
PREPARATION PROCESS, STRUCTURAL AND CATALYTIC
PROPERTIES OF BN-SUPPORTED NOBLE METALS

16:45-16:57 D. L. A. Fernandes, J. A. B. P. Oliveira & M. T. S. R. Gomes
DEVELOPMENT OF AN ARRAY OF SENSORS TO DETECT AND
QUANTIFY VOLATILE HAZARDOUS COMPOUNDS

16:57-17:09 F. Constantinescu, D. C. Popescu, I. Ivanescu & A. Toma
THE PRODUCTION OF ENVIRONMENTALLY FRIENDLY MOTOR
GASOLINE COMPONENTS BY REACTIVE DISTILLATION

17:09-17:21 M. Kunaver, A. Kržan, V. Tišler & M. Žigon
LIQUID WOOD AS THE FEEDSTOCK FOR POLYMER SYNTHESIS

17:21-18:21 **Poster presentations**

19:00- **Reception at "Beli Dvor" (The White Palace)**
Conference dinner at "Milošev Konak"

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ATMOSPHERIC POLLUTION
- 09:50-11:02 **Oral presentations**
(Chairmen: Panayotis Siskos and Zorka Vukmirović)
- 09:50-10:02 T. Yuzhakova, B. Bonnetot, C. Guimon & A. Auroux
PREPARATION AND CHARACTERIZATION OF CeO₂-M₂O₃
(M = B, Al, Ga, In) MIXED OXIDES FOR OXIDATION REACTIONS
- 10:02-10:14 S. Bennici, A. Gervasini & A. Auroux
PROPERTIES AND CATALYTIC ACTIVITY IN NO_x ABATEMENT OF
Cu/Sn AND Cu/Ga BIMETALLIC OXIDE CATALYSTS SUPPORTED ON
SILICA-ALUMINA
- 10:14-10:26 C. Melis, C. Trozzi, D. Gaudioso, D. Đorđević, M. Dacić, S. Bajc,
B. Ramić & S. Kljajević
CONTRIBUTIONS OF GHG EMISSIONS FROM DEVELOPED AND
DEVELOPING COUNTRY ITALY AND SERBIA AND MONTENEGRO IN
1990
- 10:26-10:38 A. Acharid, M. Sadiki, M. Ben Arfa, R. Olier & M. Privat
QUANTUM STUDY OF MOLECULAR AND IONIC INTERACTIONS IN
ADSORBED LAYERS AT AIR / WATER INTERFACE IN RELATION
WITH POLLUTANT TRANSFER BETWEEN ENVIRONMENTAL
SPHERES
- 10:38-10:50 N. Ignatova, E. Velizarova, R. Milchev & M. Broshtilova
MONITORING OF POLLUTANTS DEPOSITION AND USING OF
MODELING FOR CRITICAL LOADS CALCULATIONS
- 10:50-11:02 Z. Vukmirović, D. Đorđević, I. Tošić & M. Unkašević
EVIDENCE OF WINDBORNE MINERAL DUST IN THE
MEDITERRANEAN ATMOSPHERE
- 11:02-11:30 **Coffee break**
- 11:30-11:45 **Session lecture:** Mila Laušević
QUADRUPOLE ION TRAP IN ENVIRONMENTAL ANALYSIS
- 11:45-12:57 **Oral presentations**
(Chairmen: Mila Laušević and Anatoly Golovko)
- 11:45-11:57 C. E. West, S. J. Rowland, C. A. Lewis, S. T. Belt, M. J. Hetheridge,
G. Roberts & Q. Lui
ILLUMINATING THE PHOTOCHEMICAL FATE OF PROZAC AND
VALIUM
- 11:57-12:09 C. Redshaw, S. Rowland, C. Whitby, M. Frenzel, M. Hetheridge & G. Roberts
UNEARTHING THE FATE OF PROZAC, VALIUM AND THEIR HUMAN
METABOLITES IN SEWAGE SLUDGE AMENDED SOILS

- 12:09-12:21 J. M. Joumier
APPLICATION OF GC-TRIPLE QUADRUPOLE MS/MS FOR MULTI-
RESIDUE ANALYSIS OF PESTICIDES IN COMPLEX MATRIX
- 12:21-12:33 J. E. Graham, K. G. Boyd, S. W. Gibb & J. G. McHenery
THE DETERMINATION OF EMAMECTIN BENZOATE IN ENVIRON-
MENTAL MATRICES
- 12:33-12:45 S. D. Mhlanga, B. B. Mamba, R. W. Krause & T. J. Malefetse
QUANTITATIVE ANALYSIS FOR THE REMOVAL OF NATURAL
ORGANIC MATTER AND DEGRADATION BY-PRODUCTS FROM
WATER USING CYCLODEXTRIN NANOPOROUS POLYMERS
- 12:45-12:57 Z. Đurić, I. Jokić, D. Vasiljević-Radović, O. Jakšić, D. Randelović &
J. Lamovec
MICRO/NANO-ELECTROMECHANICAL SENSORS FOR
ENVIRONMENTAL PROTECTION
- 12:57-14:15 **Announcement of poster presentations**
- 14:15-15:30 **Lunch**
- 15:30-16:42 **Oral presentations**
(Chairmen: *Mila Laušević and Anatoly Golovko*)
- 15:30-15:42 A. Kronimus & J. Schwarzbauer
NON EXTRACTABLE ORGANIC XENOBIOTICS IN RIVERINE
SEDIMENTS ANALYSED BY PYROLYSIS AND
THERMOCHEMOLYSIS
- 15:42-15:54 V. Guzsány, A. Madžgalj, P. Trebše, F. Gaál & M. Franko
DETERMINATION OF NEONICOTINOID INSECTICIDES BY LIQUID
CHROMATOGRAPHY COUPLED WITH THERMAL LENS
SPECTROMETRIC DETECTION
- 15:54-16:06 S. Ražić, A. Onjia, S. Đogo & L. Slavković
CHEMOMETRICS APPROACH TO ELEMENTAL ANALYSIS OF
PLANT AND SOIL SAMPLES
- 16:06-16:18 L. Bertin, S. Capodicasa, G. Cagnetta, D. Dionisi, L. Marchetti & F. Fava
DECONTAMINATION AND VALORIZATION OF SLUDGES DERIVING
FROM BIOLOGICAL WASTEWATER TREATMENT PLANTS
THROUGH ANAEROBIC DIGESTION
- 16:18-16:30 J. Lukić, A. Orlović, D. Skala & J. Jovanović
ASSESMENT OF WASTE INSULATING OIL REREFINING BY
EXTRACTION WITH N-METHYL-2-PYRROLIDONE REGARDING
OXIDATION STABILITY AND POLYCYCLIC AROMATIC
HYDROCARBON CONTENT
- 16:30-16:42 Sh. S. Itkulova & G. D. Zakumbaeva
EFFECT OF WATER ON REFORMING OF METHANE BY CARBON
DIOXIDE OVER SUPPORTED CATALYSTS
- 16:42-17:00 **Coffee break**
- 17:00-18:00 **Poster presentations**
- 18:00-18:15 **Closing**

"Workshop of the Mediterranean Green Chemistry Network (MEGREC)"

will be organized on **Friday, December 9th** at **3:00 PM** at **Faculty of Technology and Metallurgy** (Karnegijeva st. 4, Belgrade) in the Dean's Room.

Contact person: Prof. Teodor Ast, e-mail: ast@tmf.bg.ac.yu, phone: +381-64-1246103

Saturday, December 10th

11:00-14:00 **Belgrade city tour**

(optional)

Poster presentations

Wednesday, December 7th

Announcements: 18:25-19:30

Poster presentations: 19:30-20:30

1. Sustainable development

1. J. Kanazir, Đ. Basić, I. Vujković & R. Todosijević
SUSTAINABLE INDUSTRIAL DEVELOPMENT AND MANAGEMENT
2. S. Lazarević, I. Janković-Častvan, V. Pavićević, Đ. Janačković & R. Petrović
ADSORPTION OF Pb²⁺, Cd²⁺ AND Sr²⁺ IONS ON HAP POWDER OBTAINED BY
HYDROTHERMAL DECOMPOSITION OF UREA AND CALCIUM-EDTA CHELATES
3. D. Životić, I. Gržetić & V. Simić
POTENTIALLY HAZARDOUS TRACE ELEMENTS IN COAL FROM THE KOSTOLAC
BASIN
4. M. Ilić, S. Zlatanović, O. Cvetković, V. Pavelkić & S. Blagojević
INORGANIC CO₂ SEPARATIONS MEMBRANES
5. R. Biočanin
ENVIRONMENT PROTECTION AND CHEMICAL ACCIDENTS
6. L. Keznikl, I. Landa & L. Pokorny
ELIMINATION OF MIGRATION ABILITY OF DANGEROUS SUBSTANCES DURING
MAINTENANCE OF REGIONS DAMAGED BY WAR
7. A. Zarubica, M. Purenović & M. Miljković
INFLUENCE OF EMULSION "ANTIINKRUSTAL PURONI 2000" ON THE INHIBITION
OF IRON AND STEEL CORROSION
8. M. Stojanović, S. Zildžović, D. Kovačević, D. Iles, M. Grubišić & D. Radulović
IN-SITU URANIUM STABILIZATION BY NATURAL APATITES
9. C. Gaidau, M. Ionescu, M. Crudu & L. Miu
COMPACT PROCESSING OF LEATHER - AN ECOLOGICAL ALTERNATIVE
10. V. Joldžić
SUSTAINABLE DEVELOPMENT FROM THE ASPECT OF ENVIRONMENTAL
LAW - PROBLEM OF CONTINUAL DEVELOPING AND APPLAYING

2. Life cycle assessment

11. D. Đukic-Ćosić, M. Ćurčić & V. Matović
MONITORING OF TOXIC METALS Cd AND Pb IN HERBS *Hypericum sp.* AND
Thymus sp. FROM SERBIA
12. Z. Al Chami, D. Mondelli & T. Miano
BIOAVAILABILITY OF MICRONUTRIENTS AND HEAVY METALS AND THE
EFFECTS OF ORGANIC MATTER IN BINDING MECHANISMS

3. Risk assessment

13. D. D. Đurović, N. Z. Blagojević & V. Delević
CONTENT OF Pb, Al AND Cr IN DRINKING WATERS FROM WELLS IN THE
SURROUNDING AREA OF ALUMINUM FACTORY PODGORICA

14. G. Đukanović, R. M. Zejnilović & S. Šolaja
APPRAISAL OF KAP-S INFLUENCE ON CHANGE OF ZINC CONCENTRATION IN UNDERGROUNDWATERS IN KAP-S SURROUNDINGS
15. N. Todorović, M. Stevančević & M. Radovanović
SOLAR ACTIVITY - POSSIBLE CAUSE OF LARGE FOREST FIRES
16. D. Stanković, B. Krstić & R. Igić
CONCENTRATIONS OF LEAD (Pb) AND MANGANESE (Mn) IN SOME WOODY PLANTS ALONG M-21 ROAD THROUGH "FRUŠKA GORA" NATIONAL PARK
17. L. Jovanović
THE DEPENDENCE OF HUMAN HEALTH UPON DEFICIENCY AND SUFFICIENCY OF BIOGENIC ELEMENTS
18. A. Voulgaropoulos, M. Todorović, L. Cruceru, D. Manojlović, D. Trbović, B. Nešić & V. D. Krsmanović
DETERMINATION OF ARSENIC, COPPER AND LEAD IN DANUBE WATER: RESULTS OF THE 2nd REGIONAL INTERLABORATORY STUDY

4. Green chemistry

19. E. Portjanskaja, S. Preis & J. Kallas
AQUEOUS PHOTOCATALYTIC OXIDATION OF LIGNIN AND HUMIC SUBSTANCES WITH SUPPORTED TiO₂
20. V. Marjanović, R. Ninković, J. Miladinović, Lj. Trumbulović-Bujić & R. Drobnjak
CHEMICAL THERMODYNAMICS OF MIXED AQUEOUS SOLUTIONS OF SODIUM SULPHATE AND ZINC SULPHATE AT 298.15K
21. G. Cvijanović, N. Milošević, D. Cvijanović & M. Vesković
THE IMPORTANCE OF MAIZE SEED INOCULATION WITH FREE NITROGEN FIXERS WITHIN THE SYSTEM OF ENVIRONMENTAL PROTECTION
22. D. Pepić, M. S. Nikolić, M. Žigon, A. Kržan, M. Kunaver & J. Donlagić
HYDROLYTIC AND ENZYMATIC DEGRADATION OF BIODEGRADABLE POLY(ETHER-ESTER) COPOLYMERS
23. S. Sredojević, V. Dragičević, F. Bača, S. Gošić-Dondo, G. Drinić & M. Vrvic
THE CHEMICAL, PHYSICAL AND THERMODYNAMICAL PARAMETERS IN DETERMINATION OF GENOTYPES' REPLY TO ENVIRONMENTAL FACTORS: I. MERCHANT PESTICIDES COMBINATION SELECTED FOR MAIZE SEED PRODUCTION
24. S. Sredojević, V. Dragičević, M. Srebrić, P. Piper, G. Dražić & M. Vrvic
THE CHEMICAL, PHYSICAL AND THERMODYNAMICAL PARAMETERS IN DETERMINATION OF GENOTYPES' REPLY TO ENVIRONMENTAL FACTORS: II. THE SELECTION OF SOYBEAN VARIETIES AND SOIL TYPES TO LOW TEMPERATURE IN SPRING
1. The bioproduction and water content of seedlings
25. S. Sredojević, V. Dragičević, M. Srebrić, P. Piper, Ž. Jovanović & M. Vrvic
THE CHEMICAL, PHYSICAL AND THERMODYNAMICAL PARAMETERS IN DETERMINATION OF GENOTYPES' REPLY TO ENVIRONMENTAL FACTORS: II. THE SELECTION OF SOYBEAN VARIETIES AND SOIL TYPES TO LOW TEMPERATURE IN SPRING
2. The hydrolysis, biosynthesis and germination
26. I. Pešenjanski, B. Stepanov & B. Miljković
INVESTIGATION OF WHEAT STRAW LOW-TEMPERATURE COMBUSTION BY THERMOGRAVIMETRIC ANALYSIS

27. R. Đurović & M. Marković
HEADSPACE SOLID-PHASE MICROEXTRACTION IN MULTI-CLASS PESTICIDE
RESIDUE ANALYSIS
28. V. Tsoleva & S. Marinova
SUITABILITY OF CLAYEY SUBSTRATA CONTAINING INDUSTRIAL GYPSUM FOR
AGRICULTURAL UTILIZATION

5. Soil contamination, depollution technologies

29. A. Vaněk, L. Borůvka, O. Drábek & V. Ettler
CHEMICAL AND MINERALOGICAL STUDY OF HEAVY METAL BINDING IN
ALLUVIAL SOILS OF THE MINING/SMELTING DISTRICT
30. A. Antić, O. Cvetković, B. Jovančičević, S. Nikolić, S. Blagojević & M. Zdravković
DISTRIBUTION OF SOME HEAVY METALS IN SOILS FROM VELIKA MORAVA
RIVER VALLEY
31. B. Combourieu, S. Durand, C. Chamignon, P. Besse, M. Sancelme, C. Forano & A. M. Delort
MOBILITY OF ORGANIC POLLUTANTS ADSORBED ON CLAYS MONITORED BY
VARIOUS MAS NMR APPROACHES
32. G. Dević, V. Jovanović & P. Pfendt
SEQUENTIAL EXTRACTION OF METAL IONS FROM A BROWN COAL: PARTITION
OF THE METALS HAVING HIGH Me-HUMIC ACID COMPLEX STABILITY
CONSTANTS
33. M. Komárek, P. Tlustoš & J. Száková
ALTERATION OF HEAVY METAL MOBILITY USING ORGANIC AND INORGANIC
AMENDMENTS - IMPLICATION FOR ENHANCED PHYTOEXTRACTION OF HEAVY
METALS FROM CONTAMINATED SOILS
34. M. Pucarević, P. Sekulić & S. Rajović
POLYCYCLIC AROMATIC HYDROCARBONS IN THE TOPSOIL FROM THE CITY OF
NOVI SAD
35. N. Z. Blagojević, D. D. Đurović & V. M. Delević
CONTENT OF Pb, Cd, Cu AND Zn IN THE SOIL IN THE SURROUNDING AREA OF
ALUMINUM FACTORY PODGORICA
36. S. M. Mrkić, P. Pfendt, B. Jovančičević, M. Vrvic & P. Nikolić
XYLENE DEGRADATION IN THE CLAYS OF AN ALLUVIAL AQUIFER
37. S. Sakan, I. Gržetić & D. Đorđević
EVALUATION OF HEAVY METAL POLLUTION AND DISTRIBUTION IN THE TISA
(TISZA) RIVER SEDIMENTS
38. S. Dragović, A. Čučulović, Lj. Janković, A. Onjia & G. Bačić
GAMMA DOSE RATES OF NATURAL RADIONUCLIDES IN SURFACE SOILS OF
SERBIA AND MONTENEGRO
39. B. Žarković & S. Blagojević
EFFECT OF SOME AGROTECHNICAL MEASURES ON THE UPTAKE OF LEAD BY
MAIZE PLANTS
40. V. Doichinova
HEAVY METALS IN URBANIZED FOREST SOILS OF SOFIA REGION
41. V. Chrástný & M. Komárek
EFFECTS OF FLOODING ON LEAD AND CADMIUM SPECIATION IN SEDIMENTS
FROM A DRINKING WATER RESERVOIR
42. D. Veselinović, D. Marković, A. Savin, S. Filip, D. Bengin & B. Ristić
THE CORRELATION OF THE LEAD AMOUNTS IN THE WATER AND IN THE SOIL

43. D. Belić, B. Nešić, I. Brčeski & J. Petrović
TESTING OF POLLUTANT CONTENT IN SOIL AT CERTAIN LOCATIONS IN
BELGRADE
44. M. Mojašević, [N. Protić] & S. Vitorović
ORGANOCHLORINE INSECTICIDE RESIDUES IN SERBIAN SOILS
45. A. Cachada & A. Duarte
DEVELOPMENT OF A METHODOLOGY TO EVALUATE SOIL QUALITY - A TOOL
FOR URBAN RESOURCE MANAGEMENT
46. A. Cachada, A. Duarte & E. Ferreira da Silva
THE INFLUENCE OF A CHEMICAL COMPLEX IN POTENTIAL TOXIC METAL
DISTRIBUTION OF NEARBY URBAN SOILS
47. Z. Golić, V. Raičević, S. Antić-Mladenović, Lj. Jovanović, D. Kiković & B. Lalević
CHROMIUM-RESISTANT BACTERIAL POPULATION FROM MILIĆI BAUXITE MINE
SOILS
48. D. Kiković, Lj. Jovanović, V. Raičević & B. Lalević
EFFECTS OF HEAVY METALS ORIGINATED FROM INDUSTRY AND MINING ON
SOIL MICROORGANISMS IN KOSOVSKA MITROVICA
49. M. Maze, C. Bailleul, J. C. Dur, D. Tessier, K. Laval & M. Legras
EFFECT OF PHYSICO-CHEMICAL CHARACTERISTICS OF AGRICULTURAL SOILS
ON FUNGAL BIOMASS - CASE OF MEADOW AND CROP

6. Ecotoxicology

50. A. Perović, S. Nikčević, N. Bushati, J. Wolz, T. B. Seiler, D. Šundić, L. Erdinger & H. Hollert
AN EVALUATION OF RESULTS FROM MONITORING AND ECO-TOXICITY
TESTING OF THE SKADAR/SHKODRA LAKE BY TRIAD APPROACH
51. M. Milošević, A. Horvat & M. Demajo
EFFECTS OF METAL IONS ON Mg^{2+} -ATPase ACTIVITY IN PLASMA MEMBRANES
ISOLATED FROM THE RAT UTERUS
52. B. J. Drakulić, S. D. Petrović, D. Mijin & I. O. Juranić
A QSAR STUDY OF ACUTE TOXICITY OF *N*-ARYL-SUBSTITUTED
FLOUROACETAMIDES TOWARD RATS. CLASSICAL AND MOLECULAR
PROPERTY SPACES APPROACH
53. C. Lamelas & V. I. Slaveykova
DO LEAD - NATURAL ORGANIC MATTER COMPLEXES CONTRIBUTE TO Pb
BIOAVAILABILITY TO FRESH WATER MICROALGAE?
54. J. Petrović, T. Cvetić & D. Marković
COMPLEXES OF CHLOROPHYLL WITH COPPER, ZINC AND LEAD IN SOLUTION
AND PHOTOSYNTHETIC ORGANELLES: CHLOROPHYLL FLUORESCENCE
STUDIES
55. J. M. Đinović & A. R. Popović
QUALITY OF PETKA SPRING WATER IN THE VICINITY OF COAL ASH DUMP OF
THE KOSTOLAC POWER PLANTS (SERBIA)
56. M. Miljković, M. Purenović, G. Nikolić & V. Rakić
SPECTROSCOPIC, STRUCTURAL, AND QUANTITATIVE CHARACTERISTICS OF
THE ARTIFICIAL FOOD DYE E124 IN SOME FOOD PRODUCTS
57. S. Đogo, S. Ražić & L. Slavković
HERBAL DRUGS ORIGINATING FROM MEDICINAL PLANTS OF THE
FAMILY *Lamiaceae*

58. S. Perović, A. Lapanje, A. Perović, H. Hollert, L. Erdinger, T. B. Seiler, D. Drobne, P. Zidar, J. Strus & R. Kostanjsek
MONITORING OF THE LAKE SKADAR BY TRIAD APPROACH AND MICROBIAL DIVERSITY PROFILING
59. V. Chiosa, I. Hutchins & C. Mandravel
ACUTE TOXICITY EVALUATION FOR SOME CHEMICALS WITH SMALL MOLECULAR WEIGHT
60. Z. Leka, M. Ivanović, B. Damjanović & N. Latinović
INFLUENCE OF NEW DITHIOCARBAMATE, (NH₄)₃IDADTC, ON DEVELOPMENT OF *Phomopsis viticola* Sacc. FUNGI
61. M. Ricking, J. Schwarzbauer, H. Neumann-Hensel & E. Claus
CHEMICAL ANALYSIS OF SEDIMENTS AND CORRESPONDING PORE WATER AND ELUTRIATES AS A BASE FOR CORRELATION OF CHEMICAL COMPOSITION AND ECOTOXICOLOGICAL EFFECTS

Thursday, December 8th

Announcements: 13:21-14:15

Poster presentations: 17:21-18:21

6. Ecotoxicology

62. S. O. Podunavac-Kuzmanović & S. L. Markov
BIOLOGICAL ACTIVITY OF COPPER(II) COMPLEXES WITH SOME BENZIMIDAZOLE DERIVATIVES
63. N. Miljević, D. Golobočanin, A. Maksić & M. Nadeždić
CHEMICAL BEHAVIOR OF NITROGEN AND PHOSPHORUS IN THE VELIKA MORAVA CATCHMENT
64. B. Amidžić & R. Biočanin
PESTICIDES IN WORKING AND HUMAN ENVIRONMENTS AND FACTORS AFFECTING HUMAN HEALTH
65. D. Radić-Jovanović, M. Rašić & M. Vlajković
COMPARATION OF DIFFERENT METHODS FOR DETERMINING BIOAVIABILITY AND BIOACCESSIBILITY FACTORS FOR PAH SUBSTANCES
66. B. J. Drakulić, M. D. Soković & I. O. Juranić
ANTIBACTERIAL ACTIVITY OF 4-ARYL-4-OXO-2-BUTENOIC ACIDS AGAINST *Escherichia coli*. A QSAR STUDY
67. A. Tomašević, D. Mijin, E. Kiš, I. Deršek-Timotić, V. Batas & S. Janković
PHOTOCHEMICAL BEHAVIOR OF METHOMYL
68. E. Fulladosa, I. Villaescusa, J. Debord, J. C. Bollinger & J. C. Murat
EVALUATION OF TOXICITY FOR ORGANIC ARSENICAL COMPOUNDS USING *Vibrio fischeri* BACTERIA AND MICROCALORIMETRIC BUTYRYLCHOLINESTERASE INHIBITION
69. T. Bokić, T. Zečević & M. Ristić
COPPER ACCUMULATION AND DISTRIBUTION IN VINEYARD SOILS OF SERBIA
70. Lj. Marković, Ž. Vuković, M. Pavlović & O. Jozanov-Stankov
THE PHYSICO-CHEMICAL AND BIOLOGICAL MONITORING OF THE RIVER SAVA POLLUTION
71. J. Stojanović, S. Solujić-Sukdolak & V. Jakovljević
THE INFLUENCE OF DETERGENT, ETHOXYLED OLEYL-CETYL ALCOHOLE AND

SODIUM TRIPOLYPHOSPHATE ON THE BIOPRODUCTION OF SOME ORGANIC SUBSTANCES OF THE FUNGI SPECIES *Penicillium verrucosum* PEYRONEL

72. Y. A. Erdogan, N. Deveci & B. Sunman

ADSORPTION OF CADMIUM ON THE MEDITERRANEAN SEAGRASS

Posidonia oceanica

73. M. Vávrová, K. Bednařík, L. Vojtová, J. David & J. Jančář

ECOTOXICOLOGICAL EVALUATION OF POLYURETHANE FOAMS

7. Water treatment, reuse

74. A. Bojić, M. Purenović, J. Perović, T. Anđelković, D. Bojić, A. Veselinović & M. Vodeničarski

PHOTOCATALYTIC DEGRADATION OF HUMIC ACIDS IN WATER BY UV LIGHT

75. D. Vione, V. Maurino, C. Minero & E. Pelizzetti

EFFECT OF SOME INORGANIC ANIONS ON THE FENTON DEGRADATION OF PHENOL

76. M. Mizdraković, J. Lakušić & D. Đorđević

DECOLORIZATION OF TEXTILE WASTEWATER BY UV-TREATMENT AND COAGULATION PROCESSES

77. B. B. Mamba, R. W. Krause, T. J. Malefetse & E. N. Nxumalo

SYNTHESIS OF MONOFUNCTIONALIZED CYCLODEXTRIN POLYMERS FOR THE REMOVAL OF ORGANIC POLLUTANTS FROM WATER

78. H. Kawakami, M. Aoki & K. Fujiwara

TOXICITY AND BIOSORPTION OF HEAVY METALS IN GREEN ALGA

Chlorella kessleri

79. U. Iriarte-Velasco, J. I. Álvarez-Uriarte & J. R. González-Velasco

ARRHENIUS EQUATION FOR CHLOROFORM FORMATION DURING HUMIC ACID CHLORINATION: DEPENDENCE ON pH AND REACTION TIME

80. O. Terzić, J. Krstić, A. Popović & D. Jovanović

THE REMOVAL OF CYANIDE FROM WATER USING SYNTHETIC ACTIVATED CARBONS

81. M. Stanković, L. Pezo, A. Jovanović, D. Arandelović, B. Simonović & M. Jovanović

INDUSTRIAL SCALE SOLUTION OF OIL CONCENTRATION REDUCTION FROM WASTE WATER

82. V. Jovanović, V. Dondur, Lj. Damjanović, G. Jordanov, M. Petković, I. Juranić & M. Tomašević-Čanović

ADSORPTION OF PESTICIDES ON FUNCTIONALIZED SYNTHETIC ZEOLITES

83. M. Vukčević, S. Dimitrijević-Branković & M. Laušević

EXAMINATION OF THE ACTIVATED CARBON ANTIMICROBIAL ACTIVITY

84. N. Kuburović, V. Valent, M. Todorović, A. Orlović, S. Drmanić, T. Šolević & J. Nikolić

THE USE OF ADVANCED OXIDATION PROCESSES AS A CONTRIBUTION TO THE DETOXIFICATION OF WATER

85. N. Benderdouche, B. Bestani, M. Termoul & M. Belhakem

DEPOLLUTION OF PHENOL AND 4-CHLOROPHENOL CONTAMINATED WATER BY AN ACTIVATED CARBON PREPARED FROM OLIVE STONES

86. K. Živković, R. Zejnilović & N. Blagojević

TREATMENT OF THE FECAL WASTEWATER ON THE PLANT IN PODGORICA

87. V. Rakić, V. Rac, Z. Mrkonja, D. Brnjos, B. Dragoi & A. Auroux

STUDY OF REMOVAL OF PHENOL AND NICOTINE FROM WASTE WATERS BY THE USE OF VARIOUS SOLID ADSORBENTS

88. Y. A. Erdogan & N. Deveci
DETERMINATION OF THE ADSORPTIVE PROPERTIES OF ACTIVATED CARBON AND ITS PVA COMPOSITE
89. Z. Sandić, S. Kljajević, Lj. Malović, I. Mrkić, D. Đorđević & A. Nastasović
MACROPOROUS FUNCTIONAL POLYMERS FOR THE COPPER REMOVAL FROM WASTE WATERS
90. T. Milošević, K. Marjanović, S. Solujić, S. Sukdolak & M. Milošev
INFLUENCE OF VARIOUS NUTRIENT MEDIUM ON CELLULASE PRODUCTION IN CMC DEGRADING FUNGI
91. S. Đekić, R. Pfendt, Z. Jankanj & M. Borna
TESTING OF GROUND WATERS IN THE VICINITY OF THE PANČEVO INDUSTRIAL ZONE
92. C. Busset, P. Mazellier & J. De Laat
CARBONATE RADICAL REACTIVITY IN AQUEOUS SOLUTION
93. J. Reinik, J. Kallas & K. Jakobsson
COPING WITH MILITARY PAST POLLUTION IN ESTONIA
94. D. Klauson, E. Portjanskaja, M. Krichevskaya, A. Kachina, S. Preis & J. Kallas
THE INFLUENCE OF IRON IONS ON THE EFFICIENCY OF AQUEOUS PHOTOCATALYTIC OXIDATION OF ORGANIC POLLUTANTS
95. A. Golob-Mišić, R. Marković & V. Trujić
DEFINITION OF TOXICITY OF SAMPLES OBTAINED BY NEUTRALIZATION METHOD FROM METALLURGICAL WASTE WATER
96. R. Kovačević, R. Marković & J. Pavlović
DETERMINATION OF ARSENIC, ANTIMONY AND BISMUTH IN SLUDGE ACHIEVED FROM METALLURGICAL WASTE WATER BY ICP-AES
97. D. Manojlović, D. R. Ostojić, B. M. Obradović, M. M. Kuraica, V. D. Krsmanović & J. Purić
USE OF NEW OZONE GENERATOR FOR TREATMENT OF WATER WITH HIGH CONCENTRATIONS OF PHENOLS
98. A. Popara, D. Manojlović, J. Jovičević, B. M. Obradović & M. M. Kuraica
REMOVAL OF ARSENIC FROM DRINKING WATER BY DIRECT OZONIZATION AND FILTRATION
99. A. Zarubica, M. Miljković & M. Purenović
NEW METHOD OF CATALYTIC REMOVAL OF ORGANIC ACIDS (ACETIC AND FORMIC) BY MICRO ALLOYED ALUMINIUM BASED COMPOSITE

8. Biodegradation of toxic compounds

100. S. Lutz, F. Monteau, S. Jurjanz, G. Rychen, B. Le Bizec & C. Feidt
BIOAVAILABILITY OF SOIL-BOUND PAHs INGESTED BY DAIRY COWS
101. D. Lapole, F. Monteau, G. Rychen, S. Jurjanz, B. Le Bizec & C. Feidt
ABSORPTION AND BIOTRANSFORMATION OF PYRENE, PHENANTHRENE AND BENZOAPYRENE IN THE DAIRY GOAT
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105. I. Marova, L. Babak, M. Vavrova, L. Vojtova & J. Jancar
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111. M. Kunaver, A. Kržan, V. Tišler & M. Žigon
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114. S. Milošević, A. Čosović, V. Adamović & M. Grbavčić
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- 114a. M. D. Zuga & L. Alexandrescu
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121. M. Stanković, L. Pezo, A. Jovanović, N. Lazić, B. Simonović, D. Dabić & M. Jovanović
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143. S. Grujić, T. Vasiljević & M. Laušević
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164. N. Villota, F. Mijangos & F. Varona

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Oral presentations

Plenary lecture - Wednesday, Dec. 7th, 9:45

THE EMERGENCE OF STABLE ISOTOPES IN ENVIRONMENTAL AND FORENSIC GEOCHEMISTRY STUDIES

P. Philp

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Stable carbon and hydrogen isotopes have been used for many decades in the petroleum industry as an exploration tool. The development of gas chromatography-isotope ratio mass spectrometry (GCIRMS), permitting determination of both carbon and hydrogen isotopic compositions of individual compounds has lead to a virtual explosion of this technique in petroleum exploration and environmental forensic studies. This paper will present an overview of stable isotope geochemistry and discuss a number of applications to various environmental problems.

The first part will introduce the concept of stable isotopes, with particular attention to carbon, hydrogen, these being the isotopes of greatest importance for environmental studies. Secondly the techniques for determination of the bulk isotope values will be described along with a discussion of the various standards against which the values are measured plus the range, and significance of values that may be expected for each isotope. Thirdly GCIRMS will be described along with advantages, disadvantages, and operating problems associated with this technique.

The second part of the paper will discuss the use of stable isotopes in various types of environmental problems. The first is applicable with either bulk isotope determination or GCIRMS and concerns the use of the isotopes in conjunction with data from other techniques such as GC or GCMS to determine whether or not products are related to each other. This is particularly important where there might be multiple sources potentially responsible for a particular spill and it is necessary to see whether any of them were actually responsible for the spill. The second major type of application is where the contaminant is a refined product or coal tar, with multiple components, and the GC and GCMS data are ambiguous and the relationship between suspected sources and product might only be determined through the use of the stable isotopes. The third approach is where the contaminant is a single component, such as MTBE, PCE, or toluene for example and where GC and GCMS will be of no use in any attempted correlation. The final type of application to be discussed is probably one of the most powerful applications, for compounds such as MTBE, PCE, and volatile aromatics such as benzene and toluene, where the isotope values can be used to evaluate the onset of natural attenuation of these compounds.

Stable isotopes have only been used for a relatively short period of time in environmental studies, but as will be shown in this paper, the approach is a very powerful tool and in some cases, particularly with single components, maybe the only tool available to determine the relationship between a contaminant and suspected sources, or to study the fate of a specific compound in the environment.

Section lecture - Wednesday, Dec. 7th, 10:45

ENVIROMENTAL POLLUTANTS IN THE FOOD CHAIN

N. Katsaros

Director of reasearch NCSR "Demokritos", Greece

During the last fifty years fertilizers have been used extensively in agriculture in order to increase the food production. As a result of that surface water, drinking water fruits and vegetables were contaminated from nitrates mainly. In wells and drills it was found more than 50 mg/L the limit approved by E.U. for drinking water. Similar was the case for fruits and vegetables. Were the levels of nitrates were also above limits. Techniques and methodologies to reduce the amount of nitrates in water will be presented along with the E.U. regulations.

The extensive use of agrochemicals had as a result residues from agrochemicals to be traced in many agricultural fruits and vegetables. Agricultural chemical affect the central nervous system and the hormonal systems. Although the immediate effect of these agrochemical are known the overall effects of various agrochemicals to the organism is not known neither the long term effects E.U. regulations and directives will be printed.

Polychlorobiphenyls, PCB's were extensively used during the last fifty years in generators and transmitters due to their insulating properties. When later it was discovered that PCB's and their by products when burned, dioxins affect the hormonal system and suspicious for carcinogenesis and teratogenesis it was already too late. By E.U. regulations PCB's should be removed from machineries by the year 2007. In the meantime in fish and meat.

Mercury, lead, cadmium, and others heavy metals were found in water, in agricultural products, fish and meat due to the extensive use of these heavy metals when particularly leaded gasoline was used and mercury and cadmium batteries were a priority with the mercury residues thrown into the sea. Methods and elimination producers will be presented.

During the last years there is concern about the genetically modified foods, since are not well known the long term effects in health and the environment. This issue will be extensively presented.

Section 2: Life cycle assessment - Wednesday, Dec. 7th, 11:00

PALLADIUM AND PLATINUM TRANSFER TO MILK AND ORGANS OF LACTATING GOATS

C. Ducoulombier-Crépineau, C. Feidt & G. Rychen

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The use of catalysts by the automobile industry has increased the levels of Platinum Group Elements (PGE) in environmental matrices. Platinum and palladium are used as components of modern three-way catalytic converters. Little is known about the potential transfer pathway of Pt and Pd in the food chain if the metals are ingested by animals (ruminants) eating contaminated grass. Few is known in the case of products (milk) coming from exposed animals. A single oral dose of 200 mg Pt and 200 mg Pd (PtCl₂ and PdCl₂) was administered to goats. The concentrations detected in the milk after the oral administration of Pt are very low, below 0,5 ng/g DW, and showed no significant increase when compared with the control milk. The analysis of the organs of the goats revealed a significant increase of the Pt concentrations in the kidney and liver, respectively of a factor of 73 and 32. The concentration of Pd detected in milk showed a significant higher concentration (9 ng/g DW) than the control milking (1 ng/g DW). The highest concentration was detected in the kidney in which the Pd concentration ranged from 0.5 ng/g DW (control) to 268 ng/g DW at the end of the experiment. This first study demonstrated that the Pt in this form is not transferred to milk contrary to Pd which is rapidly transferred. However, Pd and Pt are both highly detected in the studied organs suggesting a real absorption of these metals. Further studies will be carried out to assess the transfer pathway of other Pt and Pd salts and to measure the effect of a continuous low dose.

Section 2: Life cycle assessment - Wednesday, Dec. 7th, 11:12

EXTRACTION *in vitro* OF SOIL-BOUND PAHs IN THE RUMEN

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PAH contamination of the food chain can be enhanced by exposure of lactating ruminants during grazing, whereby they can ingest up to 1 kg of soil. Extraction of soil-bound PAH in the rumen remains unknown whereas their extraction in the digestive tract of monogastrics has been demonstrated.

A pasture soil was artificially contaminated with the reference molecule benzo[a]pyrene **BaP** and the very ubiquitous phenanthrene **PHE** to study their extractability in the rumen after aging of 1d, 15d or 30d. Radio-labeled molecules were used to facilitate counting of proportions of PAHs extracted from the soil. Three different solvents were compared in order to distinguish the actors of the suspected ruminal effect: water (physical effect), artificial rumen juice (chemical effect) and rumen juice with bacteria (biological effect).

Extraction of PHE was highest (10.6%) before aging (independently from the used solvent). An aging of 2 weeks reduced the extracted proportion at less than 4% of soil-bound PHE using water or artificial rumen liquid. Nevertheless addition of ruminal bacteria allowed to extract as much PHE as before aging. BaP was extracted from soil at 8.3% by the bacteria containing milieu but less than 4% by water or artificial rumen liquid. Contrarily to PHE, no effect of aging was observed for BaP.

This study demonstrated that about 10% of soil-bound PAHs can be extracted in ruminal conditions. This extraction rate in the whole digestive tract of ruminants may be higher *in vivo* as ingested soil is exposed after the rumen to acidity (stomach), bile salts and pancreatic enzymes (small

Section 2: Life cycle assessment - Wednesday, Dec. 7th, 11:24

NATURAL ESTUARINE PARTICLES AND THEIR UPTAKE OF NITROGEN IN ESTUARIES (NEPTUNE)

A. D. Tappin*, M. F. Fitzsimons & G. E. Millward

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Globally, total nitrogen (N) loadings to estuaries will continue to increase due to changes in climate, urbanisation etc. Currently, organic N (ON) constitutes >50% of the total N input to estuaries. However, the speciation and reactivity of ON in estuaries are poorly quantified, thereby invoking major uncertainties regarding the factors controlling the flux of N within and from estuaries. A key uncertainty concerns the particle-water interactions of ON and the role of estuarine master variables in modifying ON partitioning and reactivity.

Suspended particles (SPM) within turbid estuaries such as the Tamar, SW England, can be broadly separated into those that are permanently (P-SPM) and temporarily (T-SPM) suspended. The residence time of P-SPM approximates to that of the surrounding water, and is much shorter than T-SPM. Furthermore, the physicochemical and biological properties of the two fractions are reported to be significantly different. On this basis we aimed to test the hypothesis that the reactivity and flux of ON in turbid estuarine systems is significantly controlled by specific fractions within the SPM population.

We have characterised dissolved constituents and suspended particle fractions from the estuary for contrasting seasons, and have begun to determine the reactivity of the particle fractions to ON, using ¹⁴C-labelled amino acids as proxies for ON, in relation to particle characteristics and the potential master variables of salinity, dissolved organic carbon and bacterial activity. This presentation will provide a synopsis and discussion of the data acquired thus far.

Section 2: Life cycle assessment - Wednesday, Dec. 7th, 11:36

LEACHING BEHAVIOR OF A SOLID WASTE IN LABORATORY TESTS AND LANDFILL

U. Kirso, G. Urb, N. Irha, J. Reinik & M. Laja

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Assessment of the environmental hazard and ecotoxic potential of industrial wastes has become acute problem in many countries including Estonia. To predict the environmental impact of spent shale deposits in Northeastern part of Estonia, it is important to know which compounds could be released to the environment and understand the processes involved. Only based on this information it is possible to characterize the hazard of waste in site-specific conditions, transport and long-term changes in the utilization/disposal conditions.

This study focused on the leaching behavior of the fresh spent shale (semi-coke) and aged material in laboratory as well as in the field conditions. In a laboratory setting a standard two-stage batch-leaching test was applied for samples. The selected compliance test belongs to the so-called shake test, in which the maximum leachable amount is being investigated at the materials own pH-value. In the field the new type of lysimeters, which do not disturb the surface, were used. High amount of hazardous organic compounds, e.g., phenols and polycyclic aromatic hydrocarbons were found in all leachates studied. The matrix composition is found to be more important in field conditions and in laboratory treatment of aged material. The composition of water extracts is highly dependent on test conditions.

The conclusion has made that the adequate hazard identification of a solid waste only on the bases of a one-step laboratory-leaching test is problematic. For risk assessment of an aged solid waste deposit the use of field lysimeters is recommended.

Section 3: Risk assessment - Wednesday, Dec. 7th, 11:48

A RELATION BETWEEN PHYSIOLOGICAL, BIOCHEMICAL AND ENERGETIC RESPONSES IN TERRESTRIAL ISOPODS *Porcellio scaber* AFTER EXPOSURE TO DIFFERENT PESTICIDES

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The environmental hazards of potentially toxic chemicals are usually assessed on basis of toxicity experiments in which selected organisms are exposed to a range of dose levels and exposure responses are evaluated.

In our work we try to assess the physiological, biochemical and energetic parameters of non-target organisms terrestrial isopods as a sensitive indicators of a stress due to exposure to different pesticides, such as organophosphorus pesticides and neonicotinoids. Since both pesticides do not belong to the same group of chemicals, different responses were expected. Adult and juvenile terrestrial isopods were exposed to a laboratory simulated concentrations of organophosphorus pesticide, diazinon and neonicotinoid, imidacloprid. After two weeks of food exposure (up to 150 ug/g dry food for diazinon and up to 25 ug for imidacloprid) of they were evaluated for AChE and GST activity, lipid, protein and glycogen content, feeding activity, weight change and survival. In the case of diazinon a linkage between AChE activity and mortality was observed, but in the case of imidacloprid, the relation between feeding parameters and GST activity was observed. The results of the present study suggest that the most commonly measured physiological parameters do not always provide the most sensitive criteria for establishing ecotoxicological effects. On the other hand, biochemical parameters seem promising to assess and predict the effects of toxicants on nontarget organisms.

Section 3: Risk assessment - Wednesday, Dec. 7th, 12:00

SET OF CORE INDICATORS FOR WATER DURING THE PREPARATION OF LOCAL ENVIRONMENTAL ACTION PLANS IN MACEDONIA

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The Local Environmental Action Plan (LEAP) is a planning document on municipality level that involve developing a community vision, assessing environmental issues, setting priorities and identifying the most appropriate strategies for addressing the top environmental problems in order to achieve the sustainable development of the country.

The preparation of the LEAPs for the Macedonian municipalities started in 1997 and till now around 35 municipalities (from the total 85) have prepared and adopted the LEAPs.

Mostly the State of Environment Assessment in the LEAPs already prepared was presented on very descriptive way, very poor technical data were provided for the representative picture of the environmental conditions and there was no any connection between all presented data in the form of environmental indicators that can provide very simple, easy to show trends over the time.

The new approach includes the adaptation and introduction of the Driving Force, Pressure, State, Impact and Response (DPSIR) methodology and introduction of the environmental indicators for each element of the DPSIR methodology.

The aim of this paper is to present the adaptation and introduction of the DPSIR methodology and environmental indicators (Set core of indicators) for WATER medium in the phase of preparation of the State of Environment Assessment in the National Methodology for the preparation of LEAPs in Macedonia.

Section 3: Risk assessment - Wednesday, Dec. 7th, 12:12

DIETARY EXPOSURE OF THE VOJVODINA POPULATION TO PERSISTENT ORGANIC POLLUTANTS IN THE DANUBE FRESHWATER FISH

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The greatest part of human exposure to persistent organic pollutants (POPs) is attributed to the food chain. Due to processes of bioaccumulation and biomagnification, POP enter practically all environmental compartments, and especially water. Water basins act as the final recipient of toxicants. Thus, aquatic organisms used in human diet are the most significant source of POP exposure of humans. Dietary exposure of human population of Vojvodina to POPs in freshwater fish was assessed on the basis of POPs content in edible parts of fish and average dietary habits of the randomly chosen population groups. The content of POPs was determined by gas chromatography (GC/ECD) in various fish species collected from the Danube in the vicinity of Novi Sad. Dietary habits of 400 randomly chosen subjects (both genders, age 2-65) were assessed using a questionnaire, applied 4 times in a season 2003/2004. Average dietary intake of isomers of HCH and DDT metabolites are 0.10 and 3.64 µg/kg-day, which is below acceptable daily intake (ADI) recommended by FAO/WHO. However, ADI for PCBs is 1 µg/kg-day, and it was calculated that dietary exposure of total population of Vojvodina to PCBs in fish is very high - 6.5 and 5 times higher than ADI for male and female population, respectively. Average daily PCB intake is especially high for children, which may have adverse effects for their growth and development.

Section 3: Risk assessment - Wednesday, Dec. 7th, 12:24

ESTIMATION OF POTENTIAL DERMAL AND INHALATION OPERATOR EXPOSURE TO MALATHION IN REPRESENTATIVE FIELD CONDITIONS

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One of the elements in the risk assessment procedure for the placement of a plant protection product on the market is the estimation of potential exposure of the operators. For EU countries, this procedure is described in the Directive 91/414/EC and is generally based on the use of two mathematical models. In the present study the potential operator exposure was estimated and compared in two experiments run in Serbia (Topola) and Greece (Heraklion) in June-July, 2004. Both experiments were conducted in triplicate and followed the same protocol with two malathion EC formulations. In the first experiment a knapsack mistblower was used to spray apple trees in an orchard in Topola with Ethiol. In the second experiment a high pressure hand held lance was used for the application of Malathion 50-EC to orange trees in Heraklion. For monitoring of dermal exposure the whole body dosimetry method was applied using 100% cotton coveralls. Inhalation exposure was measured using personal air pumps and tubes with XAD-2. For the monitoring of hand exposure, nitrile gloves were used. The potential dermal exposure of the operators ranged from 19.2 to 49.3 ml of spray solution per hour (s.s./h) for the whole body, and from 0.0 to 2.3 ml s.s./h for hands in both experiments. The potential inhalation exposures were estimated to be in the range of 0.01 to 0.06 ml s.s./h based on an breathing rate of 25 L/min. The coefficient of variation or the whole body exposure was 43% for the Topola experiment and 0.7% for the Heraklion one.

Section 3: Risk assessment - Wednesday, Dec. 7th, 12:36

DETERMINATION OF POPs IN GASEOUS PHASE BY ACTIVE AND PASSIVE SAMPLING METHODS

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Damaging of industrial and military targets, natural resources, infrastructure, and homes in the Former Republic of Yugoslavia during the Balkan conflict situation and war accident resulted in the release of the large quantities of chemicals, including persistent organic pollutants (POPs), into the environment. The results of recent investigations of the POP contamination within the project APOPSBAL INCO COPERNICUS - ICFP501A2PR02 in the vicinity of damaged industrial and military objects indicated serious pollution problems in Croatia, Serbia and Bosnia and Herzegovina.

The aim of this research is to determine and define the content of POPs in air samples in gaseous phase in the town of Kragujevac, the zone potentially impacted by the POPs, using active and passive sampling method. Paper presents selected original results obtained during air sampling campaign conducted in July 2004 (active method) and during the period September 2004 - June 2005 (passive method). Passive air samplers were employed in this study as a technically feasible and cost-effective alternative for investigating chemical signatures in the air, capable of semi-quantitative measurements of the air pollution as well as relative comparisons of the individual sampling sites.

This type of air analysis on presence of PCBs, HCHs, DDT/metabolites and PAHs was performed for the first time in Serbia.

The residual concentrations of POPs on investigated localities were detected.

Section lecture - Wednesday, Dec. 7th, 13:00

POLYCYCLIC AROMATIC HYDROCARBONS AND TRACE ELEMENT DISTRIBUTION IN NOVI SAD

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Concentrations of 16 EPA polycyclic aromatic hydrocarbons (PAHs) and eight trace elements in the surface soil samples of Novi Sad city urban area and in the Danube bank sediment sample were measured. The results correspond to a network of six representative sampling sites in which the main soil properties, organic matter, water content, pH and particle size have also been determined. The total content of PAHs, i.e. P AHs level ranged from 310 to 1,450 µg/kg while arithmetic mean value of 946 µg/kg and median of 375 µg/kg obtained from soil samples throughout Novi Sad urban area. Data were compared with the ones found for soil and river sediment throughout the world, and with target values set by Dutch authorities.

It was introduced the total carcinogenic potency that was calculated for each sampling site on the base of the Benzo(a)pyrene Equivalent factors. The reference total carcinogenic potency was suggested to be calculated on the base of Dutch target concentrations of PAHs for unpolluted soil. It revealed only one sampling site through Novi Sad with carcinogenic potency below the value calculated for unpolluted soil. Also, our data were compared with the Polish standard soil PAHs contamination.

The geometric mean content of Zn, Cu, Cd and Pb obtained from soil samples throughout the Novi Sad urban area (61.32, 28.39, 0.151 and 2.70 mg/kg, respectively) was compared with the geometric mean concentration in world soils and with the allowed ones set by Dutch authorities. The special soil metal index was proposed for the whole soil heavy metal burden and calculated for each investigated locality. On the base of these data it was detected only one site with Zn and Cu content higher than the allowed ones set by Dutch authorities used for investigation of a site for possible rehabilitation (Dutch A values).

Section 4: Green chemistry - Wednesday, Dec. 7th, 13:15

DEGRADATION OF POLLUTANTS IN AQUEOUS SOLUTION BY A POWERFUL COMBINED PHOTOCATALYTIC SYSTEM (IRON-TiO₂)

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Heterogeneous photocatalysis with titanium dioxide has been largely investigated as a method for pollutant degradation. The principle of photocatalysis is well known: by irradiation of semiconductor with light of energy higher than the band gap ($\lambda < 400$ nm) the pair of charge carriers (electron-hole) is formed. In the absence of suitable scavengers, recombination of electrons and holes occurs within a few nanoseconds. The recombination of electrons and holes is the reaction limiting the efficiency of this process. To suppress this reaction, different substances, which are able to trap electrons and prevent electron-hole recombination are added. Among them transition metals have been used to prevent the electron-hole recombination. In the work reported here we investigated the influence of ferrous and/or ferric ions, which was one of the most efficient and used transition metals.

Kinetics of oxidative photodegradation of Monuron (3-(4-chlorophenyl)-1,1-dimethylurea) in different photocatalytic systems (iron, TiO₂ and combined system iron + TiO₂) were investigated and compared. The influence of iron addition on TiO₂ photocatalyst and of TiO₂ on the photocatalytic cycle Fe(III)/Fe(II) were carefully studied. A very positive effect of iron addition was observed. This phenomenon was more and more pronounced when TiO₂ concentration was lower. In a suspension of TiO₂ (24 mg·L⁻¹) with addition of Fe(III) (3·10⁻⁴ mol·L⁻¹) the measured rate constant was similar to that obtained in a suspension of TiO₂ with a concentration more than 20 times higher (500 mg·L⁻¹). The mechanistic approach carried out in this study allows us to identify the main reactions governing the combined system and a photochemical cycle was proposed. The optimisation of the photocatalytic systems was obtained when each photocatalyst plays a specific role: Fe(III) as a main ·OH radicals source and TiO₂ as an oxidizing agent of Fe(II).

Section 4: Green chemistry - Wednesday, Dec. 7th, 13:27

ASYMMETRIC SYNTHESIS OF α -AMINO ACIDS USING NOVEL CHIRAL FUNCTIONALIZED INORGANIC CATALYSTS

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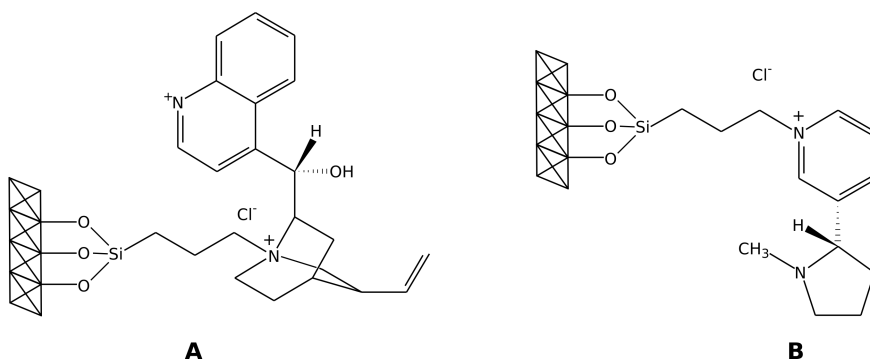
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Asymmetric synthesis of α -amino acids has been extensively studied using homogeneous chiral catalysts for many years. However, these catalysts often cause problems related on their recovery and recycle. Soai and co-workers described for the first time the use of functionalized alumina or silica as heterogeneous chiral catalysts in enantioselective alkylation's reactions with high stereoselectivities. Encouraged by these results, we prepared novel functionalized chiral catalysts on activated silica gel and examined their catalytic activity on the asymmetric synthesis of α -amino acids. Specifically, we synthesized two novel functionalized catalysts **A** and **B** outgoing from the chiral auxiliaries, (+)-cinchonine and (S)-(-)-nicotine. The novel catalysts result in high chemical yields and in some cases in virtually complete asymmetric induction of α -amino acids (ee > 98%) using protected glycine derivatives. The advantages of the novel catalysts are their easy removal from the reaction mixture by simple filtering and their recycling. Thus, the novel functionalized organo-inorganic catalysts **A** and **B** should play an important role in the new greener industry by replacing hazardous and environmentally threatening chemicals. Further studies of these novel phase-transfer catalysts are now under investigation.



Section 4: Green chemistry - Wednesday, Dec. 7th, 13:39

OPTIMIZATION OF PETROLEUM RAW MATERIAL TO OBTAIN ECOLOGICALLY PURE PETROLEUM PRODUCTS

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The quantity of sulfur and high-sulfur oils in the total balance of the oil refining in Russia and abroad is continuously increasing at the simultaneous toughening of environmental requirements to the quality of commercial products.

Sulfur is believed to be the most important element among the oil heterorganic elements due to its wide occurrence and significant negative effects mainly caused by the presence of the sulfur compounds (SC) in petroleum products.

A highly toxic and corrosion-active sulfur dioxide is formed during combustion of sulfur-containing fuels in motors and furnaces. Ever-increasing environmental requirements make to strictly limit the allowable sulfur content in petroleum products, especially in motor fuels that are extensively burnt in modern devices in the largest amounts.

A significant part of the sulfur-containing oil compounds is found in the composition of the light products upon refining. Thus, the sulfur moiety in diesel fractions of low-sulfur oils may reach 0.3-0.4 wt%, and in case of high-sulfur oils - 1.0-1.5 wt% and sometimes it even may surpass 3 wt%.

The list of sulfur-containing compounds of oils includes the elemental sulfur, hydrogen sulfide and sulfur organic compounds, including mercaptanes (thioles), R_1-S-R_2 (thioesters), where R_1 and R_2 are alkyl, cycloalkyl or aryl groups, alkylthiaclopentanes (thiophanes), alkylthiacyclohexanes, thiaindanes, thiophenes, their various naphtheno- and arenoderivatives, as well as disulfides and cyclic compounds containing N or O atoms in the molecules, except for sulfur atom. Organic sulfur compounds always make no less than 98% of total SC in oils.

Alkylthiols, dialkylsulfides and disulfides are present only in light oil distillates; their concentration drastically decreases with the rise in the boiling point, becoming negligible in the fractions b.p. $>300^{\circ}\text{C}$. These compounds are instable and decompose at the temperatures below 100°C and even lower, contributing to the corrosion of the refinery equipment.

As far as concerns the cyclic SC, only the lowest cyclic SC, containing no more than 2-3 rings, pass into the composition of the light (gasoline and diesel) distillates.

During a prolonged contact with air (for example, during storage of petroleum products) the saturated sulfoxides are comparatively readily oxidized by air and turn into sulfoxides, which are less stable than the initial SC and start decomposing with significant rates at the temperature about 70°C already.

Aromatic SC - arenothiols (thiophenols) and arenothiophenes are much more stable and possess about the same thermal stability as aromatic hydrocarbons with similar carbon molecular frameworks.

Modern technologies of the production of low-sulfur petroleum products are usually divided into 1) those based on the catalytic hydrogenation and 2) those based on non-catalytic methods for SC removal from the raw material composition:

1. Catalytic desulfurization of petroleum products
2. Non-hydrogenation methods for motor fuel desulfurization:
 - shift of the boiling point via alkylation
 - desulfurization via extraction
 - desulfurization via the processes of conversion and extraction
 - selective oxidative desulfurization
 - desulfurization through deposition
 - adsorption desulfurization

Selective oxidative desulfurization of sulfur compounds into hydrocarbons and volatile sulfur products is very attractive. An important economic benefit may be obtained by the replacement of the expensive hydrogen that is usually used to manufacture the petroleum products with a very low sulfur content.

Ozone is one of the promising reagents for preliminary oxidative treatment of petroleum distillates requiring the SC removal. It actively interacts with many sulfur-containing compounds and polycycloaromatic hydrocarbons although has not been applied in refinery practice yet.

Currently the transformations of oil components during ozone treatment have been extensively studied at the Institute of Petroleum Chemistry, SB RAS.

Electrophilic reactions of ozone addition at the S atom in saturated sulfides over the C=C bonds in the molecules of olefins, thiophenes, and benzothiophenes occur with extremely high rates (the constants of reaction rates $k=10^4$ - 10^5 l/mol·s) that weakly depend on the temperature. As an ozone treatment result, the saturated oil sulfides may be practically quantitatively transformed into sulfoxides, which are gradually oxidized into sulfones in the presence of ozone excess. Thiophene and benzothiophene derivatives quickly fix O_3 molecules over C_2 - C_3 bonds and form ozonides that decompose under heating or action of alkali solutions to yield acidic products extracted by an alkali from hydrocarbonaceous medium.

Taking into account the feasibility of different versions of treatment and removal of the ozonolysis products from the reaction mixtures, one should agree that this approach gives considerable opportunities at the desulfurization of oil fractions.

A new method for preparation of straight-run distillates for catalytic hydrodesulfurization has been proposed that consists in raw material ozonolysis followed by the thermal treatment of reaction products at the temperatures above the decomposition points of the organic peroxides (ozonides) formed (theoretically above $\sim 110^\circ\text{C}$). These consecutive operations allow more than a half of sulfur (54%) of the oil fraction 140-380 $^\circ\text{C}$ to be removed.

The adsorption purification of the non-thermolized and thermally treated products of raw material ozonolysis provides for 75-78% of the desulfurization degree. The introduction of the thermal treatment stage in the above process series enables the reduction of the undesirable loss of hydrocarbons in the form of the adsorbates obtained.

These results evidence that the ozonolysis of the straight-run diesel fractions followed by thermal treatment and adsorption purification of the conversion products may become a promising alternative method for desulfurization of motor fuels that does not require the application of catalysts, hydrogen and high temperatures.

Section 12: Marine chemistry and marine pollution - Wednesday, Dec. 7th, 13:51

FATE OF POPs IN THE VENICE LAGOON: INSIGHTS FROM AN OVERVIEW OF ENVIRONMENTAL, BIOLOGICAL AND HUMAN MILK CONCENTRATIONS

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Since decades the Venice Lagoon has been receiving discharges of many classes of pollutants from its drainage basin and from urban and industrial areas laying on lagoon borders. POPs, which are mainly resulting from industrial activities, have therefore been accumulating in sediments and might represent a threat to human health. In particular, intensive harvesting of Manila clam (*Tapes philippinarum*) and other traditional fishing activities carried out in the lagoon, represent the highest direct source of risk for human health.

In order to evidence different levels of POPs' contamination and disentangle the main sources of these pollutants, data of dioxins and other POPs for atmospheric depositions, water and sediments collected in several sites of the Venice Lagoon, are presented. Moreover, dioxins and PCBs data, and dioxins fingerprints for both sediments and Manila clam evidence that sediments are the main direct source of contamination for this benthic bivalve, and highlight the main source of POPs for different areas of the lagoon. A regression model between sediment and clam's toxicity is identified as a valuable tool for health risk assessment. In fact, it allows for estimating clam toxicity from known concentrations of dioxins in bottom sediments, while human health risk is assessed on the basis of total daily intake estimated for local population. Finally, recent data of POPs in breast milk of mothers living in Venice confirm a non-negligible human health risk for regular shellfish consumers. Conclusions suggest for keeping some lagoon areas restricted to fishing and for maintaining current situation under monitoring.

Section 12: Marine chemistry and marine pollution - Wednesday, Dec. 7th, 14:03

VARIABILITY OF MERCURY FLUXES BETWEEN A TIDAL ESTUARY AND THE SEA

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Ria de Aveiro (Portugal), a coastal lagoon that exchange with the Atlantic Ocean, received during 50 years the effluent of a chlor-alkali industry and consequently several tons of mercury were buried in the sediments of an inner basin. Previous studies reported exportation of mercury from the contaminated area to the rest of the lagoon. Besides, levels found in estuary mouth during ebb tide evidenced the transport of mercury to the coastal zone.

In this paper, the tidal dynamics of mercury species at the outer part of the lagoon were studied during 4 tidal cycles, in contrasting season and tidal regimes, in order to quantify the importance of the lagoon waters as carriers of mercury to the nearby coastal area. Fluxes between the estuary and the coastal area for each tidal cycle were estimated from the water flux as derived from a two-dimensional vertically integrated hydrodynamic model and using the concentrations measured at the lagoon mouth. The results showed that both the magnitude and the sign of fluxes are highly dependent of the season and tidal regime. It is known that mercury leaves the contaminated inner basin essentially associated with suspended matter. This study shows that after estuarine transit, mercury continues being transported mainly by particulate fraction playing a major role in the exchange of mercury between the Aveiro lagoon and the sea. The fluxes of dissolved mercury seem to exhibit high variability with season and tidal regime with consequences in bioavailability to coastal organisms.

Plenary lecture - Wednesday, Dec. 7th, 15:30

RAPID DEVELOPMENT OF THE ANALYTICAL INSTRUMENTATION AND ITS INFLUENCE ON THE ENVIRONMENTAL SCIENCE

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The development of the analytical instrumentation is a good example of an excellent cooperation between different sciences and technologies. This good cooperation has enabled very rapid development of the adequate and easy to use instrumentation. Provided with adequate and easy to use analytical instrumentation the Environmental Science has experienced an evident positive development and also very positive influence on the development of the awareness of the majority of the population and governmental authorities in charge for the environmental issues.

In the past the analytical instrumentation has been based mostly on the wet chemical and electrochemical methods and the optical spectroscopy. The fast development of the micro electronics and well financed military and space projects have enabled the use of the new technologies in the analytical instrumentation development and even deploying part of it on the space platforms opening a new era of remote sensing. Also the availability of the powerful coherent light sources has enabled the realization of a number of the surface laser based remote sensing methods. The very similar development of the instrumentation in Meteorology and Hydrology has made the very valuable data from these fields of science readily available for the analysis and the mutual correlation to the results of the environmental measurements. The ample data management has become one of the hot issues and the application of the artificial intelligence for data analysis and correlation is opening possibilities for saving the time and man power for the other more demanding tasks.

The complete review of the modern environmental instrumentation is almost impossible in a given limited time and space. The emphasis will be given to the air pollution instrumentation and its influence on the Environmental Science. Within this, certainly not limited field, the special accent will be given to the instrumentation for remote sensing and the mass spectrometry based instrumentation.

The outlook for the further development of the environmental instrumentation is very bright owing to the on march of micromachining methods, microelectronics and nanotechnology. The time when the hand held instruments for the complex and complete analytical measurements will be broadly available is coming soon.

Section 5: Soil contamination, depollution technologies - Wednesday, Dec. 7th, 16:05

ARE POLYETHYLENE FILMS WITH PROOXIDANTS BIODEGRADABLE?

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Biodegradability of high density polyethylene film (HDPE) and low density polyethylene film (LDPE) both additivated with balanced content of antioxidants and prooxidants was studied with defined microbial strains particularly with *Rhodococcus rhodochrous* and *Nocardia asteroides* in mineral medium. The abiotic pretreatment consisting of thermooxidation and photooxidation corresponding to about three years of outdoor weathering resulted to complete loss of mechanical properties and disintegration into small fragments. The samples were then inoculated, incubated up to 200 days and during this period the metabolic activity was monitored by measuring ATP content. Simultaneously the cultures were controlled also by optical microscopy and FTIR spectroscopy. In a first initial phase of fast growth was observed, it was due to the presence of low molecular extractable compounds as shown from ¹H NMR analysis of the incubation medium. Then along period of stabilized metabolic activity took place, suggesting that microorganism continued to gain energy from the substrate but evidently at much slower rate. Complementary analysis carried out at the end of the incubation showed that during the experiment time biodegradation processes probably affected superficial layer of materials only. This new polymer material represents perspective solution to the problem of visual pollution by plastic litter but its ultimate degradability must be further studied.

Section 5: Soil contamination, depollution technologies - Wednesday, Dec. 7th, 16:17

DISTRIBUTION AND SPECIATION OF IODINE AND BROMINE IN TWO FOREST SOILS

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Halogen compounds are present in soil as a result of natural and man-made processes. Their sources in the environment are diverse and include atmospheric deposition, bedrock material, agricultural products, marine biota, etc. Among these, atmospheric deposition is considered to be the most important source.

The aim of this study was to examine the natural enrichment processes of halogens in soils at two forest sites in the vicinity of Heidelberg, Germany. The bedrocks at the sites differ, one of them is a limestone while the other is a sandstone. The bromine and iodine distributions were examined in soil, soil solutions, rocks, wet deposition, leaves and leaf litter using various methods such as INAA, XRF, ICP-MS and IC/ICP-MS.

Bromine concentrations in rain were 2.5 ± 0.4 µg/l while iodine concentrations were 0.38 ± 0.01 µg/l. Iodine and bromine concentrations in soil ranged from 0.6-15 mg/kg and in soil solutions they varied between 0.5 and 43 µg/l. The distribution of iodine and bromine in the soil profiles showed similar trends. Speciation results revealed the presence of two "mechanisms" controlling the iodine and bromine distribution in soil. In the topsoil, halogens tended to be more in an organic form (60-100%), while in the lower soil sections the inorganic fractions increased compared to upper sections. Furthermore, in organic rich soil horizons the halogens are influenced by soil organic matter. The iodine and bromine sources are mainly atmospheric deposition while in one site an additional influence from basement rocks was observed.

Section 5: Soil contamination, depollution technologies - Wednesday, Dec. 7th, 16:29

EFFECT OF DAIRY EFFLUENTS PRE-TREATMENT ON N₂O EMISSIONS AND N-ORGANIC DEGRADATION AFTER SOIL APPLICATION

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Nitrous oxide (N₂O) is a potent greenhouse gas that plays a key role in climatic forcing contributing to the greenhouse effect by about 4%, and also contributes to stratospheric ozone depletion. On another hand, cattle slurries are commonly applied to agricultural soils, inducing an increase of soil nitrous oxide emissions. Therefore, many procedures were developed for slurry pre-treatment in order to improve soil slurry application and reduce nitrogen losses, namely N₂O emissions.

The aim of this work was to compare N₂O emissions and the kinetic of N organic degradation from treated and untreated cattle-slurry after incorporation in agricultural soils.

Laboratory incubations of mixture soil/slurry were performed under controlled temperature (20°C) and moisture content (28%), and the N₂O emissions and the mineral nitrogen content of soil were measured during 94 days. The whole slurry (WS) was compared to the liquid (LF) and solid fractions (SF) obtained by mechanical separation of the whole slurry, and to the superficial (PAM-sup) and sediment (PAM-sed) fraction obtained by chemical separation of the liquid fraction with a chemical agent, polyacrylamide (PAM). Results obtained showed that slurry pre-treatment allows decreasing N losses from soil (total N emissions) observed after slurry incorporation. Furthermore, it was observed a liquid mineralization of 4.8% of the WS organic N, and immobilization of 23.1% in treatment with SF, 23.9% with LF, 4.6% with PAM-sed and 6.9% with PAM-sup.

Section 5: Soil contamination, depollution technologies - Wednesday, Dec. 7th, 16:41

A 25-YEAR RECORD OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOILS AMENDED WITH SEWAGE SLUDGES

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We studied polycyclic aromatic hydrocarbons in crop soils amended with 1,000 tons dry weight of sewage sludges per 10,000 m² from 1974 to 1992. Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds widely occurring in various media such as soils, sediments, waters, aerosols, food and living organisms [1]. PAHs are of environmental concern because some PAHs such as benzo[a]pyrene have shown mutagenic and carcinogenic properties. Furthermore, light aromatic hydrocarbons occurring in contaminated soils and tars inhibit the growth of plants. The knowledge on the fate of PAHs in soils amended with sewage sludges is scarce, notably in the long term. Here we report PAH levels in experimental maize crop soils during sludges addition (1974-1992) and after sludges addition (1993-1999). The first major result is that control soils do not show any increase of PAH levels, despite the location of control plots within a frame of other plots that were heavily amended with sewage sludges. This finding gives evidence for the absence of significant horizontal contamination from amended plots. The second major observation is that the total PAH level is still twice higher than background 7 years after the last sludges addition, despite conditions which should have favoured their degradation and washing.

References:

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Section 5: Soil contamination, depollution technologies - Wednesday, Dec. 7th, 16:53

CHEMICAL DECHLORINATION OF POLYCHLORINATED BIPHENYL (PCB) IN DIELECTRIC OILS ENHANCED BY ULTRASOUND

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In the last decades polychlorinated biphenyl compounds (PCB) were commonly used in transformer oils as additives for their excellence dielectric properties. Due to their recognised high toxicity and the more stringent environmental law they must be reduced to very low level. Recently, many investigations have been devoted and many methods have been developed for processing these compounds. This paper reports the results of an experimental approach based on the chemical dechlorination of some transformer oils through out a nucleophilic substitution of the chlorides of the PCBs by poly(ethylene glycol) to produce an aryl poly(ethylene glycolate) and KCl. In the studied two-phase system the displacement of a chloride ion from the chlorinated substrate should be rapid only if the glycol alkoxide agent and the PCB are in the same phase.

The influence of temperature, PEG/ KOH content and ratio, were investigated. Ultrasound was used in some cases whose effect was in the sense of a marked reduction of both test duration and process yield. In all cases, the process was followed by determining the chloride content at defined time in the glycol phase.

PCBs content in the oil phase was determined using a gas liquid chromatography (GLC). Dechlorination of PCB by chemical treatment is effective but strongly dependent on the nature of matrix oil. PCBs can be removed up to lower than 20 ppm also at less severe operating condition ($T < 95^{\circ}\text{C}$). Stirring condition seems to affect markedly the process yield influencing the homogeneity of two phase system (oil / glycol). Ultrasound can improve the process efficiency by making operating condition less severe.

Section 5: Soil contamination, depollution technologies - Wednesday, Dec. 7th, 17:25

HEAVY METAL POLLUTION IN SUVA HARBOR SEDIMENTS, FIJI

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Pollution of the environment is a major world-wide issue. In Fiji, contamination of the coastal environment by heavy metals is proving to be a real concern.

The work reported here was carried out to ascertain the extent of anthropogenic contamination by heavy metals in the <0.063 mm surface sediments of Suva harbour. Sediment samples from 40 sites selected within the harbour were collected and analyzed for five heavy metals. The levels of the metals range from 21.4 to 143.0 ± 0.1 ppm Cu, 1.40 to 4.87 ± 0.07 wt% Fe, 22.1 to 93.5 ± 0.3 ppm Pb, 40.2 to 269.0 ± 0.3 ppm Zn and 1.1 to 2.6 ± 0.2 ppm Sn.

With reference to the pristine area of the Great Astrolabe, in Kadavu, the acquired data from the harbour are indicative of heavy metal pollution. This could be attributed to the numerous industrial and commercial activities at Wailada and Walu Bay industrial areas, the municipal dump located at the Suva foreshore and the Suva wharf. This pollution is further compounded by the high population density in Suva city.

Section 5: Soil contamination, depollution technologies - Wednesday, Dec. 7th, 17:37

EFFECT OF CHELATES ON CHROMIUM AND NICKEL MOBILITY AND ON THEIR UPTAKE BY *Datura innoxia* FROM AN INDUSTRIAL SOIL

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Phytoextraction of metals from polluted soils is an attractive method because it is environmentally friendly and cheaper than conventional physical and chemical methods. Two approaches are possible: the use of hyperaccumulator plants, which produce a low biomass or the use of tolerant plants, which produce a high biomass, coupled with the addition of chelates.

In a phytoremediation perspective, several chelates (EDTA, citric acid, DTPA and histidine) have been tested. An application of these chelates has been carried out at different concentrations on an industrial soil contaminated by chromium and nickel, in order to solubilize both metals. EDTA and citric acid have been the most effective and an "optimal" concentration has been determined ($0.05 \text{ mol}\cdot\text{L}^{-1}$) for an application on the soil.

Thereafter, we investigated the effect of EDTA and citric acid, on chromium and nickel uptake and accumulation by *Datura innoxia*. The "optimal" concentration being too high for a good development of plants, lower application rates are used to evaluate the efficiency of these chelates. Two application modes have been used. In one case a single dose was applied after the transfer of *Datura* on the polluted soil and in the other case there were two doses, the first after the transfer on the soil and the second after seven days of culture.

The results showed that citric acid has been the most effective for uptake and translocation of both metals, Cr and Ni. Cr uptake was more effectively than Ni and was mainly accumulated in the stems.

Section 8: Biodegradation of toxic compounds - Wednesday, Dec. 7th, 17:49

PHOTOTRANSFORMATION OF CARBAMAZEPINE IN ESTUARINE WATERS

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This work deals with the phototransformation of organic pollutants in estuarine waters. Carbamazepine proved to be a good chemical probe for examining indirect photolysis due to its limited reactivity by either direct photolysis or dark reaction pathways and its ubiquity at trace level in the Rhône river delta waters (France). A multivariable kinetic model of aqueous carbamazepine photo-degradation was developed as a function of dissolved organic matter (DOM), nitrate, iron and chloride ions (Cl⁻) at concentration values commonly observed in natural estuarine waters. Several pathways were available for carbamazepine photodegradation in this system, including direct photolysis and indirect photooxidation. By-product identification by liquid chromatography tandem mass spectrometry indicated that carbamazepine is converted to acridine, a stable product associated with direct photolysis alone. With respect to indirect photolysis, an enhancing effect of chloride ions was observed at environmentally relevant pH and dissolved iron was the most relevant variable responsible for the increase of the rate of carbamazepine degradation. The Fe(III)-photoinduced reaction depends on the pH of the solution, degradation rate being much higher at acidic pH than at neutral pH. At pH 2 hydroxylation pathways prevailed. However, in presence of a high Cl⁻ concentration (15 g·L⁻¹) a chlorination pathway also took place. This competitive pathway resulted in a decrease of the carbamazepine photodegradation rate, because part of the absorbed light was channeled into a series of reactions leading to Cl₂^{•-} (2.09 V vs NHE) radical rather than to the more reactive hydroxyl radical (2.8 V vs NHE). At pH 7 hydroxylation hardly took place, while in presence of Cl⁻ chlorination pathway was still active. This later pathway accounted, to a large extent, for the observed increase in carbamazepine degradation rate in neutral solutions containing both iron and Cl⁻ with respect to solutions containing iron alone. This work should contribute to get more insights into the environmental significance of abiotic chemical processes for organohalogen production in saline waters.

Section 8: Biodegradation of toxic compounds - Wednesday, Dec. 7th, 18:01

CARBON, OXYGEN AND SULPHUR ISOTOPIC PICTURE OF MICROBIAL BIODEGRADATION OF CONTAMINANT HYDROCARBONS

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We have analyzed about 30 samples of water contaminated by hydrocarbons (a restricted industrial area). The mean concentration of DIC (Dissolved Inorganic Carbon) in groundwater, varied from 228.90 mg/dm³ (winter) to 519.47 mg/dm³ (summer). Likewise, the mean $\delta^{13}\text{C}_{\text{DIC}}$ value in winter was -16.16‰, and that in summer was -19.92‰. It was observed that increasing concentration of ¹³C-depleted DIC, was accompanied by decreasing concentration of ³⁴S- and ¹⁸O-depleted SO₄²⁻ ions dissolved in water. This resulted from an advanced microbial oxidation of ¹³C-depleted hydrocarbons and simultaneous microbial reduction of ³⁴S- and ¹⁸O-depleted SO₄²⁻ dissolved in water. It was calculated from isotope mass balance that, from about 16 to 33% and from about 50 to 72% of DIC in groundwater formed due to microbiological decomposition of hydrocarbons during winter and summer, respectively.

Section 8: Biodegradation of toxic compounds - Wednesday, Dec. 7th, 18:13

CHARACTERIZATION OF BIOCOMPATIBLE HYDROGELS: DEGRADATION AND ENVIRONMENTAL IMPACT OF THE PRODUCTS

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Copolymers of lactic and glycolic acid have been recognized as biocompatible, bioresorbable and biodegradable polymers. Nowadays, these compounds are used as controlled drug delivery systems and also as materials for surgical sutures and osteosynthesis. An important property of these polymers is the possibility of modulation of their life-time and/or their physical properties by changing their composition. The importance and application range of these materials have been increasing gradually. Nevertheless, in spite of the fact that the degradation mechanism of these copolymers has been a subject of numerous studies, it is not fully understood till now, because the results of various degradation studies are somewhat unclear and in some cases even controversial.

The aim of this study was the elucidation of the degradation pathways and environmental impact of degradation products of special well-defined "smart" amphiphilic, end-functionalized hydrogels prepared from biodegradable and biocompatible monomers gained preferably from renewable sources. The polymers selected for the study were synthesized by co-polymerization of poly(D,L-lactide-co-glycolide) (PLGA) and/or poly(D,L-lactide-co-glycolide) grafted with poly(ethylene glycol) (PLGA-g-PEG) and additionally modified by itaconic acid. They were subjected to degradation under strictly controlled conditions and the degradation products were characterized by chromatographic methods (SEC, RP-HPLC), selected spectral methods (IR, NMR, MS) and by toxicity tests.

Acknowledgement: Financial support from Ministry of Education, Youth and Sports under MSM 021630501 is greatly appreciated.

Plenary lecture - Thursday, Dec. 8th, 9:00

ASSESSMENT OF AIR QUALITY IN THE COLOGNE CONURBATION USING PINE NEEDLES AS A PASSIVE SAMPLER

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The negative influence of human activities on air quality has been known for decades now and numerous measures and regulations against excessive air pollution have been implemented. Withstanding these efforts to maintain high air quality, especially in densely populated areas, emissions from power plants, domestic heating, industry and especially motorized traffic are still a matter of concern. Within Europe the issue of (transboundary) air pollution is addressed by e.g. the first EU Daughter Directive and assessed and reported by EMEP. The rigid directive requires an atmospheric quality standard that is not met by large conurbations in several countries. In 2005 the major German cities of e.g. Hamburg, Munich, Cologne and Berlin had exceeded the allowed number of 30 daily peak values for fine particulate matter (PM₁₀) already during the first quarter. Envisaged atmospheric-environmental protection measure included a driving ban to be issued for diesel-powered vehicles in inner city-regions. Such measure do impose a very dramatic impact on local socio-economic structures and thus have yet not been enforced. However, European Union environmental legislation does require that actions will have to be taken in the very near future to ensure adequate atmospheric quality, even in busy conurbation areas.

Environmental monitoring networks in most conurbations do not allow for spatially and temporally highly resolved analyses of variability in air quality and assessment of urban-rural gradients in atmospheric pollution. For budgetary reasons the establishment of a dense monitoring network using active air sampling is beyond realization. Thus remote sensing operations and modelling are applied to gain insight into regional variability. Spatial resolution in remote sensing, however, in most cases does not allow for identification of local air quality gradients.

Alternatively, biomonitoring has been implemented as a means of local, regional and supra-regional control of air quality. Advantages of biomonitoring, beside in general being most affordable include the following. Spatial resolution in biomonitoring can be set according to needs in most cases and due to low costs often allow for high density observation networks. Biomonitoring can be applied in a way that abundance and composition of indicator plant species and their condition can on the one side be directly used as an air quality assessment tool. On the other side, vegetation can be used as passive sampler for gaseous and particle-bound atmospheric pollutants, whereby perennials may offer means to obtain time-integrated pollution records for up to several years. Thus at locations where enhanced pollution load has been detected, temporal trends in air quality can be reconstructed. A variety of plants are in use for biomonitoring air quality amongst others including mosses, lichens, cabbage, grasses, deciduous and conifer trees.

For a biomonitoring study of variability in air quality in the Cologne Conurbation we selected Black/Austrian Pine (*Pinus nigra*) as passive sampler of atmospheric pollutants. Austrian Pine is frequently used as ornamental tree and thus available throughout the entire study area. In comparison to other pine species like *Pinus sylvestris*, which is often used in other studies, *Pinus nigra* is far more abundant in inner city areas and easier to sample because of low growing branches. We determined the

following pollutants and pollution proxies on pine needles in the Cologne Conurbation. Magnetic susceptibility was taken as a proxy for combustion particle load, which was verified by analyses of iron content of pine needles and REM-analyses of needle particulates. The good correlation between susceptibility and iron was attributed to the presence of magnetite spherulites generated upon combustion in power plants and vehicle engines. Determination of magnetic susceptibility offers a very cost-effective means to identify pollution gradients and hot-spots that may be investigated in more detail using more sophisticated but also more expensive techniques.

Various environmentally relevant trace elements (Pb, Cd, Hg, Ni, Ba, Sb, etc.) by their absolute concentration allow identification of problem areas. Their relative composition gives a fingerprint that may be used for identification of possible sources and/or apportioning thereof. Since the ban of tetraethyl-lead as anti-knocking agent in Germany in 1988, the concentration of traffic-sourced Pb-pollution has decreased dramatically. In the Cologne Conurbation we note Pb-concentrations in pine needles ranging from 0.2 to 6 ppm with a median at 1.0 ppm. The Pb-loads generally correlate with the Cd-concentrations in needles that span the range from 0.02 to 0.4 ppm. Locally strongly enhanced Cd-concentrations were detected exclusively in industrial areas. The lack of covariance of other metals (Ni, Co, Cr) with combustion-derived Fe points against a traffic or power-plant source for these elements but indicates a predominantly industrial origin. A suite of platinum elements including Pt, Pd, Rh, Ru are characteristic for catalytic converter emission that may approach significant loads in heavy traffic areas. We note concentrations in pine needles ranging from 4-25 ppb for Pt, 3 to 20 ppb for Pd and 1.5 to 7 ppb for Ru. High loads of catalytic converter elements were associated with sites adjacent to major inner city roads.

Upon incomplete combustion of fossil fuels polycyclic aromatic hydrocarbons (PAH) are emitted in large quantities. PAH depending on molecular size and properties as well as ambient atmosphere are transported in a continuum between exclusively gaseous and fully particle-bound modes. Two-ring PAH including EPA-listed acenaphthene and acenaphthylene were not included in our study due to severe co-elution with sesquiterpenoid needle resin components and accumulation histories of pine needles well beyond equilibrium conditions.

PAH-distributions (50-410 ppb) were dominated either by 3-ring compounds phenanthrene and anthracene or by 4-ring components fluoranthene and pyrene. PAH comprising 5 to 7 rings (benzopyrenes, benzofluoranthenes, benzoperylenes, indenopyrene, coronene) occurred in sub-ppb concentrations. Source discrimination of PAH based on their respective distribution pattern is problematic. A general pattern of co-variance between PAH loads and magnetic susceptibility may allow to use the simpler, faster, and very cost-effective magnetic tool as a screening technique for identification of areas with problematically high PAH loads, which may then be analysed in detail by solvent extraction, PAH purification and GC/MS- or HPLC-detection.

The isotopic composition of carbon and nitrogen in needles is primarily governed by climatic, nutritional and physiological factors. However, a high atmospheric load of $\delta^{13}\text{C}$ -depleted CO_2 , resulting from combustion of isotopically light fossil fuels, has been proposed to lead to $\delta^{13}\text{C}$ -depletion in leaf/needle photosynthate of roadside vegetation in France. We observe opposite trends of $\delta^{13}\text{C}$ -enrichment in needles taken in Cologne conurbation and attribute these to environmental stress due to air pollution. The same accounts for $\delta^{15}\text{N}$ -signatures of pine needles, which show a trend to heavier $\delta^{15}\text{N}$ -values with increasing exposure to high ambient NO_2 -concentrations. This observation was substantiated by a good correlation between NO_2 -concentration measured for five urban locations by the environmental agency of the City of Cologne and our $\delta^{15}\text{N}$ -determinations on needles of nearby pine trees. The trend to heavier $\delta^{15}\text{N}$ -isotopes in pine needles as a result of air pollution only accounts for inner city regions. In rural regions pine needle nitrogen isotopes are very light (-10 to -4 permil) in forests whereas they are very heavy (+2 to +7 permil) in agricultural areas. The $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ isotopic composition of pine needles shows a robust correlation with magnetic susceptibility.

Thus under specific boundary conditions carbon and nitrogen isotopic signatures of pine needles serve as indicators of environmental stress caused by high NO₂ and CO₂-concentrations in urban air. Comparable to magnetic susceptibility analyses, bulk isotope determination on pine needles comprises a fast and cost-effective way of screening spatial and temporal variability in air quality of large conurbations. Once hotspots and strong gradients in atmospheric pollution have been detected, more sophisticated and costly techniques including trace element and persistent organic pollutant analyses offer reception of highly reliable and time-integrative records of environmental quality that may guide politicians or other municipal and government decision makers.

Section lecture - Thursday, Dec. 8th, 9:35

RECENT ASPECTS IN DIMETHYL CARBONATE CHEMISTRY

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Dimethyl carbonate (DMC) is a valuable methylating reagent which can replace methyl halides and dimethylsulfate in the methylation of a variety of nucleophiles and phosgene in carboxylation reactions. It couples tunable reactivity, and unprecedented selectivity towards mono-*C*- and mono-*N*-methylations (>99% at complete conversion). It is a prototype example of a *green reagent*, since it is non-toxic, made by a clean process, it is biodegradable, and it reacts in the presence of a catalytic amount of base thereby avoiding the formation of undesirable inorganic salts as by-products. Depending on the reaction conditions, DMC can be reacted under plug-flow, CSTR, or batch conditions. Other remarkable reactions are those where DMC behaves as an oxidant.

The high selectivity in methylations is due to the double reactivity of DMC which reacts on its hard centre (the carbonyl group) with harder nucleophiles and on its soft one (the methyl group) with softer nucleophiles. Recently achieved selectivity with nucleophiles on N, O, S and C will be given.

Activation of DMC on acidic catalysts like zeolites and the related reaction mechanism will be reported as well.

Production of DMC, applications and reaction mechanisms will be reported.

Section 6: Ecotoxicology - Thursday, Dec. 8th, 9:50

EFFECTS OF CHEMICAL POLLUTANTS ON DIGESTIVE GLANDS INVESTIGATED BY MICROSCOPY TECHNIQUES

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In our work, light microscopy and electron microscopy was used to study effects of chemical pollutants on digestive glands of *Porcellio scaber* (Isopoda, Crustacea). The lysosomal damage was determined by lysosomal latency assay and the neutral red retention (NRR) assay. Both were conducted on digestive glands of *in vitro* and *in vivo* laboratory exposed animals and on field populations. The results indicate decreased lysosomal membrane stability (LMS) in digestive glands of animals after laboratory exposure to copper and mercury compared to the control animals, as well as decreased LMS in metal polluted environments. Application of a focused ion beam (FIB) / scanning electron microscope (SEM) was used to observe morphological changes of digestive gland cells under normal physiological conditions and under metal induced stress. These results were compared to that obtained by light microscopy. The FIB / SEM system is a promising method to be used in toxicity studies, however at present it is in early stage of application in life sciences. We discuss advantages, disadvantages and future perspectives of light and electron microscopy in toxicology.

Section 6: Ecotoxicology - Thursday, Dec. 8th, 10:02

NON-TARGET SCREENING ANALYSES OF ORGANIC POLLUTANTS IN RIVERINE SYSTEMS

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Assessing the anthropogenic impact on the aquatic environment the compound related pollution is considered dominantly. Beside inorganic contaminants (heavy metals) especially the organic compounds are characterized by a wide diversity of molecular structures and corresponding physico-chemical properties. Since the molecular structure does not only influence the physico-chemical properties but also biodegradability, the fate and distribution of organic pollutants are manifold and complex. However, base for every environmental evaluation of the impact of pollutants on environmental systems is the structural elucidation of the relevant compounds.

With respect to surface water bodies, in particular riverine systems, the environmental analyses historically focus on pre selected spectra of substances (e.g. Priority Pollutants). Such monitoring programs can neglect partially additional pollutants. Hence, for a comprehensive view on the state of pollution detailed non-target screening analyses are essential.

In our presentation we introduce results of non-target screening investigations applied on water and sediment of several river systems in Germany (Lippe River, Elbe River, Rur River, Rhine River...). These studies focused on the structure elucidation and subsequent quantification of still unknown or unnoticed organic pollutants. These identifications included e.g. brominated phenylpropionic acids, mercury organic compounds, sulphur containing substances etc. and was based dominantly on GC/MS data. Verification of structures was performed by comparison with synthesized reference material, which was, further on, analysed by complementary but independent analytical methods (e.g. NMR- and IR spectroscopy). Finally, the individual concentration profiles are discussed with respect to possible emission sources and aspects of transport and distribution.

Section 6: Ecotoxicology - Thursday, Dec. 8th, 10:14

DISTRIBUTION OF HEAVY METALS IN THE SKADAR LAKE SEDIMENTS

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Skadar lake represents the biggest, and the most important, aquatic place in Montenegro. The main inflow into the lake (from Montenegro part) is coming from Morača and Crnojevića River. These rivers flow through industrial and urban settlements, and are potential polluters of the lake water system.

In this work, parameters that determine distribution, behavior and origin of heavy metals in sediments of Skadar lake and its tributaries have been investigated. The metals were chosen upon their ecochemical importance, and possibility for natural and anthropogenic pollution. The examined metals were copper, zinc, cadmium, lead, chromium and nickel. In order to have the complete insight into the nature of heavy metals associations in lake sediments, the samples were examined by sequential extraction method (five phases).

The results of the research indicate that the aquatic environment of the Skadar lake doesn't show any indication of anthropogenic pollution, except for some locations where certain anthropogenic pollution has occurred.

Distribution of examined metals in appropriate phases shows very low presence of anthropogenic fraction, while ecochemically least important, fifth phase, is most abundant. After comparison with US EPA (2002): "A guidance manual to support the assessment of contaminated sediments in freshwater ecosystems", it was confirmed that concentrations of metals found do not endanger life in Skadar lake.

The fact that both maximum and minimum concentration of specific metals were found in estuaries of the main tributaries into the lake indicates their dominant influence on the chemistry of the lake waters, and with that defines assets that determine a "fate" of the heavy metals in examined aquatic environment.

Section 6: Ecotoxicology - Thursday, Dec. 8th, 10:26

HUMAN PHARMACEUTICALS IN SCOTTISH WASTEWATER EFFLUENTS

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In recent years there has been a growing interest in monitoring the presence of pharmaceuticals in the environment. In most cases, pharmaceuticals are not completely removed during wastewater treatment processes and can find their way into the environment. Investigations in countries including Canada, Italy, Greece and Germany have already revealed the presence of human pharmaceuticals in effluents arising from wastewater treatment plants. However, to date no such studies have been conducted in Scotland.

The aim of this study was to ascertain the occurrence of human pharmaceuticals in effluents released from two typical Scottish wastewater treatment plants. The first serves a small town (including hospital facilities) and discharges to the North Sea while the second serves a small village and discharges into a river. From the 3000 pharmaceuticals used in the U.K., twelve target compounds were selected according to their persistence, bioaccumulation, toxicity and potential risk to the environment. Compounds include anti-cancer agents, antibiotics, nonsteroidal anti-inflammatories and antidepressants.

Effluent samples were collected daily from both sites, filtered, subjected to solid phase extraction and analysed using new methodology involving high performance liquid chromatography with tandem mass spectrometric detection. Results show that erythromycin, ibuprofen, mefenamic acid, diclofenac, propranolol and trimethoprim were present in effluents from both plants with erythromycin (an antibiotic) being the most abundant at a concentration of up to 1 µg/L. These initial results will be used to inform a future sampling strategy to examine the occurrence and distribution of human pharmaceuticals in natural waters in Scotland.

Section 6: Ecotoxicology - Thursday, Dec. 8th, 10:38

ENVIRONMENTAL FATE OF LANSOPRAZOLE, OMEPRAZOLE AND AMOXICILLIN

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The presence of pharmaceuticals in surface and ground waters is an increasingly relevant issue in environmental chemistry. These substances enter into the aquatic environment due to the ineffectiveness of sewage treatment plants, and thus they are potential pollutants for the aquatic ecosystem, possibly with adverse effects on aquatic organisms.

The impact that these xenobiotics can have is not very clear because there are limited data on their environmental fate. These chemicals can be transformed through abiotic processes (hydrolysis, photolysis) into different products, which may be even more persistent and/or more toxic than the parent molecules. Many searches are now addressed to the identification of these transformation products, but a lot of work has yet to be done considering the number of drugs on the market.

Here the environmental fate of three drugs is reported: lansoprazole, omeprazole (proton pump inhibitors) and amoxicillin (penicillin-like antibiotic). Chemical and photochemical investigations were performed in flask-model experiments in order to understand their environmental behaviour. The pharmaceuticals were kept in the dark (at different pHs) and/or irradiated in aqueous media under different conditions and the transformation was followed by HPLC and/or NMR. The transformation products were separated by chromatographic techniques and were characterized by their spectroscopic features. In some cases degradation pathways were tentatively described.

Here we report also preliminary data for an ecotoxicity evaluation. The pharmaceuticals and the corresponding products were examined with regard to their acute and chronic toxicity towards algae, rotifers and microcrustaceans of the aquatic environment to detect the effects due to the exposure of non-target organisms which are sensitive to the pharmaceutical's mode of action.

Section 6: Ecotoxicology - Thursday, Dec. 8th, 10:50

***Scrobicularia plana* ANNUAL BIOACCUMULATION RATES IN A HUMAN INDUCED MERCURY GRADIENT (RIA DE AVEIRO, PORTUGAL)**

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Scrobicularia plana is one of the most important and exploited natural resources in temperate estuarine systems, and may therefore represent a major pathway for human contamination, through bioaccumulation and bioamplification processes in polluted estuarine ecosystems, a widespread concern.

The main aim of this work was to study the annual and life-cycle mercury bioaccumulation in the well-documented bivalve species *Scrobicularia plana* along a human induced mercury gradient in the Ria de Aveiro coastal lagoon (Portugal), and the risks associated with its consumption by humans. A nearby, non-polluted estuary (Mondego estuary) was assumed as reference.

Total mercury ranged from 0.019 mg·kg⁻¹ (wwt) in 4+ year old organisms in the reference site, where a significant negative correlation ($p < 0.05$) was found between [Hg]_{tot} and size, resulting in negative bioaccumulation rates (detoxification), and as high as 1.8 mg·kg⁻¹ (wwt) in 3 year old bivalves from the most contaminated area, where a strong positive correlation was found ($p < 0.01$) and annual bioaccumulation rates reached as high as 0.5 mg·kg⁻¹·yr⁻¹. No increment was found with age in organic mercury contents, which corresponded to a decrease in organic mercury percentage with age and suggests passive accumulation and no methylation processes occurring within the organisms.

In terms of management and population health, our results suggest that *S. plana* of commercial size (above 2.5 cm) collected from locations with sediment [Hg]_{tot} levels above 6 mg·kg⁻¹ exceed the maximum [Hg] for human consumption, and therefore harvesting in these areas should be prohibited.

Section lecture - Thursday, Dec. 8th, 11:30

HYDROMETALLURGICAL TREATMENT OF SOLID WASTES AND WASTEWATERS TOWARDS AN ENVIRONMENTAL PROTECTION

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This study addresses environmental pollution problems associated with solid and liquid wastes/effluents produced by ferrous metallurgy in the European countries and by non-ferrous metallurgy in Western Balkan area, in order to develop preventive and remedial technologies aiming at waste minimization, remediation of waste disposal sites and ultimately prevention of the regional water resources contamination.

The hydrometallurgical processing of EAF steelmaking dust (Paul Wurth S.A., Luxembourg) was investigated under the high pressure leaching in autoclave. The behaviour of zinc and iron with sulphuric acid as leaching agent is discussed. The dependencies of temperature and liquid : solid ratio were investigated. The main goal was to transfer zinc into solution while iron should stay as solid precipitate.

Treatment of industrial wastewaters and leachates from RTB Bor will be considered using neutralization process. This investigation targets at the recovery of metals or groups of metals in a marketable form and at the recycling of pure water in the industrial activities where possible. Especially the cascade line of three reactors of 10 liter will be shown in order to present one continuous process for the purification of solution.

It is envisaged that the application of the proposed technologies at an industrial scale will improve working conditions at mining/metallurgical sites and therefore the quality of life and the ecology at the affected regions.

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 11:45

POSSIBLE PATHWAYS OF TRANSFORMATION OF NEW DISINFECTION AGENT ALKYLDIMETHYLBENZYLAMMONIUM CHLORIDE IN CONDITIONS OF DRINKING WATER PREPARATION

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The revealed adverse effects of molecular chlorine as a disinfecting agent used for the drinking water preparation have induced an extensive search for the safer chemicals for this purpose. Ozonization, chlorination with sodium hypochlorite and UV-irradiation are used at small scale at the experimental installations in Moscow. Recently a new disinfecting agent, alkyldimethyl-benzylammonium chloride was proposed as a reasonable alternative. This reagent has been widely used for disinfecting surfaces. It is cheap, relatively stable, water-soluble and does not produce organochlorines being applied. Since it will be used at a certain stage of the water treatment process its application may be accompanied by chlorination, ozonation or UV-irradiation. Thus, these three reactions were carried out in the laboratory to identify the products of degradation of alkyldimethylbenzylammonium chloride in experimental conditions, resembling these used at the water treatment stations.

As the degradation products of the proposed disinfectant could be quite harmful, GC-MS and LC-MS were used as analytical tools to establish individual composition of the transformation products. About 40 products were identified and quantified. Oxidation and dequaternization were the most important reactions, while dimethylalkylamines were the major products. The most dangerous among other products were benzylchloride, benzaldehyde, aliphatic aldehydes and a number of organochlorines arising at the advanced stages of chlorination. Organochlorines appeared even during Ozonization or irradiation as a result of reactions of intermediates with chloride-anions. A number of diphenylalkyl derivatives were detected. They arise due to dimerization of benzyl containing oxidation products.

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 11:57

Fe(III)-ENHANCED SONOCHEMICAL DEGRADATION OF METHYLENE BLUE IN AQUEOUS SOLUTION

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Sonochemistry is one of Advanced Oxidation Processes for water and wastewater decontamination. Application of ultrasounds to aerated aqueous solutions in the frequency range 30-1000 kHz induces the formation of cavitation microbubbles. These bubbles undergo nucleation, growth, and implosive collapse. The very fast adiabatic collapse of the microbubbles induces a huge increase in temperature and pressure at their interior, under which circumstances pyrolysis of the gas-phase compounds can occur. Pyrolysis of water vapor yields hydroxyl radicals, $\cdot\text{OH}$, which can induce degradation processes in the gas phase, at the gas-water interface, and in the solution bulk [1].

The practical applications of sonochemistry to water treatment have been limited so far by the high costs [2]. This work [3] shows an approach to increase the rate of sonochemical processes upon addition of the rather inexpensive reactant Fe(III). The primary sonochemical process induces water splitting into H^{\cdot} + $\cdot\text{OH}$. Hydrogen atoms then undergo a diffusion-limited reaction with dissolved oxygen to yield the hydroperoxyl radical, HO_2^{\cdot} , which produces H_2O_2 upon dismutation. Fe(III) can be reduced to Fe(II) in the system by $\text{HO}_2^{\cdot}/\text{O}_2^{\cdot-}$ and H_2O_2 , and the Fenton reaction between Fe(II) and H_2O_2 to yield additional $\cdot\text{OH}$ would then follow. Due to this sono-Fenton process, the sonochemical degradation rate of Methylene Blue is significantly enhanced upon addition of Fe(III), and a further enhancement is observed in the presence of $\text{Fe(III)} + \text{H}_2\text{O}_2$.

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Section 7: Water treatment, reuse - Thursday, Dec. 8th, 12:09

PERSPECTIVES OF WATER DISINFECTION IN MUNICIPAL WATER-SUPPLY TAKING INTO ACCOUNT PRODUCTS OF TRANSFORMATION

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One of the most important issues for the sustainable development of a modern city is the quality of drinking water. Nowadays more and more industrial chemicals appear in the natural water. Together with humic matter these compounds bring to formation of a notable array of by-products during the process of disinfection of the drinking water. As a result a lot of unknown compounds influence human health.

In present work we have investigated the transformation of seven model compounds (cyclohexene, n-butanol, diphenylmethane, acetophenone, aniline, 1-methylnaphthalene and phenylxylyl-ethane) in reaction with active chlorine and under UV irradiation. These compounds are widely used in modern industry and are detected very often in water samples all over the world. The products of chlorination and irradiation were detected by means of GC-MS. The mutagenicity was tested in the Ames test on the strains TA98 and TA100 and in micronuclei test. Interacting with aquatic chlorine all the selected compounds brought to a representative array of chlorinated derivatives. The schemes of aquatic chlorination of the compounds studied were proposed. Comparative study of model chemicals and their by-products confirmed that chlorination products were more toxic and dangerous than the initial compounds. Besides that by-products revealed mutagenic and cancerogenic activity. In contrast to chlorination only derivatives of butanol and phenylxylylethane were detected after UV irradiation. These by-products were not more harmful than initial substances. The other model chemicals remained unchanged in these conditions. Preferences and disadvantages of different water treatment methods were discussed.

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 12:21

PHOTOCATALYTIC ACTIVITY OF DOPED TiO₂ IN DEGRADATION OF METHYLEN BLUE AND MALIC ACID IN WATER UNDER VISIBLE OR UV LIGHT

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The use of solar photocatalysis for water treatment is a very useful and attractive method. The usual photocatalyst is TiO₂. Its catalytic activity under solar radiation can be improved by doping. We prepared, by sol-gel method, large surface area titanium oxide doped by Li, La and Cd (1-5% in atomic ratio). The effects of the doping metals on the crystal structure and porosity parameters have been studied by different physical technics (XRD, TEM, XPS, N₂ adsorption). The band gap was investigated by UV absorption. The photocatalytic activity of the solids was tested on the methylene blue and malic acid degradation under UV or Visible light and compared to that of P25 Degussa TiO₂ catalyst taken as reference.

Our investigations showed that doping decreases the band gap of materials compared to that of P25 catalyst but this decrease weakly depends on the nature and the content of the doping metal, the band gap is then close to that of anatase. Nevertheless the catalytic activity strongly depends on the concentration and the nature of the metal. Under UV light the best catalyst remains P25 but under visible irradiation doping leads to more active catalysts, following Li 5% > La 5% > P25 ≈ La 2%

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 12:33

ELECTROCHEMICAL BEHAVIOR OF AZO BOND ON DIFFERENT ELECTRODE MATERIALS. FUNDAMENTS FOR COLOR REMOVAL IN WASTE WATERS

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The effluents from textile dyeing are colored so these waters will have to be treated before being released back to environment. Various synthetic alimentary azo dyes have been shown to induce a variety of tumors in mice and rats and to exhibit inhibitory effects on the biosynthesis of proteins.

The removal of pollutant species by electrochemical methods can be carried out in an electrochemical cell directly without the addition of redox chemical reagents, working at room temperature. Another advantage is that these techniques use as the main reagent the electron, which is a "clean reagent" and by controlling the potential the oxidation can be selective carried out.

The main purpose of this paper is to obtain data regarding the electrochemical behavior of some textile and alimentary dyes on different electrodes - CV (glassy carbon), Au (gold) and BDD (boron doped diamond electrode) - and conditions (pH, electrolytes, concentrations). The obtained fundamental results were used for the synthetic waste water discoloration. On BDD electrode the average values for absorbance decreasing was 97-99%, COT 88-90% and COD 85-91%, depending of the azo dyes nature and experimental parameters.

For the purpose of this work, cyclic voltammetry and coulometry (using BAS 100W and AUTOLAB PGSAT 12 computer aided electrochemical systems), UV-Vis spectrophotometry (UNICAM Helios β) and (TOC) and (COD) determination (Shimadzu Corporation, Tokyo, Japan equipment) have been used for the control of the azo dyes concentration during the electrochemical discoloration.

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 12:45

URANIUM UPTAKE BY FRESHWATER ALGA *Chara globularis*: POSSIBLE APPLICATIONS IN CONTAMINATED WATER TREATMENT

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Phytoremediation of soils and surface waters contaminated with heavy metals, particularly uranium, is of great interest. Certain species of water plants show considerable potential in uptake of uranium from contaminated waters.

In this study we present results from our investigation on uranium uptake by freshwater alga *Chara globularis* and dry material obtained from this alga. The study has been carried out under conditions of variable pH and carbonate content, using methods of UV-VIS spectrometry, fluorimetry and total beta radioactivity measurements. The results obtained for alga and dry material were compared and discussed in terms of their ability for uranium sequestration. Obtained data show that alga *Chara globularis* has potential in both *in situ* and off line treatment of water contaminated with uranium.

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 12:57

ION EXCHANGE ISOTHERMAL SUPERSATURATION (IXISS) OF MAGNESIUM-AMMONIUM PHOSPHATE (STRUVITE) SOLUTIONS IN COLUMNS

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Recovery and recycling of phosphorus (P) from effluents and waste waters of different types represent one of the most important tasks of the modern environmental chemistry. The phosphates are removed and recovered from the water under treatment as a double magnesium-ammonium phosphate known also as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) or other low solubility P compounds. The advantage of P recovery in the form of struvite consists in the possibility to use it as valuable mineral fertiliser. Ion exchange can be used to both recover phosphates from waste waters and to synthesise struvite of sufficiently high purity. The paper describes results obtained by studying conditions of synthesis of struvite by using the Ion Exchange Isothermal Supersaturation (IXISS) technique. The IXISS phenomenon is observed when using certain ion-exchange separation techniques permitting concentrating the target substance (or undesired impurity) up to the level exceeding its solubility at a given temperature. Moreover, this supersaturated solution remains stable for a long period, while after leaving the column it crystallises spontaneously. The experiments reported in this paper have been carried out using two different types of resins, the Lewatit CNP 80 which is a carboxylic macroporous resin and the Lewatit S 100 which is a sulphonic gel type resin. Stable supersaturated struvite solutions were obtained by stripping of magnesium from both cation exchange resin using ammonium phosphate solutions in column-wise operation. X-ray diffraction analysis of precipitates obtained confirmed the formation of high-purity struvite crystals for the Lewatit CNP 80 but the yield was of 14% on the other hand the results for the Lewatit S100 was of around 60% but the precipitate was a mixture of struvite and newberyte.

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 13:09

PHOTOCHEMICAL TRANSFORMATION OF EMERGING POLLUTANTS: EXAMPLE OF ETHINYLESTRADIOL AND DICLOFENAC

L. Méité, P. Mazellier* & J. De Laat

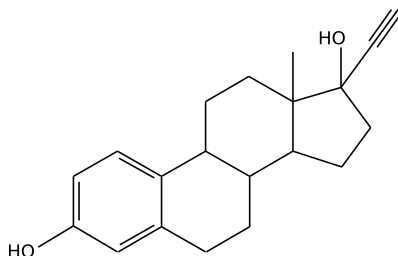
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The aquatic compartment is contaminated by chemicals arising from human activities. Beside pesticides, surface water analyses regularly show that different chemicals are detected in the concentration range ng/L - µg/L. Among these chemicals, pharmaceutical residues and hormones represent products which have been shown to be able to modify the ecological equilibrium.

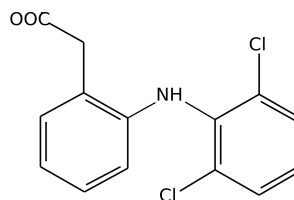
These compounds evolve in the aquatic compartment according to biological, physical or chemical transformation. Among these reactions, phototransformation may be significant and lead to degradation products that can be accumulated in water.

17 α -ethinylestradiol (EE2) is a synthetic estrogenic steroid used for women therapeutic as an oral contraceptive. EE2 is known to have the potential to disrupt the normal activity of the endocrine system.

Diclofenac is a nonsteroidal anti-inflammatory drug (NSAID). It is employed in human medicine as an analgesic, an antiarthritic or an antirheumatismal.



Ethinylestradiol



Diclofenac

The photochemical transformation of these two compounds was studied upon monochromatic irradiation (254 nm used for disinfection in water treatment) and polychromatic with $\lambda > 290$ nm, (simulation of solar irradiation). The quantum yields of direct photolysis are about 0.20 of diclofenac and about 0.03 for ethinylestradiol for UV irradiation. From these values, it is possible to evaluate the rate of transformation when the compound is submitted to a UV disinfection process or its half live in the environment. Photoproducts were identified by LC-MS experiments and will be described in the presentation.

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 15:30

INVESTIGATIONS OF OCCURANCE AND ELIMINATION OF HAZARDOUS COMPOUNDS IN WASTE WATER TREATMENT PLANTS

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The focus of environmental research has recently been widened to endocrine disrupting compounds (EDCs), pharmaceuticals and personal care products. These trace organic contaminants enter the environment through regular domestic use. Thus, loads of bioactive compounds are entering the wastewater, and if not completely removed through sewage treatment also reach the receiving water bodies. Number of effect studies in the aquatic environment is limited, but some reported effects in the range of environmental concentrations (e.g. ethinylestradiol). Thus, the removal efficiency of sewage treatment plants (STPs) should be more precisely monitored and enhanced wherever applicable.

Main task of the presented project is the monitoring and assessment of the concentration of several trace organics in all process steps (water and sludge samples) of different STPs. All investigated substances are of great environmental and/or ecotoxicological relevance caused by persistence, toxicity or its potential of bioaccumulation (EU-waterframework). This will help to identify the removal performances of the plants in view of sorption to sludge or biodegradation.

Samples were prepared by solid-phase-extraction, liquid-liquid-extraction and/or accelerated-solvent-extraction. Additionally, some substances need to be derivatized, to enable sensitive gas chromatography. Identification and quantification is performed by gas or liquid chromatographic separation and detection by mass spectrometry (LC-MS, GC-MS). The results show the different behavior of single substances or groups of compounds. As an example the removal of octylphenol or the plasticizer DEHP is assumed to be mainly based on degradation. On the other hand the musk fragrance Tonalid is adsorbed to great extent to the primary and secondary sludge.

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 15:42

EFFECT OF MICROORGANISMS ON THE SORPTION OF LANTHANIDES BY QUARTS AND GOETHITE AT THE DIFFERENT pH VALUES

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The effect of *Rhodopseudomonas pallustris* on the amount of various forms of lanthanides sorbed by quartz sand and goethite precipitated as coatings on a sand matrix at the different pH was studied. Goethite (α -FeOOH) was prepared by adding 0.17M Fe(NO₃)₂ and 0.52M NaOH in an evaporating dish. After cultivation of bacteria and filtration of liquid medium the suspension of microorganisms in water ($4.8 \cdot 10^8$ cells in ml⁻¹) was added to quartz sand or goethite with the mixed solution of lanthanides (C=15 ppb). The experiment was carried out at pH 4, 7 and 9. Tubes with microorganisms and controls (no inoculum) were incubated without shaking at 22°C. Exchangeable (extracted by 0.5M NH₄NO₃) and nonexchangeable (extracted by 0.3M NH₂OH-HCl in 1M HNO₃) forms of elements were recovered from the surfaces after experiments.

pH of sorption solution seems to be most important parameter in the biosorption and sorption process. Sorption of lanthanides by quartz was essential at pH 9 only. In spite of same chemical properties of lanthanides there were differences in the sorption by quartz at alkaline conditions. Microorganisms decreased concentrations of elements in the sorption solution at pH 7 and higher. At pH 7 microorganisms increased exchangeable and non-exchangeable, at pH 9 - increased exchangeable and reduced non-exchangeable forms of elements with compare quartz. Sorption of lanthanides by goethite was rise at pH 7 and higher. Microorganisms decreased the sorption of lanthanides by α -FeOOH at alkaline pH due to the reducing in its exchangeable forms.

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 15:54

APPLICATION OF REGIONAL HYDROCHEMICAL IN-SITU BARRIERS IN SIGNIFICANT GROUNDWATER RESERVOIRS

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The regional protection before the disperse of pollutants in water utilization groundwater structures and reservoirs generally include **a)** passive protection elements (Protection Zones) and **b)** active elements, when the treatment technology of extracted groundwater is modified.

When the significant degradation of groundwater quality is observed - for example in the areas with intensive anthropogenic environmental damage - it proves that the protection zones are not effective and currently used water purification/treatment processes are very expensive or problematic.

We are engaged in possibilities of in-situ ground water treatment when the quality of extracted water is modified directly in the aquifer. This is going on since the mid nineties of the twentieth century within a long-term project framework. Creating aerobic conditions using the air oxygen is the most economic solution based on experience. It is a commonly known fact that during aerobic conditions concentrations of Fe and consecutive Mn decrease in extracted groundwater and also the concentrations of biodegradable organic pollutants, heavy metals etc. High efficiency of this technology was verified on the groundwater sources (water yield more than 40 l per sec.) and it shows that the principles are available not only on local but also on regional basis. Hydrochemical barriers are created without the destructive impact to the geological environment which is obvious during the building of the permeable barriers with active hydrochemic cell.

This contribution summarises the results of experimental and practical projects that took place on the local groundwater resources in Czech Republic and Russia. The results are available for regional groundwater protection projects using the methods. The specific applications for the projecting similar systems are presented.

Section 7: Water treatment, reuse - Thursday, Dec. 8th, 16:06

COMPETITIVE ADSORPTION OF TRIVALENT AND HEXAVALENT CHROMIUM ON GRAPE STALKS ENCAPSULATED IN CALCIUM ALGINATE GEL BEADS: KINETICS STUDY

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In recent years, several studies have been carried out to evaluate the use of low cost sorbents as a replacement for current costly methods for removing heavy metals from aqueous solutions. Chromium is usually released in the environment by effluent discharge from steelworks, chromium electroplating, leather tanning and chemical manufacturing. Cr(VI) adsorption is being of special concern due to its toxicity. Recently, we have reported the biosorption of hexavalent chromium using grape stalks wastes coming from wine production [1]. In order to improve the mechanical strength of the sorbent in view of its application in industrial waste water treatment, the grape stalks were encapsulated in calcium alginate gel beads. Beads containing 2% w/v grape stalks (2% GS-CA) have been proven to be an efficient low cost sorbent for Cr(VI) ions [2].

Nevertheless, in real applications, chromium is usually encountered in water streams in both Cr(III) and Cr(VI) oxidation states. Therefore, in this work, the competitive adsorption of Cr(III) and Cr(VI) has been studied with the aim of obtaining more realistic data about chromium sorption on 2% GS-CA. Experiments were carried out to study adsorption kinetics. The kinetic data were treated mathematically according to different adsorption kinetic models in order to obtain the information concerning the limiting steps of the sorption process. The pore diffusion model was found to fit the data obtained during the first ten minutes the pseudo-second order model the overall range of kinetic data. Adsorption results showed that in binary mixtures, both Cr(III) and Cr(VI) sorption are enhanced due to the presence of each other.

To give a qualitative analysis of the main functional groups that might be involved in the adsorption of Cr(III) and Cr(VI), a FTIR-ATR analysis in solid phase were carried out.

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Section lecture - Thursday, Dec. 8th, 16:18

TRACE ELEMENT CONTAMINATION AROUND A COPPER SMELTER COMPLEX IN BOR REGION (SERBIA) STUDIED BY MOSS BIOMONITORING

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The moss biomonitoring technique was employed to study the atmospheric deposition around the big copper smelter complex in the town Bor (eastern Serbia). Samples of *Hypnum cupressiforme* were collected at 41 sampling sites during 2000 and 2001. A combination of instrumental neutron activation (INAA) and atomic absorption spectrometry was used to obtain data for 40 elements in these moss samples and the analytical data were subjected to factor analysis. The factor analysis showed a strong component associated with the copper smelter complex in Bor, with very high loadings for Cu, Zn, As, Se, Mo, Ag, Cd, In, Sb, and Pb. Most of these elements showed a very uniform distribution around the smelter with concentrations of about 10% of the maximum level at 40 km distance from the source. In the case of Cu the corresponding decline was a factor of 100, indicating that copper is emitted mainly with a larger aerosol fraction than the other elements. No other point sources of metal emission were identified, with the possible exception of Ag where the data indicated an additional source somewhat east of the copper smelter. No appreciable transboundary contribution from sources in Romania or Bulgaria could be clearly identified. Contamination of the moss samples with soil particles was identified by the factor analysis as a substantial problem. Still the obtained data may be useful as a reference level for comparison with future measurements of heavy metal pollution in this area.

Section 9: Industrial clean technologies - Thursday, Dec. 8th, 16:33

PREPARATION PROCESS, STRUCTURAL AND CATALYTIC PROPERTIES OF BN-SUPPORTED NOBLE METALS

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The support characteristics play an important role in supported noble metal catalysts. The use of high surface area boron nitride powders as catalyst supports exhibits several advantages over traditional oxide supports like alumina, titania, zirconia or silica. In this study we report on the preparation and characterization of metals (Pd, Pt, Au and Ag) deposited on boron nitride powders with potential applications as catalysts for oxidation reactions. The deposition and the dispersion of the active phase were strongly influenced by the preparation process and in particular by the compound used as dispersing phase. The support and catalysts were characterized by several techniques (BET, XRD, SEM, TEM) including TPR-TPO experiments and calorimetry. The size and dispersion of the particles and the role played by the organic or inorganic phases used as solvents (benzene, glyme, water, THF, diglyme, glycol, isopropanol) were determined. The catalytic performances were tested in the combustion of methane traces in excess oxygen and in presence of water. The light-off temperatures (50% methane conversion) increased in the following order: Ag < Pt < Au < Pd /BN.

Section 9: Industrial clean technologies - Thursday, Dec. 8th, 16:45

DEVELOPMENT OF AN ARRAY OF SENSORS TO DETECT AND QUANTIFY VOLATILE HAZARDOUS COMPOUNDS

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The use of organic solvents is common in industrial processes. Organic solvents are used in the manufacture of adhesives, glues, varnishes, cements, paints, plastics, coatings, gums, oils, resins, lacquers, thinners, waxes, floor and shoe polishes, fuels, antifreeze, degreasing, inks, pharmaceutical and pesticide products, used as cleaning and dry cleaning agents and in laboratory processes. All solvents should be considered potentially hazardous. The harmful effects may follow inhalation of the vapour, eye or skin contact with liquid or vapour, or by ingestion. The severity and type of effect depends on the vapour concentration, duration of exposure, and toxicity of the solvent. Prolonged repeated exposure to some solvents may impair perceptions and cause behavioural changes with degeneration of nerve cells in the peripheral nervous system, which causes several organic malfunctions, some of them irreparable, and in most severe cases death can follow.

In this work, an electronic nose composed of an array of six acoustic wave sensors was specially developed for the detection and quantification of a series of volatile solvents. Each of the sensing piezoelectric quartz crystals was coated with a different sensitive layer. Although none of the individual sensors was specific for a single compound, a neural network algorithm showed that a specific solvent, out of a range of 10 possibilities, for which the system has been trained, was correctly identified, and could also be quantified.

Section 9: Industrial clean technologies - Thursday, Dec. 8th, 16:57

THE PRODUCTION OF ENVIRONMENTALLY FRIENDLY MOTOR GASOLINE COMPONENTS BY REACTIVE DISTILLATION

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Following restrictions of environment pollution, the tertiary aliphatic ethers from C₅-C₈ are more and more used as octanic components for environmentally friendly gasoline, replacing success—fully the lead tetraethyl. The industrial way for synthesis of these ethers is the addition reaction of inferior alcohols (methanol, respective ethanol, rarely isopropanol) to tertiary olefines C₄-C₆. The present synthesis processes consist in individual etherification of olefines from composition, in the presence of ion exchange resins, in units with clasical structure: reactors-separation columns.

The present paper describe a new proceeding of getting tertiary ethers (TAME, ETBE and TAEE) through catalytic distillation, process what supposes concomitant evolution (integration) in a single device, the catalytic distillation column (DC), for the reaction and separation steps of the products.

The integration of chemical transformation with separation step can be totally or partially, the conversion results only partial in catalytic distillation column DC, the rest taking place in a reactor which precede the column or works in paralel with it. This process has a number of advantages, among which there are:

- The improvement of reactive olefines conversion to ethers, due to the movement of reaction thermodynamic equilibrium;
- The diminution of secondary products flow rate through the increase of transformation selectivity;
- The decrease of operating and capital costs following of the devices number and energetic consums reduction.

In the paper there are presented laboratory data regarding the thermodynamic and kinetic reaction aspects and some pilot experiments results in respect to obtaining of aliphatic tertiary ethers. Also there is presented the flow sheet of a industrial unit for the proposed process.

Section 9: Industrial clean technologies - Thursday, Dec. 8th, 17:09

LIQUID WOOD AS THE FEEDSTOCK FOR POLYMER SYNTHESIS

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Wood is a complex mixture of natural polymeric materials, among them cellulose, lignin and hemicelluloses, which can be liquefied to yield a potential renewable feedstock for the production of polymers. In our previous work we prepared liquid wood using glycols and organic acids that yielded oligomeric polyesters with incorporated wood degradation products.

Our research was directed toward exploring the potential uses of liquid wood using aspects of polyester chemistry with an emphasis on unsaturated polyester resins, saturated polyester polyols and alkyd resins. Liquid wood contains numerous compounds with a high amount of hydroxyl groups. These highly reactive soluble oligomers were used for polymer synthesis. Untreated or neutralized liquid wood was polymerized to appropriate molar masses and other properties such as hydroxyl and acid numbers using conventional materials used in industrial resin production.

Unsaturated polyesters were prepared by reacting liquid wood with maleic and phthalic acids. Resins contained up to 25% wood in dry matter. It was possible to prepare resins with reactivities comparable to commercial resins.

Polyester polyols were synthesized in a similar reaction by using adipic acid. The final products had hydroxyl numbers in the range 150-500 and polyurethane foams with densities of 0.03-0.05 g/mL could be prepared. The foams could incorporate unliquefied wood residues as fillers and could be used for isolation purposes.

Air drying alkyds were prepared in a similar manner with the use of unsaturated fatty acids. Due to residual hydroxy groups, alkyd resins had higher polarity and therefore lower miscibility with nonpolar solvents. Their drying time was also longer than of the conventional alkyds.

Plenary lecture - Friday, Dec. 9th, 9:00

SOURCES AND FEATURES OF ATMOSPHERIC PARTICULATE MATTER IN THE MEDITERRANEAN - CONSEQUENCES FOR THE AIR QUALITY MONITORING

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Atmospheric particulate matter (PM), or simply aerosol, is a complex mixture of solid and/or liquid substances (except pure water), suspended in a gas, that enters into the atmosphere by several mechanisms including natural sources. Organic matter, sulphate, nitrate, ammonium, elemental carbon, mineral dust and sea-salt are the main PM contributors ($\sim\mu\text{g}/\text{m}^3$), whereas some elements such as As, Cd, Cr, Cu, Ni, P, Pb, V or Zn (among others) are typically found as trace contributors (few ng/m^3). Aerosols present a size between a few nanometers (nm) and tens of microns (μm), depending on the sources, formation mechanisms and "age" of the particles. Human activities alter the natural PM composition and increase its ambient air levels several times above its natural concentrations. Owing to PM impairs ambient air quality, causing adverse effects on human health and natural ecosystems and influence on processes related to climate, standards for ambient air PM levels exist within the EU territory. The EU Directive 1999/30/EC established limit values for PM₁₀ ($\text{PM}<10\ \mu\text{m}$) concentrations, both in an annual ($40\ \mu\text{g}/\text{m}^3$ for 2005 and $20\ \mu\text{g}/\text{m}^3$ for 2010) and daily basis ($50\ \mu\text{g}/\text{m}^3$ not to be exceeded more than 35 times by 2005 and 7 times by 2010). The II Position Paper on PM (2004) proposes to establish also limit values for PM_{2.5}, a daily limit value of $35\ \mu\text{g}/\text{m}^3$ not to be exceeded more than 35 times/year and an annual mean limit value between 12 and $20\ \mu\text{g}/\text{m}^3$.

This study synthesises results obtained in several projects performed during the last years. Most of the data discussed here have been obtained in research projects developed in Spain and focused on the PM source contribution (e.g. natural vs. anthropogenic) and in the strategies for a suitable PM monitoring in ambient air (e.g. Rodríguez et al., 2002; Alastuey et al., 2004; Querol et al., 2004; and references therein). These studies have mostly been multidisciplinary, including *in-situ* chemical and physical characterisation of PM, meteorological analysis and satellite remote sensing aerosols observations. Moreover, PM data obtained in recent projects (still under develop) and from the literature have been included in order to compare the PM features in the different EU regions (some of them also included in Putaud et al., 2004 and Querol et al., 2004, and other extracted from EMEP, 2004; Almeida et al., 2005 and Götschi et al., 2005; among others). Although not all Mediterranean regions are properly covered, these results allow obtaining a comprehensive picture of the Mediterranean aerosol behaviour in the western regions.

The Mediterranean basin is characterised by a set of features affecting levels and composition of PM. Although some of these features are not "homogeneous" throughout the Mediterranean area, most of the basin: **1**) is characterised by an abrupt topography and is not affected by the frequent air masses renovation that occurs in Central-Northern Europe due to the mid-latitudes general circulation (westerly winds, cold fronts and rain), **2**) is frequently affected by natural sources of mineral dust such

as African desert dust outbreaks and mineral matter resuspension in some semi-arid regions, **3**) is affected by high radiation intensity favouring photochemical processes. These factors affect levels, composition, day-to-day variations and seasonal evolution of PM. As consequence of this, the "Mediterranean PM" exhibits features different to those observed in Central and Northern Europe.

PM events in the Mediterranean. The following main episodes have been identified in Spain and Northern Italy: local urban PM pollution events (cold season), regional PM pollution episodes (warm season), Atlantic/Northern clean air events and African dust outbreaks. Clean air events are mostly associated with abrupt entries of Atlantic or Northern air masses into the Mediterranean basin, whereas pollution episodes are enhanced by the "calm air" conditions dominating between these Atlantic air masses entries and the reduced dispersion conditions linked to the topography (e.g. Milan and Turin in the bottom of the Po valley, or Barcelona confined by the Catalan coastal range). Summer regional recirculation of air masses in Eastern Spain results in PM and O₃ regional episodes at rural sites, being PM₁₀ mostly constituted by ammonium-sulphate, organic matter and mineral dust (due to natural resuspension). In Barcelona and Milan, high PM_{2.5} concentrations (>60 µg/m³) are frequently recorded during winter local urban pollution events, when the most important contributors to PM_{2.5} are ammonium-nitrate and organic matter.

African dust contributions to Mediterranean PM. Desert dust outbreaks over the Mediterranean occur in a synoptic scale, affecting large areas of Southern Europe. During African dust event, the daily mean concentration of mineral matter in Eastern Spain, Northern Italy, Corsica and Sardinia, are in the ranges 10-15 µg/m³ in PM_{2.5} and 15-30 µg/m³ in PM₁₀ both at rural and urban sites. However, extremely high daily mean PM levels at rural sites, such as 100 µgPM₁₀/m³ in mainland Spain, 135 µgPM₁₀/m³ and 65 µgPM_{2.5}/m³ in Portugal, 190 µgPM₁₀/m³ and 90 µgPM_{2.5}/m³ in Crete and up to 600 µgPM₁₀/m³ and 65 µgPM_{2.5}/m³ in the Canary Islands, also occurs as consequence of this African dust transport. Around 10 African dust events per year (2-4 days duration each) occur in many parts of the basin, resulting in an important interference of the anthropogenic PM pollution.

PM levels and composition: the Mediterranean vs. Central-Northern Europe. A PM data compilations from different EU regions shows that annual mean rural-background PM₁₀ levels are typically into the ranges 14-21 µg/m³ in the Western Mediterranean (WM), 14-24 µg/m³ in Central Europe (CE) and 8-16 µg/m³ in Northern Europe (NE), being the natural contribution maxima in the Mediterranean areas: 4-8 µg/m³ of mineral dust + 2-4 µg/m³ of marine aerosol in the WM, 1-2 µg/m³ of mineral dust + 2-4 µg/m³ of marine aerosol in CE and 2-4 µg/m³ of mineral dust + 1-4 µg/m³ of marine aerosol NE (the remaining fraction being sulphate, nitrate, ammonium and carbonaceous matter). For PM_{2.5}, rural background levels are typically in the ranges 12-16 µg/m³ in the WM, 12-20 µg/m³ in CE and 7-13 µg/m³ in NE, being the differences of the natural contribution in the different regions smaller than in the PM_{2.5} fraction, because of the coarse grain size nature (2.5-10 µm) of a significant fraction of mineral dust and sea-salt.

Metrics or parameters for ambient air PM monitoring. Owing to the fact that different PM components exhibits different size distribution (depending on the sources, formation mechanisms and "age" of the particles), different PM "metrics or parameters", based on mass concentration (PM₁₀, PM_{2.5} or PM₁: µg/m³) or number concentration (N: cm⁻³), should be used depending on the type of aerosols to be monitored. Fumigations of SO₂ plumes (containing fresh sulphuric-acid & sulphate particles) are much better traced by PM₁ than by PM_{2.5} and PM₁₀, mainly because of the influence of mineral dust particles >1 µm in semi-arid Mediterranean regions and the >1 µm nature of sea-salt. In contrast, in environments affected by emissions of primary PM, both anthropogenic (ceramic, cement production, mining, road dust resuspension) and natural (mineral dust resuspension), PM₁₀ or PM_{2.5}-10 are better indicators of the air quality than PM₁. Although the influence of mineral dust is much lower in PM_{2.5} than in PM₁₀, this mineral matter load may still be reduced if monitoring PM₁ (which is basically made of sulphate, nitrate, ammonium and carbonaceous matter). It should also be taken

into account that the load of nitrate may also be reduced if monitoring PM₁ instead of PM_{2.5}. The number concentration ($N: \text{cm}^{-3}$) is an alternative measurement that provides another "view" on aerosols. The contribution of particles $>1 \mu\text{m}$ to N is almost negligible (even if their contribution to the total PM mass is important), being the particles $<0.1 \mu\text{m}$ (mostly carbonaceous matter) the main contributors to N , and the 0.2 to $0.8 \mu\text{m}$ particles the main contributors to PM₁ mass. Owing to this, the aerosol number concentration and its size distribution is mainly influenced by the processes related to the emissions and/or formation of carbonaceous matter, ammonium-sulphate and ammonium-nitrate, not being significant the influence of mineral dust. The relationship between the number and mass concentrations depends on the type of aerosols, its age and the microphysical processes occurring during the different seasons and events. In urban environments, the submicron aerosol number $N(<1 \mu\text{m}; \text{cm}^{-3})$ and mass PM₁ ($\mu\text{g}/\text{m}^3$) concentrations frequently show correlated time series during periods of non-extreme N ($<1 \mu\text{m}$) and/or PM₁ concentrations. However, high N ($<1 \mu\text{m}$) and low PM₁ concentrations are observed during "nucleation episodes" and/or "impacts of aerosols precursor's plumes (e.g. SO₂ or organic compounds)" under clean air conditions. In contrast, increases in PM₁ and decreases in N ($<1 \mu\text{m}$) levels are observed during some aged polluted air episodes (e.g. winter stagnant conditions over cities or long range transport of pollutants), owing to the role of coagulation (reducing N) and condensation (increasing PM-mass) processes. Thus, mass and number concentrations are not always equivalent. These results show that, because of the complex nature of PM, suitable measurements of PM require on programs for monitoring multiple physical and chemical properties-parameters of PM.

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Section lecture - Friday, Dec. 9th, 9:35

THE ROLE OF PRIMARY AND SECONDARY AIR POLLUTANTS IN ATMOSPHERIC POLLUTION

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The question to which extent primary and secondary air pollutants are relevant to atmospheric pollution and their effects on human health and environment can be answered in a straight-forward manner: in most cases the secondary products of atmospheric photo-oxidation are the more important ones, of industrial chemicals as well as of natural products. The formation of secondary products represents the critical property determining the establishment of certain air standards, rather than the actually emitted substance, although there are notable exceptions.

One typical example is volatile organic chemicals leading to formation of photo-oxidants of diverse structure and from various sources. Oxidation intermediates and reaction products often have higher biological activity than the respective precursors. Secondary air component are also important as nucleation particles for formation of aerosols, which eventually develop into fog and acid rain. Other examples will be given in the presentation.

Section 11: Atmospheric chemistry, air pollution, modeling of pollutants diffusion - Friday, Dec. 9th, 9:50

PREPARATION AND CHARACTERIZATION OF CeO₂-M₂O₃ (M = B, Al, Ga, In) MIXED OXIDES FOR OXIDATION REACTIONS

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Ceria-containing materials have a wide range of applications to catalytic processes such as the treatment of exhaust gases, combustion, and deNO_x. However the major drawbacks of an oxygen storage system based on pure CeO₂ are its thermal resistance, low-temperature activity, and textural stability, which are insufficient to meet the requirements of high-temperature applications. The present work focuses specifically on the combination of ceria with another oxide from group III in order to improve the catalytic properties. CeO₂-(B₂O₃, Al₂O₃, Ga₂O₃, In₂O₃) mixed oxides with a wide range of M₂O₃ contents have been prepared via a coprecipitation route and via a sol-gel method. The catalysts have been characterized in terms of their structural, textural and surface properties, including the acid-base and redox features, by a variety of techniques (BET, XRD, Raman, SEM, TG, TPR-TPO, TG-DSC). The adsorption of probe molecules (NH₃ and SO₂) was used to investigate the acid-base properties by calorimetry and XPS. Only boria created significant acidity, and the samples prepared by the sol-gel method displayed less surface acidity than their coprecipitated analogues. The basicity compared to pure ceria was sharply decreased for boria-ceria, slightly decreased for alumina-boria, and slightly increased for gallia-ceria and india-ceria. The TPR profiles were examined in relation with the nature of the phases and the extent of reduction. For example, the temperature of the maximum of the reduction peaks for CeO₂-In₂O₃ samples prepared by coprecipitation decreased with increasing In₂O₃ loading while the samples prepared by sol-gel gave a very different TPR profile. The properties were shown to strongly depend on the preparation procedure, chemical stability and structural features including the phase composition and the kinetics of the oxygen uptake/release.

Section 11: Atmospheric chemistry, air pollution, modeling of pollutants diffusion - Friday, Dec. 9th, 10:02

PROPERTIES AND CATALYTIC ACTIVITY IN NO_x ABATEMENT OF Cu/Sn AND Cu/Ga BIMETALLIC OXIDE CATALYSTS SUPPORTED ON SILICA-ALUMINA

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In the last decades, catalysts containing copper oxide have received a lot of interest in particular for emission control reactions (NO_x and SO_x abatement). In this work, we study the surface properties and the catalytic activity of two series of bimetallic oxide catalysts, containing Cu coupled with Ga or Sn.

The catalysts were prepared by successive adsorptions; first Cu was deposited on the silica-alumina support and then Ga (or Sn) was deposited on the uncalcined Cu-containing material. The calcinated catalysts contained the same total number of metal atoms ($6 \cdot 10^{20}$ atom·g⁻¹) distributed in different proportions on the support (Cu:Me = 1:0, 1:0.25, 1:0.50, 1:0.75, 0:1, with Me = Sn or Ga). They were characterized by XRD, XPS, FT-IR, TEM, SEM-EDS, s-TPR, calorimetry, using various probe molecules (NH₃, C₆H₅-NH₂, CO).

Amorphous materials with high surface area (350-500 m²·g⁻¹) and a well-dispersed oxide phase (2-4 nm) were obtained. The predominantly Brönsted surface acidity of silica-alumina was converted into Lewis acidity upon metal addition, as revealed by XPS on the samples saturated by NH₃. The number of acid sites and the relative proportion between Lewis and Brönsted acid sites were obtained by comparing the XPS and calorimetry results.

Different reactions for NO_x abatement were studied, from direct decomposition of N₂O (with/without O₂) to selective reductions of N₂O and NO (SCR by C₂H₄ and CH₄). The catalysts maintained a high activity for N₂O decomposition, even in presence of O₂. The CuO-phase was responsible for the catalytic activity, while the addition of Ga or Sn oxide mainly influenced the SCR selectivity.

Section 11: Atmospheric chemistry, air pollution, modeling of pollutants diffusion - Friday, Dec. 9th, 10:14

CONTRIBUTIONS OF GHG EMISSIONS FROM DEVELOPED AND DEVELOPING COUNTRY ITALY AND SERBIA AND MONTENGRO IN 1990

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The greenhouse gases - GHG (CO₂, CH₄, N₂O, CO, NO_x, NMVOCs, HFCs, PFCs, SF₆ and SO₂) are emitted from energy, industry, land-use change, agriculture and waste sectors. The GHG concentrations that were less than 280 ppm in the atmosphere have increased to about 370 ppm now and are constantly increasing. If GHG concentrations stabilise at 450 ppm by the end of the 21st century, global average temperature will increase by 0.7°C, accompanied by a sea level rise of 10-65 cm.

Besides limiting GHG emissions, cumulative emissions between now and 2100 would be about 1500 Gt of C_{eq}, with annual emissions reaching 20 GtC_{eq} per year and accelerating upward. The world could expect a warming of 1.4 to 2.9°C and a sea level rise of 19 to 86 cm by 2100 under this scenario.

The largest share of historical and current global emissions of greenhouse gases has originated in developed countries. The per capita emissions in developing countries are still relatively low, but their share of global emissions will grow to meet their social and development needs.

Contribution of GHG emissions of developed country Italy and developing country Serbia calculated according to Revised 1996 IPCC Guidelines for National Greenhouse Gas Inventories shows that Total emission of CO₂ equivalent from all sectors of Italy was 485.545 Gg and of Serbia was approximately 72.500 Gg.

The emissions are calculated for 1990 year that is accepted as a base year on global level.

Section 11: Atmospheric chemistry, air pollution, modeling of pollutants diffusion - Friday, Dec. 9th, 10:26

QUANTUM STUDY OF MOLECULAR AND IONIC INTERACTIONS IN ADSORBED LAYERS AT AIR / WATER INTERFACE IN RELATION WITH POLLUTANT TRANSFER BETWEEN ENVIRONMENTAL SPHERES

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Results on adsorption of 2-pollutant mixtures (ionic/aromatic compound mixtures) in aqueous solutions have already been reported by our team. While heavy metal salts do not adsorb at the air - water interface when alone in solution, they exhibit positive relative adsorption at that interface when organic solutes such as those previously mentioned are present. As a consequence, bubbling mechanism leads to co-polluted aerosol formation. Given the importance of bubbling in pollutant transfer between water sphere and atmosphere and the importance of aerosol electrical charge, it appears necessary to better understand the structure of the adsorption layer and particularly the place of ions.

Statistical simulation seems, nowadays, to be the best way to describe the behaviour of ions in solutions and at interfaces but, for that purpose, it is necessary to precise what are the nature and strength of interactions between the different species present in the adsorbed layer at a molecular level.

This is why we tried, as a first attempt, to model interactions between Pb^{2+} ions, water and benzene molecules by quantum mechanical theory at the B3LYP level. Our results are consistent with experimental trends previously described and give hints to understand how the nature of the anions and of benzene-ions, water-ions and benzene-water interactions modify the superficial behaviour of these mixtures.

Section 11: Atmospheric chemistry, air pollution, modeling of pollutants diffusion - Friday, Dec. 9th, 10:38

MONITORING OF POLLUTANTS DEPOSITION AND USING OF MODELING FOR CRITICAL LOADS CALCULATIONS

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Real depositions of acidifying pollutants and heavy metals have been measured in 12 adjacent forest stands by means of 50 permanently opened collectors installed under the crowns of the main forest species. Statistical treatment of the results has been used for supplying data for geo-statistical modeling of the depositions distribution. This data has been interpolated for all areas of the studied forest catchments in EMEP grid cells of 50 x 50 km. A similar model has been developed for the concentrations of acidifying pollutants in air.

The steady state mass balance method for sustainable development of water and forest ecosystems in accordance with ICP Modeling and Mapping under the long-term transboundary air pollution convention was used to calculate the critical loads of acidifying pollutants for the Bulgarian forested catchments areas.

The critical load is the highest input rate of acidifying pollutants and heavy metals, below which harmful effects on ecosystems would not occur at the site of interest in a long-term perspective according to the current knowledge. Assessment of this critical loads modeling and its comparison to the really measured depositions offers the possibility to determine the degree of reduction of local pollutants emission required to protect the sustainable development of water and forest ecosystems.

The critical loads of the really deposited target pollutants were found to be exceeded by using the sum of both wet and dry depositions. The results of the modeling (as a software product) could be applied at the Ministry of Environment and Waters as well as in the Coordination Center of Effect of UN/CCE for sustainable management of ecosystems for calculating the required degree of reduction of a given pollutant emission.

This study is funded by the Ministry of Education and Science as well as by the Ministry of Environment and Water of the Republic of Bulgaria.

Section 11: Atmospheric chemistry, air pollution, modeling of pollutants diffusion - Friday, Dec. 9th, 10:50

EVIDENCE OF WINDBORNE MINERAL DUST IN THE MEDITERRANEAN ATMOSPHERE

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Mineral dust particles can scatter and absorb both incoming and outgoing solar radiation. In the visible part of the spectrum, the light-scattering effect is prevailing and it is an overall cooling effect, while in the infrared region, mineral dust is an absorber and acts like a greenhouse gas. The major source of mineral dust in the Mediterranean is the Sahara desert. A sampling site at Herceg-Novi (Montenegro) is included in the network for the monitoring of airborne pollutants along the Mediterranean coast. The 24-h concentrations of total suspended particles (TSP) were measured by a standardized gravimetric method in a 1-in-6 day schedule program. The available data set from the period 1995-2000 was chosen for statistical analysis. Besides the particle size distribution, the Fe content of >2% in the TSP samples was accepted for the identification of genuine Saharan dust transport. The frequency of these events of 7% a year contributed to an increase of annual TSP concentrations of 10-15%. The amorphous material was found in the sample of 31. May/1. June 1999 after the bombing of Cape Arza on the Luštica Peninsula, which is situated 5 km away from the sampling site. Using the Eta model trajectory analysis, the short-regional transport from Luštica to Herceg-Novi corroborated the origin of mineral dust. The global warming can enhance the probability of the Saharan dust storms influencing thus on the climate in the Mediterranean region with unpredictable changes.

Section lecture - Friday, Dec. 9th, 11:30

QUADRUPOLE ION TRAP IN ENVIRONMENTAL ANALYSIS

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Mass spectrometry concerns the formation, manipulation and control of the trajectories of ions as well as their detection. The emphasis in this paper will be on the control of ion trajectories using quadrupole ion trap and the application of ion trap mass spectrometry in the environmental analysis. The specific modes of operation and the ability to control trapped ion trajectories permits a wide variety of applications for the ion trap.

The identification of environmental pollutants in complex matrices has been one of the primary applications of gas chromatograph linked with quadrupole ion trap detector (GC/Q). GC/Q instruments are capable of generating full-scan in electron impact (EI) and chemical ionization (CI) over a wide dynamic range with high sensitivity. CI, with a variety of CI reagent ions, can be carried out at reagent gas pressure order of magnitude less than that employed in conventional CI sources. The example of polychlorinated biphenyls (PCBs) analysis is focused on use of selected ion CI for the determination of coeluting PCB congeners and the application of tandem mass spectrometry (MS-MS) for distinguishing toxic from non toxic congeners.

Also, quadrupole ion trap offers capabilities needed to provide routine high sensitivity HPLC-MS/MS quantitative and qualitative analysis of pollutants in various matrixes. In order to illustrate that, our results of analysis of pesticides in fruit juices as well as the analysis of antibiotics will be presented.

Section 13: Analytical methods for environmental science - Friday, Dec. 9th, 11:45

ILLUMINATING THE PHOTOCHEMICAL FATE OF PROZAC AND VALIUM

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The fate of pharmaceutically active compounds (PhACs) in the aquatic environment is governed by both abiotic and biotic processes. Abiotic transformations in surface waters occur via photolysis and/or hydrolysis, with photolysis thought to be the significant factor in determining their environmental fate. The antidepressants Prozac[®] (Fluoxetine) and Valium[®] (Diazepam) were selected for photodegradation studies from over 200 pharmaceuticals which had previously been detected in the environment.

The solar photodegradability of each drug and respective metabolites was evaluated using a Heraeus Suntest Xenon Arc lamp, designed to reproduce the effect of solar radiation. Emphasis was on the identification of photoproducts and the determination of degradation rates. Sample methods were developed for these drugs in aquatic matrices using solid phase extraction (SPE) cartridges with subsequent analysis carried out by liquid chromatography electrospray ionisation mass spectrometry (LC-ESI-MSⁿ).

Novel photoproducts have been identified by ESI-MSⁿ and mechanisms are proposed for their formation.

Section 13: Analytical methods for environmental science - Friday, Dec. 9th, 11:57

UNEARTHING THE FATE OF PROZAC, VALIUM AND THEIR HUMAN METABOLITES IN SEWAGE SLUDGE AMENDED SOILS

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The last decade has seen an increase in reports of pharmacologically active compounds in the environment e.g. in watercourses, open ocean, soil and sewage sludge. Here we report the biotic fate of two pharmaceuticals: Prozac (fluoxetine HCl) and Valium (diazepam) and their major human metabolites in sewage sludge amended soil. Since the EU banned sea disposal of sewage sludge in 1998 the application rate of sewage sludge to land has risen significantly to 52% in the UK in 2000 and is set to rise further, hence this has now become an important transport route for pharmaceuticals into the environment.

In order to assess the importance of the application of sewage sludge to land as a transport route for pharmaceuticals into the environment, and the subsequent fate of the pharmaceuticals and their metabolites, two different biodegradation experiments were performed. The first was a long term Fluoxetine HCl study (6 months) which used sewage sludge amended soil as culture. The other short term study consisted of a set of experiments using 6 different target compounds with a range of different bacterial consortia, including some that had been previously isolated. The biodegradation of the parent compounds and the formation of metabolites were monitored in all experiments. A simple extraction technique, including tandem SPE was developed, which allowed for subsequent analysis using LC-ESI-MSⁿ. Use of LC-ESI-MSⁿ resulted in the generation of quantitative and qualitative data, which will be presented.

Section 13: Analytical methods for environmental science - Friday, Dec. 9th, 12:09

APPLICATION OF GC-TRIPLE QUADRUPOLE MS/MS FOR MULTI-RESIDUE ANALYSIS OF PESTICIDES IN COMPLEX MATRIX

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There are over 800 pesticides currently in use worldwide to control undesirable weeds, insects, rodents and fungi. To ensure the safety of food for consumers numerous EU legislation has established maximum residue limits (MRL) for pesticides considered a potential health risk and the guidelines for developing analytical methods must be followed.

The analytical challenge is to maximise the number of pesticides, minimise the variety of methods, keep run times short and achieve limits of detection (LoDs) at or below the reporting level. Multi-residue analyses are increasingly gaining acceptance for the determination of residues in foodstuffs. For multi-residue analysis with a very wide scope, the sample preparation method must be non-selective in order to obtain acceptable recovery for all pesticide residues. Inherent to this approach is that clean up of extracts is only possible to a limited extent. This results in a complex sample matrix that has potential to interfere with the determination of the various analytes.

A method is described for the determination of 100 pesticide residues in various complex matrices, including fresh produce, baby food, dried herbs, spices, tobacco, ginkgo and cannabis using the Waters Micromass Quattro micro GC tandem quadrupole mass spectrometer. Despite limited sample clean up and the high complexity of the samples, little or no interference was observed for the majority of the pesticide/matrix combinations, demonstrating the excellent selectivity of this technique.

Section 13: Analytical methods for environmental science - Friday, Dec. 9th, 12:21

THE DETERMINATION OF EMAMECTIN BENZOATE IN ENVIRONMENTAL MATRICES

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Sea-lice outbreaks among farmed salmon are routinely controlled using chemotherapeutic products. The in-feed veterinary medicine SLICETM, developed by Schering-Plough Animal Health and widely used by Scottish fish farmers, is one of the most effective treatments. However its active component, emamectin benzoate, is classified as a List II Dangerous Substance. Consequently, the UK Veterinary Medicines Directorate and the Scottish Environmental Protection Agency have established safe levels for emamectin in salmon (100 ng·g⁻¹) and sediments below farm cages (7.63 ng·g⁻¹). As a result sensitive and reliable techniques to monitor emamectin benzoate in a wide range of biological and environmental matrices are required.

This study aimed to optimise an analytical method used to quantify emamectin benzoate in sediments to enable its determination in seawater, seaweed, salmon tissues and mussels. Controls fortified with 2.5 and 10.0 ng·g⁻¹ of emamectin were extracted with methanolic ammonium acetate then cleaned up on sulphonic acid solid phase extraction columns. A derivatisation step with *N*-methylimidazole and trifluoroacetic anhydride produces a fluorescent product which is analysed by reversed phase high performance liquid chromatography (HPLC).

At a fortification level of 2.5 ng·g⁻¹, the method yielded recoveries of 72.5-87.4, 57.5 and 85.1%, respectively for sandy sediment, salmon flesh and seaweed. The recoveries at 10.0 ng·g⁻¹ fortification were 73.5, 72.7 and 82% respectively. This sensitive method allows the fate of emamectin benzoate to be monitored not only in sediments but also in other biological and environmental media present around salmon farms. Thus it is well suited for routine monitoring and regulatory purposes.

Section 13: Analytical methods for environmental science - Friday, Dec. 9th, 12:33

QUANTITATIVE ANALYSIS FOR THE REMOVAL OF NATURAL ORGANIC MATTER AND DEGRADATION BY-PRODUCTS FROM WATER USING CYCLODEXTRIN NANOPOROUS POLYMERS

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Natural organic matter (NOM) is found in varying concentrations in all natural waters [1]. Its presence in water produces aesthetically undesirable problems such as colour, odour and bad taste of the water. Besides affecting many aspects of water treatment systems, NOM promotes the formation of potentially harmful disinfection by-products (DBPs) such as trihalomethanes, haloacetic acids, halo-ketones and other toxic chlorinated organic compounds [1,2]. To date, the removal of NOM and its degradation products to parts per billion levels (ppb) remains a challenge to local governments and industry. Conventional water purification technologies such as activated carbon adsorption [3], reverse osmosis [3], zeolites [4], and molecular sieves [4] have failed to remove organics to these desired levels. It is also not known whether these techniques can face the challenge of new, emerging contaminants [5].

A completely new class of nanoporous polymers called cyclodextrin (CD) polymers has recently been developed [3,4]. A study of the ability of these CD polymers to remove NOM and its degradation products was conducted. The poster to be presented will display the results obtained. Water samples spiked with some priority organic pollutants of known concentration were preconcentrated by solid phase extraction (SPE) and quantified using GC/MS. Quantification of humic substances was done by total organic carbon (TOC) measurement and UV absorbance. Quantitative analysis shows that the CD polymers are much more effective compared to granular activated charcoal (GAC) at removing the organic contaminants at µg/L and ng/L levels. The major organic pollutants investigated were the high priority chlorinated phenols, geosmin, 2-MIB and humic acid which was used to mimic NOM. Analysis of environmental samples from around Johannesburg were also conducted.

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Section 13: Analytical methods for environmental science - Friday, Dec. 9th, 12:45

MICRO/NANO-ELECTROMECHANICAL SENSORS FOR ENVIRONMENTAL PROTECTION

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Various types of novel miniature physical, chemical and biological sensors have been developed using MEMS and NEMS technologies. When combined with wireless technology, these sensors represent a new generation of sensors for environmental monitoring. Their main advantages are high sensitivity and selectivity, and the possibility of in situ measurements in real time. They are used for measurements in liquid and gaseous environments.

This paper is focused on environmental sensors based on micro/nanocantilevers similar to those applied in atomic force microscope (AFM) systems. Two basic modes of operation are analyzed. One of them is static, based on the measurement of deflection caused by strains induced by adsorption of substances to be detected on the cantilever surface. The other one is dynamic, based on the measurement of resonance frequency variations either due to the adsorbed mass or to the change of the stiffness constant of an oscillating cantilever. Apart from this, the paper also describes sensibilization of the cantilever surface depending on application, with the aim of achieving a better selectivity.

For methods based on the measurement of resonance frequency variations, our latest results regarding determination of minimum detectable signal (concentration and mass) are presented. Calculations show that the minimum mass detectable using MEMS and NEMS sensors is of the order 1 kDa (this is two orders of magnitude smaller than the mass of the protein molecules and approximately equal to the mass of one DNA base pair).

Section 13: Analytical methods for environmental science - Friday, Dec. 9th, 15:30

NON EXTRACTABLE ORGANIC XENOBIOTICS IN RIVERINE SEDIMENTS ANALYSED BY PYROLYSIS AND THERMOCHEMOLYSIS

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Anthropogenic organic compounds in sediments are partly associated with geomacromolecules (e.g. humic compounds, lignin). The interactions between macromolecular matter and the so-termed bound residues are covering the range from reversible adsorbtive forces and van-der-waals-interactions to reversible or irreversible covalent bonds. Bound residues are principally immobile and of a limited bioavailability. Therefore, the phenomenon of bound residues serves as a temporal sink for organic contaminants.

Due to the fact that bound residues are not extractable, specific analytical procedures are required for their analysis. Within this study, different thermochemical degradation methods have been applied on preextracted sediments, derived from three rivers in Germany (Mulde river, Ems river and Teltow canal), in order to release bound residues by degrading associated geomacromolecules. In detail, pyrolysis and TMAH-thermochemolysis, on-line and off-line combined with GC-MS analysis have been performed. The experiments revealed numerous halogenated compounds, e.g. brominated anisoles, chlorinated biphenyl ethers and DDT-related compounds. The results differed, depending on samples and applied methods.

It could be demonstrated that thermochemical degradation is a gainful approach in environmental analytical chemistry. However, the major restriction of the applied methods is the possibility of artefact generation due to secondary reactions during thermochemical degradation. Therefore, such approaches have to be evaluated very carefully. Consequently, additional to natural samples, spiked samples have been investigated, in order to gather methodologically induced artefact generations and to reveal corresponding reaction mechanisms.

Section 13: Analytical methods for environmental science - Friday, Dec. 9th, 15:42

DETERMINATION OF NEONICOTINOID INSECTICIDES BY LIQUID CHROMATOGRAPHY COUPLED WITH THERMAL LENS SPECTROMETRIC DETECTION

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The neonicotinoids are a relatively new class of insecticides, registered in EU since 2003. They are used worldwide for controlling insects that are developing resistance to conventional organophosphate, carbamate, and pyrethroid insecticides. It is important to determine neonicotinoids with accurate and sensitive analytical methods in order to efficiently monitor their effects and fate in the environment.

The objective of this study is to determine trace amount of neonicotinoids with liquid chromatography coupled with thermal lens spectroscopy (TLS) technique. This multiresidue-analysis method is based on a HPLC reversed phase separation (C₁₈ column), isocratic elution and collinear dual beam TLS detection. The measurements were made on a pump probe TLS configuration in flow-injection quartz cell at 244 nm excitation laser wavelength. After parameter optimization the retention times of thiamethoxam, imidacloprid, acetamiprid and thiacloprid were 4.3, 5.7, 6.4 and 8.6 min and the LOQ-s were 50.0, 100, 25.0 and 10.0 ng/cm³, respectively. In all of cases the linearity of detector response was checked in the range of LOQ-1000 ng/cm³. Generally, the retention times compared well with those obtained with identical chromatographic method using a diode-array detector (DAD). The LOQs for acetamiprid and thiacloprid provided by TLS technique, which is known to enable measurement of absorbances as low as 10⁻⁷, are however 10 times lower compared to DAD.

The applicability of developed trace level analysis was tested for spiked river water, potato and pepper samples.

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Section 13: Analytical methods for environmental science - Friday, Dec. 9th, 15:54

CHEMOMETRICS APPROACH TO ELEMENTAL ANALYSIS OF PLANT AND SOIL SAMPLES

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One part of an extensive study comprising the elemental analysis of numerous plant samples will be presented. Though, plants are just one of environmental compartments, their analysis is of special importance. The dynamic changes between nonliving media (atmosphere, water, soil) and living compartments such as plants, animals and human beings occur constantly being influenced by physical, chemical and biological processes in a different extent. The complexity of all possible processes could be partly revealed only if one can perform the analysis in the other media too. In that sense, to elemental analysis of herbal drugs samples, originated from the medicinal plants, cultivated on the plantation, under the controlled conditions, rhizosphere soil samples were also analyzed in order to highlight possible relations.

Taking into account the multivariate nature of conducted environmental research, common chemometric approach to data analysis was applied. Principal component, factor and cluster analysis (PCA, FA and CA) were used in order to get better insight to elemental patterns as well as to identify the sources that might be responsible for the influence of specific element or its grouping.

Section 10: Waste valorization - Friday, Dec. 9th, 16:06

DECONTAMINATION AND VALORIZATION OF SLUDGES DERIVING FROM BIOLOGICAL WASTEWATER TREATMENT PLANTS THROUGH ANAEROBIC DIGESTION

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Organic pollutants such as PAHs, PCBs and pesticides tend to accumulate in the primary and secondary sludges of biological plants treating domestic and industrial wastewaters. Thus, those sludges have to be submitted to a dedicated treatment, that generally consists in their thermal destruction. Anaerobic digestion could represent an alternative technology for the disposal of such sludges, as it can mediate both their decontamination and their valorization, through the production of a biogas with a high content of methane.

In this study, two sludges coming from domestic water treatment plants were spiked with PCBs or with a mix of PAHs and chlorinated aromatic compounds and employed in the development of anaerobic microcosms. The effects of the anaerobic digestion on the sludges were evaluated in terms of methane production, biodegradation of the occurring contaminants and depletion of pathogenic microorganisms, both in mesophilic or thermophilic conditions. The contribute to the digestive process of the sole fermentative eubacteria or of the sole methanogenic and sulfate-reducing bacteria, along with the possibility of enhancing its performances by stimulating the indigenous anaerobic consortium with yeast extract, were also determined. Methane production and xenobiotic removal were more efficient under mesophilic conditions, while a complete disinfection of the sludge was achieved at 55°C. Yeast extract allowed to obtain better performances under mesophilic conditions both in terms of sludge decontamination and disinfection. All the selected microbial population seemed to be involved in the biodegradation of the contaminants.

Section 10: Waste valorization - Friday, Dec. 9th, 16:18

ASSESMENT OF WASTE INSULATING OIL REREFINING BY EXTRACTION WITH N-METHYL-2-PYRROLIDONE REGARDING OXIDATION STABILITY AND POLYCYCLIC AROMATIC HYDROCARBON CONTENT

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Rerefining of waste mineral insulating oils was investigated using N-methyl-2-pyrrolidone solvent extraction process. Quality of rerefined oils was determined using oxidation stability test according to IEC61125 C standard. Rerefining of waste insulating oils showed its environmental benefits on the basis of trace amounts of PAH content measured in rerefined oils. Chemical composition of rerefined oils was investigated considering presence of different oil constituents that are found to have marked influence on oil oxidation stability. Sulfur compounds, ratio of naphthenic (CN) to paraffinic hydrocarbons (CP), aromatic hydrocarbons (CA) and polycyclic aromatic hydrocarbons (PAH) were measured using Microcolumn titration system, FTIR and HPLC. Influence of these compounds on rerefined oils oxidation stability was analyzed with respect to different rates of acid and sludge build up, during catalytic oxidation reaction. It was determined that trace amounts of PAH in rerefined oils had no pronounced effect on oxidation stability. Changes in rates of volatile acids build up was correlated to influence of CA, ratio of CP/CN and sulfur compounds content in different stages of oxidation process. In initial stage of oxidation, higher CP/CN ratios were determined to have pronounced effect on oxidation stability. In breakdown oxidation stage, synergetic antioxidant activity of monocyclic aromatic hydrocarbons and sulfur compounds was found to be detrimental in inhibition of the oxidation reaction. Increased sulfur compounds content with hydrocarbon composition (CA/CN/CP) in optimum range improved oxidation stability of rerefined oils. Optimum solvent extraction process parameters were determined with respect to rerefined oils oxidation stability: moderate extraction temperature, 1% water in NMP and low solvent/oil ratio (0.5).

Section 1: Sustainable development - Friday, Dec. 9th, 16:30

EFFECT OF WATER ON REFORMING OF METHANE BY CARBON DIOXIDE OVER SUPPORTED CATALYSTS

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Development of technologies involving carbon dioxide as renewable energy source attracts a great attention due to mitigation of CO₂. By dry reforming of methane it is possible to produce synthesis-gas being a source for the production of hydrocarbons and oxygenates. This catalytic process can be industrially introduced on condition that the active catalysts having a resistance to coke formation will be available. Also, there are some problems: - increase in hydrogen content in synthesis gas formed ($H_2/CO > 1$); - possibility to use both the real natural gas and waste industrial gases containing carbon dioxide without their cleaning from water.

In this paper the effect of water on reforming of methane by carbon dioxide over bimetallic catalysts on a base of VIII Group metals supported on alumina is discussed. It has been established that the effect of water is varied depending on its content and nature of the catalyst. Thus, introducing of a certain volume of water steam (up to 20 vol.%) into an initial gas composition ($CH_4/CO_2 = 1/1$) promotes the process of complete methane conversion over the Co-containing catalysts and leads to increasing hydrogen formation. No significant effect of water on the process has been observed over the Ni-containing catalyst. The negative effect of water has been found over the Fe-containing catalysts. Further growth of steam amount to 50 vol.% causes an increase in the process temperature over all catalysts studied.

Poster presentations

1. Sustainable development

Posters No. 1-10
Wednesday, December 7th
19:30-20:30

Poster No. 1:

SUSTAINABLE INDUSTRIAL DEVELOPMENT AND MANAGEMENT

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Sustainability is the objective that many disciplines indicate as being essential to the resolution of environmental degradation, and thus, is increasingly becoming a key social, political, scientific and engineering issue. There are increasing signs that sustainability will become a major new paradigm influencing the society of tomorrow and the engineering it requires. In this paper, a particular attention is given to the concept of sustainability and investigation how sustainable development can be related to industrial development, particularly in developing countries.

Environmental problems are defined as externalities, most of these occurring between different generations. Traditional solutions for externalities do not work in the intergenerational context, and therefore the traditional methods for evaluating the costs and benefits affecting different generations should be improved. When external costs are extended over time, those who suffer have yet to be born and the incentives are even fewer. Furthermore, an intergenerational redistribution of natural resource property rights is essential to guarantee equality of opportunities for all generations and therefore to ensure sustainability.

Poster No. 2:

ADSORPTION OF Pb^{2+} , Cd^{2+} AND Sr^{2+} IONS ON HAP POWDER OBTAINED BY HYDROTHERMAL DECOMPOSITION OF UREA AND CALCIUM-EDTA CHELATES

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Apatites are well known matrix for heavy metal immobilization and remediation of ground water and contaminated soils. The main objective of this paper was to investigate the adsorption of two heavy metal ions, Pb^{2+} and Cd^{2+} , and Sr^{2+} as radionuclide, on a hydroxyapatite obtained by hydrothermal decomposition of urea and calcium-EDTA chelates.

The calcium-hydroxyapatite was characterized by XRD, FT IR, SEM, and by determination of specific surface area and point of zero charge.

A shift in the point of zero charge towards lower pH values, which is proportional to the amount of a specifically sorbed cations, was observed. The greatest shift in the point of zero charge, and therefore the highest sorption was noticed in the case of Pb^{2+} , then Cd^{2+} , and the lowest in the case of Sr^{2+} ions. Adsorption isotherms of these cations on apatite confirmed the given sorption dependence on ion species. Further, correlation between the released Ca^{2+} ions from apatite matrix and those adsorbed Pb^{2+} , Cd^{2+} , and Sr^{2+} ions was also established.

The adsorption data suggest three possible mechanisms that could be involved in the interaction between Pb^{2+} , Cd^{2+} , and Sr^{2+} ions and the surface of apatite: specific sorption, ion exchange process and dissolution of apatite.

Poster No. 3:

POTENTIALLY HAZARDOUS TRACE ELEMENTS IN COAL FROM THE KOSTOLAC BASIN

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The concentration of potentially hazardous trace elements in coal from the Kostolac basin was preliminary analysed by inductively coupled plasma-mass spectrometry (ICP-MS) using NIST standards at Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) laboratories in Hannover, Germany. The complete procedure of sample preparation and analysis was according to Meier et al. (1996).

The Kostolac coal basin, covering the area of 145 km², is located about 90 km east of Belgrade. It is divided into three coal fields: the Drmno field in the eastern, the Čirikovac field in the central, and the Smederevsko Podunavlje field in the western part of the basin. The fields of Drmno and Čirikovac are exploited, while the field of Smederevsko Podunavlje is still under preliminary exploration.

The measurements of huminite reflectance have shown that coal from the Kostolac basin belongs to the group of soft brown coals (lignites). In the whole basin coal consists mostly of ulminite and textinite, with relatively high amount of densinite in some parts of the third coal seam in the Drmno field. The average quality of Kostolac coal is: total moisture content 40-46%, ash content 15-21% (as received basis), and net calorific value around 8 MJ/kg (with total moisture), and 24-25 MJ/kg (dry, and ash-free).

Thirteen samples of coal from the II and III coal seam from the Drmno field were collected from the P-17/2002 borehole, and analysed on fourteen potentially hazardous trace elements, namely: As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, Th and U. The analysis of geometric mean values revealed that coal has relatively high concentrations of manganese (172.45 ppm), nickel (53.94 ppm), chromium (28.42 ppm), arsenic (25.15 ppm), copper (19.09 ppm) and cobalt (8.60 ppm), which is much more than the average values for the world coals of the similar rank. The other analysed elements occur in concentrations similar to world lignites. The uranium and thorium concentrations are less than in average world lignites, but there are parts of coal seam with high uranium concentration.

Poster No. 4:

INORGANIC CO₂ SEPARATIONS MEMBRANES

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The reduction of the CO₂ emission poses great technical and economical problems. For the existing and the new generation fossil power plants several concepts are discussed for enhancing the efficiency of power plants and CO₂ separation from the exhaust gases. The CO₂ exhaust reduction can be acquired with gas separation membranes.

This review focuses on a literature study on the available CO₂ separations membranes. The study enables to understand the restrictions, possibilities of promising materials. The porous (amorphous and crystalline) membranes are described. The current status and the transport properties membrane material and published results of each type membranes are presented.

Two key technical challenges exist. Achieving higher permselectivity for the relevant application is the first of these challenges. Maintaining these properties in the presence of complex and aggressive feeds is the second challenge.

Poster No. 5:

ENVIRONMENT PROTECTION AND CHEMICAL ACCIDENTS

R. Biočanin

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Not a long time ago we were the witnesses of a number of accidents that included dangerous chemical substances during the transport. This fact is also important because we are the crossroad of numerous important European communications where a lot of such transports are passing by. Great number of such substances can seriously damage human environment for a very long period of time. The risk is defined as a product of a failure probability and its consequences. This work studies such events according to different parameters, trying to show the way how to successfully prevent them and protect from this threat as in the peace time, such as during the war operations. At the time when dangerous substances are transported we usually don't have the valuable information about everything we need to know to prevent it. The emphasis of the paper is on chemical risks caused by structural failures leading to the serious involving pressure wave, flames, explosions and toxic contamination. So, realization of the universal and united system of NBCD gives us a possibility, using modern communication equipment and very effective mobile units, to react in a real time and successfully perform monitoring, alarming, protection and decontamination.

Poster No. 6:

ELIMINATION OF MIGRATION ABILITY OF DANGEROUS SUBSTANCES DURING MAINTENANCE OF REGIONS DAMAGED BY WAR

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Currently working legislative, organizational, technological and technical conditions during migration of undesirable substances, especially of those that are dangerous for environment are based on these facts: **a)** there are enough finances, **b)** there is enough time, **c)** there are optimal organizational, technical and technological conditions.

Searching for the best solution of preventive and active protection of environment is very carefully considered usually in harmony with legislatively defined measures. As all these rules are not kept during natural disasters, a UNESCO project Ground Water for Emergency Situations (GWES) included in International hydrological program of UNESCO was started in 2004.

Evaluation of ecological problems that can appear during some extreme events is to a certain extent a new field of ecology. In spite of very detailed theoretical and methodological principles, there are significant differences - e.g. in elimination of migration abilities which needs independent research and principally new laws. Why it is so urgent to ask for these changes is clear from the list of these events, f.e.g. Yugoslavia - during the invasion extreme amounts of undesirable substances and aimed production of waste (in agreement with the EU Directives they all can be found dangerous) interfered with the environment; that is the case of setting fire to oil refineries and supplies, Chechnya - bombing of refinery in Groznyj, Iraq and Kuwait (aimed setting fire to oil derricks and pipelines).

As for methodological and theoretical interest, ecology of extreme events deals with the influence of natural disasters like extreme floods in the Czech Republic 1997, 2002; then tsunami waves in Indonesia in 2004; and hurricanes Ivan in 2004 and Katrina in 2005 on industrial properties. All parts of the environment were threatened there with industrial substances and waste that appeared as a result of these catastrophes.

The analysis of these events has shown the main purpose of all rescuing activities, and that is as fast and effective restriction of migration of especially oil substances and heavy metals as possible. In position when rapid intervention is necessary, it is impossible to use biodegradable methods of maintenance and venting or water extractions. There is an urgent need to concentrate on operative methods of storage. As a part of research work that Envirex Firm tried to solve, possibility of operative stabilization of dangerous waste by other possible or suitable waste - e.g. various ashes with relatively high effectiveness was analyzed. These ashes even can substitute lime and cement which are raw materials that are not very frequent in such extreme conditions. The results of the research of mud solidification have demonstrated very fast lowering of mobility of dangerous substances by three degrees. Excepting this technology, the authors recommend to pay attention to other methods representing extraction and attenuation of mainly biodegradable substances that gradually lose their detrimental effects on simply secured dumping grounds. Building of properly secured dumping grounds makes possible include them into renowned urbanized regions, much destroyed by this extreme situation. We would like to emphasize that because of attenuation, danger and ecological risks

gradually fall down on acceptable level. Large waste dumping grounds that appeared during this extreme situation can be utilized as a landscape-forming phenomenon, or for lay out of the terrain where some sports facilities can be built. In cases like these, the methods can successfully replace other methods of active biodegradation and maintenance technologies which are rather expensive and very demanding in organization as well. Elimination of migration of dangerous substances requires to start even with minimal ecologically aimed protective operations immediately after the extreme situation appears, regardless of possible lack of finances.

The results of laboratory and pilot plant tests have been included in this article. Considering relatively frequent and under no conduct appearing extreme situations, elementary processes of elimination have been recommended in this work.

Poster No. 7:

INFLUENCE OF EMULSION "ANTIINKRUSTAL PURONI 2000" ON THE INHIBITION OF IRON AND STEEL CORROSION

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Water, oxygen, chlorides and other corrosive agents and higher temperature may cause iron and steel corrosion. In this paper we will discuss the results of our studies of patented emulsion "Antiinkrustal Puroi 2000" inhibitory features and protection of steel constructions against corrosion.

The experiments were performed on the steel samples, which were exposed to the influence of corrosion environment in such way: in model watery solution 5% NaCl, which contains 0.1 g/dm³ CuCl₂; pH=3 and in somewhat milder solution that contains 50 mg/dm³ NaCl; 2-3°dH; pH=8. Each steel sample was studied in original model solution and then in the same one with addition different volumes (3 ml, 5 ml) of the emulsion. The emulsion effect was examined in ambient temperature conditions as well as in warm solutions. After treatment, samples were scanned with *HP* camera. The obtained changes in colours of treated samples were evaluated by spectrophotometric method (spectrophotometer "Colour Eye 3000").

The obtained results show that emulsion "Antiinkrustal Puroi 2000" is unstable in the conditions of accelerating corrosion, while it is very stable and effectively protects steel and iron in model watery solution that contains 50 mg/dm³ NaCl; 2-3°dH; pH=8. It maintains effectiveness in hot solution to its boiling point. It may be presumed that the adsorption processes are of primary significance for the emulsion inhibitory affects. Concentration of emulsion 3 ml/100 ml solution is enough to stop corrosion processes on steel.

Poster No. 8:

IN-SITU URANIUM STABILIZATION BY NATURAL APATITES

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"Technologically enhanced natural radioactivity" originate like the consequence of the human activity getting to the change of distribution and form in which are natural radionuclides. Uranium has been converted from non-reactive, geochemically stable solid into forms that are more soluble and bioavailable, increasing its chemical and radioactivity toxicity in regional scale.

For a large area of contaminated soil it is suitable in-situ remediation which involves minimizing the mobility of the uranium by transforming them to stable solid, non bioavailable phases via chemically induced transformation.

Phosphate induced stabilization is a technology based to treatment the soil, by mixing the amendment directly into the soil or by forming permeable reactive barriers. Stabilization is made possibly by binding the uranium into the stable phosphate phases by low-solubility that are stable over the geologic time. The sorption properties of domestic apatite "Lisina", was examined in this study. We experimentally at different conditions (concentration of P_2O_5 in apatite, pH, time, solid/liquid phases). Concentrate with 34% P_2O_5 at pH 7 for 30 days sorbed 98% and nature apatite, with 14% P_2O_5 , sorbed 94% of the uranium from the water solution, concentration 100 $\mu\text{g U/ml}$, make apatite "Lisina" effective for treatment contaminated soils.

Poster No. 9:

COMPACT PROCESSING OF LEATHER - AN ECOLOGICAL ALTERNATIVE

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Leather processing consisting in complex treatments, like dyeing, fatliquoring, synthetic and vegetal retanning could generate high level of water pollution though a complex organic load.

Retanning of leather represents one of the most innovative and dynamic domain in designing of new materials.

New polymers with multifunction have permitted to compact the processes for leather manufacture and to obtain leathers with complex characteristics.

Our researches have focused on designing and testing of a new blend with dyeing, fatliquoring and retanning functions.

The versatility of new product has been evaluated by manufacturing bovine leathers for shoes, upholstery and clothes.

The influence of new retanning product on main characteristics of leathers have been studied by using softness and physical-mechanical measurements in correlation with microstructural analysis performed by using SEM and chromatic spectral analysis of dyed leather.

The economical and ecological effect of compact process has been assessed in comparison with classical retanning process.

The synergetic action of blend components has allowed using of less quantity of chemical materials and water, to save time and to reduce wastewater pollution.

Poster No. 10:

SUSTAINABLE DEVELOPMENT FROM THE ASPECT OF ENVIRONMENTAL LAW - PROBLEM OF CONTINUAL DEVELOPING AND APPLAYING

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Having in mind Conference themes of the Sixth European Meeting on Environmental Chemistry it is obvious that all have their legal side. Of course precisely determined by the grooving elements of international environmental law. To present complete environmental picture connected with the theme of author's, at the past year requested study (Danube River Enterprise Pollution Reduction Project - Analytic Study Concerning the t.o.r. for: **1.** Nitrate Directive, **2.** Good Agricultural Practice, as well as **3.** The Nitrate Directive Implementation Plan), not only the text composed for the international science meeting, we strongly appoint that:

- Sustainable development,
- Life cycle assessment,
- Risk assessment,
- Green chemistry,
- Soil contamination, depollution technologies,
- Ecotoxicology,
- Water treatment, reuse,
- Biodegradation of toxic compounds,
- Industrial clean technologies,
- Waste valorization,
- Atmospheric chemistry, Air pollution, Modeling of pollutants diffusion,
- Marine chemistry and Marine pollution,
- Analytical methods for Environmental Science,
- Soil - freshwater - atmospheric systems,

in this moment each considered area has less or more strongly developed legal side, necessary for normal functioning, as well as for the protection of environmental values. Furthermore, we can not find any of mentioned areas disconnected from others. All of them are in strong interconnections and feedbacks, as for an example: soil contamination and depollution technologies with water treatment. From the reason of their importance both areas have been the objects of international and national legislatures at the same time. We shall try, in the measure how it is possible in short text, to form contour of this legal side of problem, of course form the dominant light of sustainable development.

2. Life cycle assessment

Posters No. 11-12
Wednesday, December 7th
19:30-20:30

Poster No. 11:

MONITORING OF TOXIC METALS Cd AND Pb IN HERBS *Hypericum sp.* AND *Thymus sp.* FROM SERBIA

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The beneficial effects of medicinal plants are well known from ancient times and consumption of different herbal teas is recommended all over the world.

While many investigations of the quality values of medicinal plants are being reported in current literature, less emphasis has been made on the metal content of herbal products. Toxic effects of heavy metals on plants are very complex and can affect the content of pharmacologically active compounds in medicinal plants, and thereby, seriously impact the quality, safety and efficacy of natural plant products. That's why among the other quality control analysis of the medicinal plants, determination of metals, especially toxic ones, is of special concern.

The aim of this work was to determine contents of toxic metals Cd and Pb in the herbs *Hypericum sp.* and *Thymus sp.*, collected during July 2003 from various localities of mountain Golija (Serbia). Samples of herbs were dried at room temperature and homogenized. After mineralization with digestion mixture (HNO₃ and HClO₄ in ratio 4:1), and dissolution of dry residue in 0.1 mol/L HNO₃, Cd and Pb contents were determined by AAS (apparatus GBC 932AA).

In all investigated samples of herbs *Hypericum sp.* and *Thymus sp.* Cd levels were higher than the ones proposed by WHO (0.3 mg Cd/kg dried plant materials). The levels of Pb can be classified as normally low, because all samples contained less than 10 mg/kg Pb (values proposed by WHO) on a dry weight basis. The obtained results for Cd concentration in *Hypericum sp.* samples were higher than concentration of this metal in *Thymus sp.* and confirm that *Hypericum sp.* has a tendency to accumulate this heavy metal.

Poster No. 12:

BIOAVAILABILITY OF MICRONUTRIENTS AND HEAVY METALS, AND THE EFFECTS OF ORGANIC MATTER IN BINDING MECHANISMS

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Soil organic matter has been of particular interest in studies of heavy metal retention in soils due to the tendency of transition metals to form stable complex with organic ligands.

In order to determine the effect of organic amendment such as compost with high humified organic matter, and manure, which is less humified, on bioavailability, toxicity and plant uptake of zinc, a greenhouse pot experiment was carried out in Bari University, Italy. The soil was air dried, sieved through a 2mm mesh. Solution of ZnCl₂ was added, mixed uniformly with the soil and then distributed in pots. The total zinc concentration in the soil was 665 mg/kg ss. Six treatments were carried out: **1**-Control (polluted Soil); **2**-Mineral fertilizers (NPK); **3**-Manure 10 t/ha; **4**-Manure 30 t/ha; **5**-Compost 20 t/ha; **6**-Compost 60 t/ha.

After 60 days, plants were harvested and analyzed for zinc concentration in roots and shoots. Agronomical growth parameters were also determined. Zinc speciation in the soil, redistribution between available and less available chemical form; evaluation of zinc toxicity under compost, manure and chemical fertilizer application; and plant uptake were conducted.

Compost promoted an increase in the plant growth parameters, zinc toxicity increased under manure treatments possibly due to the presence of high amount of zinc in soluble chelated forms with low molecular weight organic molecules, toxicity decreased in the case of compost, thus suggesting immobilization of the metal in the soil through organic ligands present in the compost, probably forming organo-metallic complexes and reducing its availability.

3. Risk assessment

Posters No. 13-18
Wednesday, December 7th
19:30-20:30

Poster No. 13:

CONTENT OF Pb, Al AND Cr IN DRINKING WATERS FROM WELLS IN THE SURROUNDING AREA OF ALUMINUM FACTORY PODGORICA

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Water is the source of our existence. Water is not only important for its chemical and physical characteristics, it is also necessary for the maintenance of life in general.

Surface and ground waters are today more often contaminated with the waste waters from towns and industries, therefore they lose their natural characteristics. Today it is even more difficult to find a water spring for needs of the growing number of consumers, which could satisfy the requests regarding the quality of water [1].

In the surrounding area of Podgorica there is a great number of houses which use alternative sources to provide drinking water, especially wells. These wells are mostly dug and their water is rarely analyzed.

In this paper the content of lead, chromium and aluminum in the samples taken from 10 well waters in villages in the surrounding area of Aluminum Factory Podgorica was investigated. The water from wells is used for drinking as well as for irrigation of the land around the houses. The investigated wells are exposed to the effect of ground waters, which belong to the confluence of the Morača river. Waste industrial waters are poured out to Morača river, as well as the sewage.

The samples were taken in the period from November to December 2003 in villages in the vicinity of Aluminum Factory.

The content of aluminum and chromium (VI) were determined by spectrophotometry (Varian-Cary), and the content of lead and total chromium by atomic absorption spectrometry (AAS) - flame technique - Perkin Elmer 300 model.

The concentration of aluminum is below 0.02 mg/L, concentration of chromium is below the limit of detection (0.003 mg/L) and concentration of chromium (VI) is also below the limit of detection (0.01 mg/L). They do not exceed the values in drinking water allowed by the Regulations [2].

Increased concentrations of lead were found in three wells, while other values were below the maximum allowable concentrations (MAC). The increased content of lead is probably the consequence of the vicinity of the main road and the railway which pass through the villages where the contaminated wells are placed. Considering that the samples were taken during the rain period it can be assumed that lead was partially washed off from the soil surface.

References:

1. B. Dalmacija, *Kontrola kvaliteta voda*, Novi Sad 2001.
2. *Pravilnik o higijenskoj ispravnosti vode za piće* (Sl. List SRJ br. 42/98 i 44/99)

Poster No. 14:

APPRAISAL OF KAP-S INFLUENCE ON CHANGE OF ZINC CONCENTRATION IN UNDERGROUNDWATERS IN KAP-S SURROUNDINGS

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Aluminium Plant is situated in the vicinity of Podgorica and it is considered as the main polluter of the Zeta plain. During different production processes that take place in plant it happens that large number of waste materials are being produced and either by controlled or uncontrolled manner release in air water or deposit on arranged or unarranged depots.

This work follows the flow of zink, from bauxite ore and its processing to the red mud which is put aside to the basin B (which has only pebble covering), with analysis of underground waters in vicinity of plant: rural wells and pijezo-hole.

Concentrations of zink are given in bauxite ore and hard stage of red mud for the last 4 years in monthly level. Concentration of zink in bauxite and alumina is very significant, because if in the alumina appears over 200 ppm zink, it means that the quality of late produced metal is reduced.

Zink is being followed in waters, because it is very significant element for all organisms, and it can be harmful if it appears in concentrations above allowed.

Zink is separated from bauxite ore and red mud with separable method of separating with 3 conc.acids (HCl, H₂SO₄, HNO₃), and further analyzed by instrumental method with the help of induced pressed plasma (ICP), on Kvantometar type 3580 ARL.

Concentration of zink in underground waters is also defined by instrumental method with the help of induced pressed plasma (ICP), on Kvantometar type 3580 ARL.

Obtained results show that concentration of zink in pijezo-holes in KAP-s surroundings and rural wells do not exceed MDC for zink for drinking water in total 3 mg/dm³.

Poster No. 15:

SOLAR ACTIVITY - POSSIBLE CAUSE OF LARGE FOREST FIRES

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Fires of large scales destroy forests, harvest and housing objects, and combustion products and burned surfaces become large ecological problem. Very often they emerge simultaneously on different locations of a region so a question could be asked if they always have been a consequence of negligence, pyromania, high temperatures or maybe there has been some other cause.

The subject of the paper represents an attempt of establishing the possible connection between forest fires that numerous satellites registered and activities happening on the Sun immediately before breaking the fires out. Period from November 2002 to August 2005 was especially worked out. Fires emerged on relatively large areas from Portugal and Spain on the west to the Caucasus on the east of Europe. On the basis of satellite data related to the rotation of coronary holes and Sun spots, as well as parameters related to electromagnetic and corpuscular part of the Sun radiation, we tried to found if these processes on the Sun could be the primary cause (or one of the causes) of mentioned elemental natural catastrophes [1,2]. Mostly, there are common characteristics that suggest that the processes on the Sun are very important if not the most important factor of the large forest fires origin. Together with such approach the meteorological conditions on the critical localities in certain time intervals are analyzed.

References:

1. Natural Hazards: <http://earthobservatory.nasa.gov/NaturalHazards/>
2. Fires: http://earthobservatory.nasa.gov/NaturalHazards/natural_hazards_v2.php3?topic=fire

Poster No. 16:

CONCENTRATIONS OF LEAD (Pb) AND MANGANESE (Mn) IN SOME WOODY PLANTS ALONG M-21 ROAD THROUGH "FRUŠKA GORA" NATIONAL PARK

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Within the research of the influence of traffic on heavy metal (Pb) content, there has also been performed a research of accumulation of manganese (Mn) in plants on which traffic does not influence directly, and which is essential for plants yet accumulated in larger concentrations surely results in long-term harmful effects.

The area of research was "Fruška gora" National Park which is a very complex vegetation and ecological system. Concentrations of lead and manganese were researched in plant material ie. in the leaves of 8 species of woody plants, collected on seven selected localities along the main road M-21, namely the section of the road Irig - Iriški venac - Paragovo in the length of 12 km. Concentrations of lead and manganese were determined by atomic absorption spectrophotometry.

The obtained data were processed by statistical method of variance analysis - LSD-test for the level of significance $p=0.05$ and the testing of significance of average values was determined by implementation of Duncan test.

A permanent traffic counting is performed on this part of the road by Republic Road Directorate. The data for the examined main road M-21 (taken from the conceptual design of Rehabilitation program of the road Iriški Venac - Ruma), show that the total number of vehicles per day amounts to 7001 out of which 5647 passenger vehicles using gasoline and 1354 vehicles, with a tendency of increase of the total number of vehicles in the forthcoming period, first of all passenger vehicles using leaded gasoline.

The obtained data indicate that lead and manganese concentrations found in analysed plants differ depending on the locality the samples were collected from as well as on the plant species.

The least lead concentration was registered in plants on the control locality (road that is banned for traffic) as well as on the locality 5 (2.5 km from Venac towards Paragovo), where the traffic goes only in one direction in two lanes whereby the vehicles make shorter halts. The greatest lead concentrations were found in the plants from the localities with greatest traffic frequency and longer vehicle halts at that in: wild cherry (*Prunus avium*) 19 ppm and elder (*Sambucus nigra*) 17 ppm. The obtained lead concentrations are below the values allowed by the Republic Regulation yet they far exceed the regulations of EU and WHO standards.

The least average manganese concentrations are characteristic of wild cherry (*Prunus avium*) and hawthorn (*Crataegus monogyna*) on all localities which makes us conclude that these two plant species express the least absorption of Mn. The greatest manganese (Mn) concentrations were found in the leaves of hornbeam (*Carpinus betulus*) 720 ppm on the locality 1 (on the entrance point from Hopovo), then oak tree (*Quercus petraea*) 540 ppm taken from locality 3 (Venac).

Poster No. 17:

THE DEPENDENCE OF HUMAN HEALTH UPON DEFICIENCY AND SUFFICIENCY OF BIOGENIC ELEMENTS

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The biological role of chemical elements in a human organism is very diverse. There are many known illnesses connected with the deficiency or sufficiency of different chemical elements in a human organism. This phenomenon is connected with the fact that in a human organism there is a balance of optimal concentration of biogenic elements - chemical homeostasis.

The deficiency of biogenic elements (Fe, Mn, Cu, Zn, F, Se, J, P, Ca, Mg, K, etc.) in the nutrition brings about serious problems in human health. The sufficiency of some biogenic elements can also cause harmful effects in organism, because this can disturb chemical homeostasis.

The content of biogenic elements in the organisms of the mammals shows that there are changes of the chemical composition of the organisms depending on the kind of the environment changes (air, soil, water, food).

The biogeochemical chains of nutrition create functional dependence of human health on soil composition, water and food. In this paper, the mechanisms of action of biogenic and toxic elements on human organism have been shown.

Poster No. 18:

DETERMINATION OF ARSENIC, COPPER AND LEAD IN DANUBE WATER: RESULTS OF THE 2nd REGIONAL INTERLABORATORY STUDY

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The total of 49 laboratories took part in "The 2nd South-Eastern European Interlaboratory Study WATER ANALYSIS-2004". One laboratory was from Greece, one from the Republic of Srpska - Bosnia and Hercegovina, eight from Romania and all others from Serbia and Montenegro.

The task for participants was to determine some or all trace elements (Al, As, Cd, Cu, Mn, Fe, Pb and Zn) in two samples prepared from filtered water of the river Danube near Belgrade. In another pair of samples they had to determine chloride, sulphate and phosphate. Participants could freely select the elements and anions for determination as well as the analytical methods. Interlaboratory study was successful and considerable improvement was noticed in comparison with some earlier studies.

In this paper the results obtained for determination of arsenic, copper and lead were analysed using the same methodology as in interlaboratory studies organised by IRMM-JRC (Institute for Reference Materials and Measurements: EU-Joint Research Centre, Geel, Belgium) within the IMEP (International Measurements Evaluation Programme).

4. Green chemistry

Posters No. 19-28
Wednesday, December 7th
19:30-20:30

Poster No. 19:

AQUEOUS PHOTOCATALYTIC OXIDATION OF LIGNIN AND HUMIC SUBSTANCES WITH SUPPORTED TiO₂

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The photocatalytic oxidation (PCO) of UV-radiated aqueous solutions containing humic substances and lignin was studied. The photocatalyst TiO₂ was attached to the buoyant hollow glass micro-spheres and the glass plates. The maximum oxidation efficiency as low as 1.1 and 2.54 mg·W⁻¹·h⁻¹ for humic substances and lignin respectively was achieved in neutral and alkaline media with 25 g·m⁻² of the buoyant catalyst, acidic media showed even lower efficiency. The photocatalytic efficiency with the photocatalyst attached to the glass plates was about 3 to 4 times higher than that for the buoyant catalyst. Ferrous ions added to acidic solutions did not increase the rate of PCO of humic substances. However the addition of Fe²⁺ ions, up to 0.05 mM, to the lignin solution leads to the drastic, for about 25%, increase in PCO efficiency. A further increase in ferrous ion concentration results in a decrease in PCO efficiency of lignin. Proceeding most likely by a radical mechanism, the efficiency of PCO of humic substances did not benefit from an excessive presence of hydroxyl radical promoters, such as hydrogen peroxide, although the reaction rate increased. However, PCO of lignin in acidic medium, where OH·-radical formation is suppressed, benefited from the introduction of hydrogen peroxide due to promoted radical formation.

Poster No. 20:

CHEMICAL THERMODYNAMICS OF MIXED AQUEOUS SOLUTIONS OF SODIUM SULPHATE AND ZINC SULPHATE AT 298.15K

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Aqueous solutions of electrolytes are of geochemical interest because of their presence in seawater and certain other natural brines. The principal chemical thermodynamic properties of interest for predicting solubilities are osmotic and activity coefficients. Osmotic and activity coefficients of most pure electrolytes of interest have been measured at room temperature, but many systems of practical, biological or geological as well as chemical, interest involve mixed aqueous electrolytes.

This paper deals with isopiestic measurements the osmotic coefficients of the mixed aqueous solutions of Na_2SO_4 and ZnSO_4 , at the temperature 298.15 K, with KCl(aq) treated as reference solution. Scatchard's neutral-electrolyte method, Pitzer-Kim's and Clegg-Pitzer-Brimblecombe's ionic methods for mixed-electrolyte solutions were used for the experimental results treatment. Scatchard's neutral-electrolyte method gives best results in fitting the osmotic coefficient values for the mixed aqueous solutions of Na_2SO_4 and ZnSO_4 comparing to other two methods applied. By these methods, the activity coefficients of Na_2SO_4 and ZnSO_4 were calculated and compared. The agreement between them is good, expect for the trace activity coefficients, which were determined by extrapolation for ionic strength fraction of electrolyte equal zero. In addition, the Scatchard interaction parameters are used for calculation of the excess Gibbs free energy of mixing as a function of ionic strength and ionic-strength fraction of Na_2SO_4 . The excess Gibbs energies of mixing are negative in the whole total ionic strength region.

Poster No. 21:

THE IMPORTANCE OF MAIZE SEED INOCULATION WITH FREE NITROGEN FIXERS WITHIN THE SYSTEM OF ENVIRONMENTAL PROTECTION

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The achievement of high yields in the plant production is inconceivable without the application of preparations of synthetic and chemical origin (pesticides, mineral fertilisers).

Considering that the fertilisation is a fundamental measure for achieving high and stable yields in the agricultural production, it is necessary to rationalise the application of mineral fertilisers from the aspect of the production of food of high nutritive values and agroecosystem protection. Beside other measure, this could be achieved by the application of new information within the field of biological nitrogen fixation. This process occurs in all soils and all latitudes, hence due to it more nitrogen is incorporated into soil by this process than by mineral fertilisers. Types of biological fixations are characteristic for certain microbiological associations, i.e. diazotrophs. Effects of mineral nitrogen on yield, as well as on the possibility of underground water pollution by great amounts of the nitrite form of nitrogen not absorbable by plants are known from the available literature. Based on previous results it is possible to reduce the amount of the nitrogen fertiliser by the amount bound by selected strains of diazotrophs and their combinations. In such a way soil chemisation as a form of fertilisation is reduced, soil biogeny is maintained and at the same time lower funds invested in the food production are necessary. Bacterisation with the liquid inoculum (five combinations) of ZP SC 677 maize seed was performed in the two-year experiments. The inoculum combinations included the mixture of the selected strains of diazotrophs: *Azotobacter chroococcum*, *Azospirillum Lipoferum*, *Azotobacter vinelandi*, *Pseudomonas*, *Bacillus megaterium*, *Bacillus subtilis*. The following variants with mineral nitrogen fertiliser were applied in the trial: control K, N₁ - 30 kg·ha⁻¹, N₂ - 60 kg·ha⁻¹, N₃ - 90 kg·ha⁻¹ and N₄ - 120 kg·ha⁻¹. Values of parameters of soil biogeny (total number, abundance of *Azotobacter*, enzymatic activities), as well as grain yields, were increased under conditions of bacterisation. There were no significant differences in the increase of values of observed parameters between variants N₃ and N₄, hence it can be concluded that the application of bacterisation could rationalise the application of nitrogen mineral fertilisers by 30 kg of pure nitrogen ha⁻¹, which is certainly very important from the aspects of sustainable agriculture and economic effects.

Poster No. 22:

HYDROLYTIC AND ENZYMATIC DEGRADATION OF BIODEGRADABLE POLY(ETHER-ESTER) COPOLYMERS

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The application of biodegradable polymers for packing, sanitary and agricultural purposes instead of bioresistant polymers is one way to elevate some of the problem of environment pollution by plastic waste. Aliphatic polyesters are one of the most promising biodegradable materials because they are readily susceptible to biological attack and their degradation products, are non toxic and can enter the metabolic cycles of bioorganisms. One of the ways of improving the biodegradability properties of polymers is the incorporation hydrophilic soft segments into the polymer chains.

In this work, the properties of two series poly(ether-ester)s based on poly(ethylene oxide) (PEO) and poly(tetramethylene oxide) (PTMO) as soft hydrophilic segments are presented. the content of soft segments was varied from 10 to 50 mass % in both series. The copolyesters were synthesized by transesterification reaction in the bulk. The effect of introduction of two different polyether soft segments on the structure, physical properties, as well as on enzymatic and hydrolytic degradation was investigated. It was shown that the crystallinity and degradation kinetics could be tailored by the type and content of the soft segments. The enzymatic degradation of polymer films was investigated in a buffer solution with *Candida rugosa* lipase. It could be concluded that the biodegradability depends strongly on the degree of crystallinity, but also on the flexibility of the chain backbone. As was to be expected, the poly(ether-ester) based on poly(ethylene oxide) were more susceptible to enzymatic and hydrolytic attack than those based on poly(tetramethylene oxide), biodegradability and hydrolytic properties were enhanced.

Poster No. 23:

THE CHEMICAL, PHYSICAL AND THERMODYNAMICAL PARAMETERS IN DETERMINATION OF GENOTYPES' REPLY TO ENVIRONMENTAL FACTORS:

I. MERCHANT PESTICIDES COMBINATION SELECTED FOR MAIZE SEED PRODUCTION

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In contemporary crop production, genetically predicted yield has to be supported by chemical treatment in sense of strictly controlled environmental and food protection.

The plant reaction to merchant pesticides (*Maxim*, *Cruiser* and *Gaucho* - synthetics and *Bovaria spp.* - fungus) was tested on family triplet: mother, father and their descendant in maize seed production. The water status was examined by evaporating at 40°C (bulky H₂O), 105°C (secondary, polar binding site) and 130°C (primary, ionic binding site). Water contents were expressed as concentration (g·L⁻¹) and pseudo specific density (μmol·mg⁻¹, d⁻¹ or *d*).

The reactions of hydrolysis and biosynthesis that results in seed germination, oscillated slightly, however *Bovaria* suppressed upper processes, especially germination (from 97,5; 82,5; 96 to 64; 79; 83%). The generally low biosynthesis has get low germination.

There was deep drop of concentration in ionic site of seed rest and slight in plant, while *Bovaria* elevated it at polar site of seed rest. Applied pesticides did not disturb the bulky and total water, giving uniform values of *d* (about 37 and 90 for seed rest; 51 and 690 μmol·mg⁻¹). It could be tied to hydrolyse of primary and secondary hydration sites of proteins, but not their synthesis in plant. Only the plant of descendant was ready for autotrophy growth by negative free energy values. The relation of differential entropy in seedling and its parts of family triplet separated Maxim+Gaucho and *Bovaria* combinations by highest positive and negative retreat to control, respectively.

The application of standard chemical, physical and thermodynamical parameters could deeper and omni potently determine status and changes of maize seedlings in controlled pest agents' use.

Poster No. 24:

THE CHEMICAL, PHYSICAL AND THERMODYNAMICAL PARAMETERS IN DETERMINATION OF GENOTYPES' REPLY TO ENVIRONMENTAL FACTORS

II. THE SELECTION OF SOYBEAN VARIETIES AND SOIL TYPES TO LOW TEMPERATURE IN SPRING

1. The bioproduction and water content of seedlings

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The sowing period in early spring, with temperatures about 10°C during 1-10 days, extends germination and young plants' growth. So, total germination and number of yielding plants of four soybean varieties, two temperatures: 10 and 25°C, in soils: chernozem, eutric cambisol and pseudogley were tested.

The water absorption by seed and root diluted substance from about 9000 g·L⁻¹ in seed to 220-385 g·L⁻¹ in seed rest. The pseudogley influenced the highest leaching of substance from seedlings system (38.5-69.9 mg·pl⁻¹). The pseudospecific density in cotyledons and plants was unchanged by soil, temperature and variety (39.2-46.7 and 50.7-51.5 mg·μmol⁻¹ in cotyledons and plant, respectively). The bioproduction and water content of seedlings were the highest in pseudogley; meanwhile, in root were the smallest, what means bad quality of this soil for rooting. The physiological category of relation root:shoot, expressing the balance of plant growth, underlined eutric cambisol as convenient soil type in soybean production.

If someone to current empirical determination of seedlings quality introduces universal parameters of nature - thermodynamical free energy and entropy to determine inner trends of survived plants, it have to be based on, that T₁ (in soils) gives V₁ and T₂ (control) V₂ of water level in seedling and its parts: root, shoot and cotyledons. The differential free energy and differential entropy of root and shoot have been shown qualitative segregation between genotypes in each soil type. Further, differential free energy and differential entropy of seedlings were in trend with partial seed weight, pSd (mg·μmol·P⁻¹) and partial seed rest weight, pRs (mg·μmol·P⁻¹).

Poster No. 25:

THE CHEMICAL, PHYSICAL AND THERMODYNAMICAL PARAMETERS IN DETERMINATION OF GENOTYPES' REPLY TO ENVIRONMENTAL FACTORS

II. THE SELECTION OF SOYBEAN VARIETIES AND SOIL TYPES TO LOW TEMPERATURE IN SPRING

2. The hydrolysis, biosynthesis and germination

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The two biochemical reaction, at first successive, than concomitant: hydrolysis and biosynthesis results in biological process of seed germination. According to ISTA Rules, two categories of seedlings were determined total number of germinated seeds and number of yield giving seedlings.

The upper processes can be appointed by equations and to develop coefficients of duration: relation of total and giving yield seedlings and coefficient of conversion: relation of Σ hydrolysis and Σ biosynthesis, as well as, constants of: hydrolysis, biosynthesis and germination. In this assay the both coefficients were closed in S1, S3 and S4 in eutric cambisol; meanwhile in chernozem they corresponded to control (T_2 , sand). Further, the coefficient of conversion was higher than coefficient of duration in S4 (control and chernozem) and S1 (eutric cambisol). The values of both coefficients were 1.5-2.5.

The constants of the reactions and the process led to determination of free energy: as it was expected, the free energy of hydrolysis was near to be spontaneously, reverse to biosynthesis, demanded higher energy. The Σ hydrolysis and Σ biosynthesis pointed out in the course of germination, expressed through free energy and differential free energy as a n-dimensional systems demand the participation of lower-dimensional elements like: coefficients of duration and conversion, reciprocal constant of germination against free energy and differential free energy of germination extent in the interpretation. From this point of view, S4 and pseudogley were underlined as unfavourable verity and soil type, respectively.

The seed carries in itself potential energy and capacity to give yielding plant. The researchers have to recognise and give interpretation of them through universal parameters for dynamical processes and this work is at its beginning.

Poster No. 26:

INVESTIGATION OF WHEAT STRAW LOW-TEMPERATURE COMBUSTION BY THERMOGRAVIMETRIC ANALYSIS

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Investigation of kinetics of group of reactions in domain of low-temperature wheat straw combustion were performed by thermal destruction of samples in laboratory conditions in air environment. Experiments were performed for the temperature intervals from 20°C - 500°C with the following denominated sample heating rates: 2,5; 5; 10; 25°C/min.

For referent experiment case 5°C/min granulation was varied (whole straw ~15 mm, chopped straw 0.3-0.4 mm, fine milled <0.1 mm) and humidity (4%, 8%, 26%, 60%).

Mass loss dependence from the temperature was transformed in Arrhenius coordinates, where result was a saddle-formed curve with high statistical significance which can be well approximated with regression curve of sixth degree.

Statistical tests of granulation and humidity influence are showing little significance of these variables. Tests of influence of heating rates confirm significance only in the region of high temperatures where the other half of the remaining mass reacts.

Poster No. 27:

HEADSPACE SOLID-PHASE MICROEXTRACTION IN MULTI-CLASS PESTICIDE RESIDUE ANALYSIS

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Solid phase microextraction (SPME) is an advanced and promising nonexhaustive equilibrium method for sample preparation in residue analysis without using organic solvents. It is a fast, simple, efficient and inexpensive method of selective extraction of organic compounds from a solution or gas phase using a fused silica fibre coated with a thin polymer film. Headspace (HS) extraction mode includes partition of organic analytes between the polymer layer and a headspace above the sample solution, avoiding matrix interferences in the extraction procedure.

Seven pesticides, belonging to different classes of organic compounds and ranging in volatility from hexachlorobenzene to bifenthrin were analysed applying the HS-SPME method in standard water solutions. Pesticides extraction using a 100 µm polydimethylsiloxane film was performed in the concentration range from 0.05 to 40 ng/ml, with temperature spanning from room to as high as 90°C. Detection and quantification were done by gas chromatography-mass spectrometry with an ion trap mass detector operating in the electron impact selected ion monitoring (SIM) mode.

In order to determine the optimum extraction temperature for each of the pesticides studied, extraction-temperature profiles were obtained for the one-hour extraction procedure. Equilibration time profiles were determined and times needed to reach adsorption equilibrium were estimated. Theoretical treatment of a HS-SPME process was considered. Applicability of the extraction procedure developed for pesticide standard water solutions was tested in the real fruit sample with aqueous matrix.

Poster No. 28:

SUITABILITY OF CLAYEY SUBSTRATA CONTAINING INDUSTRIAL GYPSUM FOR AGRICULTURAL UTILIZATION

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Industrial gypsum is a waste material produced in the Maritza-Iztok Thermal Electric Station. Whether to enlist it as a safe compound of the environment is a current issue. The influence of several gypsum concentrations (1, 3, 5, 7.5 and 10%) on the physical and chemical properties of ten substrata was studied in a greenhouse experiment. Substrata consisted of different proportions of clay (uncovered in coal mining) and ash (produced in coal burning). According to the results obtained gypsum negative effect was linked with the chemical properties of the mixtures. Salinization and increase in the total sulphur and sulphates content are the causes for this effect on two crops: fodder peas (*Pisum arvense*) and spring barley (*Hordeum vulgare*). Spring barley quickly adapted to new condition and ensured higher yields. Both crops had good quality and did not contained heavy metals exceeding the sanitary norms in concentrations.

Negative processes become more intensive with increasing gypsum content in clayey substrata. Increasing gypsum content favourably influenced the physical properties of substrata and partially improved their structure (Marinova et al., 2003). Gypsum in 1% content hides a minimal risk of environmental pollution. In order to estimate the acceptability of this risk, the processes of accumulation, digestion and precipitation of sulphates with depth have to be thoroughly studied.

5. Soil contamination, depollution technologies

Posters No. 29-49
Wednesday, December 7th
19:30-20:30

Poster No. 29:

CHEMICAL AND MINERALOGICAL STUDY OF HEAVY METAL BINDING IN ALLUVIAL SOILS OF THE MINING/SMELTING DISTRICT

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Alluvial soils from the historical mining and smelting area of Příbram, Czech Republic, were closely studied in order to determine the speciation of lead, zinc and cadmium. The chemical forms of heavy metals were assessed using a 5-step sequential extraction technique by Tessier. The mineralogy of heavy metal species was assessed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX). The maximum concentration reached 7590 mg·kg⁻¹ for Pb, 8728 mg·kg⁻¹ for Zn and 67.5 mg·kg⁻¹ for Cd. The chemical fractionation proved that the soil contaminated by smelting industry contains higher concentrations of mobile Pb and Zn compared to the soil contaminated predominantly by the mining activities. Calculated mobility factors (MF) showed that up to 46% of Pb and 62% of Zn are mobile in the soil polluted by smelting activities. On the contrary, the maximum MFs of Pb and Zn were 23% and 13% in the soil of the mining district, respectively. The predominant binding of Pb and Zn to the stable soil phases (Fe, Mn oxides and hydroxides, silicates) in the mining area was also proved by mineralogical studies. Differences in Cd speciation in soils contaminated by different sources were not confirmed. This is probably due to the extreme high mobility of Cd in soils.

Poster No. 30:

DISTRIBUTION OF SOME HEAVY METALS IN SOILS FROM VELIKA MORAVA RIVER VALLEY

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A modified Tessier sequential extraction procedure was applied for determination of metal's total content and the available metals were extracted with 0.005M DTPA. Samples (fifty) originated from Velika Morava River valley and included different types of soil: fluvisol, humofluvisol, molic fluvigley, eutric cambisol, distric cambisol, luvisol, chernozem, smonitza. Basic agrochemical properties of the investigated soil samples were determined by standard methods of soil chemical analysis. In all extracts metal content was determined by AAS method. The content of Zn, Cu, Cd and Pb is discussed only. Examined samples showed total Pb content from 3.0-204.0 mg/kg (mainly from second and third phase in majority of samples). Available Pb is from 1.3-7.4 mg/kg, what refers to anthropogenic pollution. Most of Cu is extracted in third phase from amorphous and partially crystallized hydrated iron oxides (to 188.0 mg/kg). Available Cu content is from 1.0-58.0 mg/kg, what refers to plant protection agent as pollutant. In all phases of extraction Cd content is very low (max. 1.13 mg/kg). Determined content of available Cd is also very low, so there is no pollution. The highest content of Zn was extracted from fifth phase in majority of the examined samples and varies from 50.0-182.0 mg/kg. Available and total content ratio of Zn is less than 10%, and that fact eliminates possibility of anthropogenic pollution. Determination of Zn, Cu, Cd and Pb content in the soils gives contribution to estimation of ecological status of Velika Morava valley.

Poster No. 31:

MOBILITY OF ORGANIC POLLUTANTS ADSORBED ON CLAYS MONITORED BY VARIOUS MAS NMR APPROACHES

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The adsorption-desorption mechanisms at the interface between organic and inorganic soil colloids influence movement of pesticides, thus their bioavailability and biotransformation process. Direct analyses of dry parts of soils have been reported in the literature using solid-state Nuclear Magnetic Resonance spectroscopy on dry samples [1]. We recently demonstrated the potential of the ¹H HR-MAS NMR technique to study such mechanism *in situ* on highly hydrated samples. By using a well-characterized model of soil it was possible to distinguish unambiguously the mobile and immobile pesticide [2]. In the present communication the results obtained during the adsorption of some pollutants such as phosphonomethylglycine (glyphosate) or mesotrione will be presented. More precisely, we will focus on the comparison of various MAS NMR techniques to study dry or hydrated samples. For example, several species of glyphosate - corresponding to different degrees of freedom - have been observed by ³¹P HR-MAS NMR during its adsorption on anionic clays taken as a model of solid colloid. T1 measurements on dry and hydrated samples have been also performed to assess the mobility of the organic pollutants. Finally, the feasibility of direct (CRAMPS, Hahn echo) and indirect (FSLG) ¹H detection to study the interaction between these organic compounds and the solid matrices will be discussed.

References:

1. Delort *et al.*, *Environ. Chem. Let.*, 2004, 1, 209.
2. Combourieu *et al.*, *Chem. Commun.*, 2001, 21, 2214.

Poster No. 32:

SEQUENTIAL EXTRACTION OF METAL IONS FROM A BROWN COAL: PARTITION OF THE METALS HAVING HIGH Me-HUMIC ACID COMPLEX STABILITY CONSTANTS

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Brown coal mines, mainly due to the heavy metal content of coals, are known potential water and sediment pollution sources. The development of coal mines into a pollution source is expressed by the acid mine water formation processes, which include chemical as well as microbial oxidation reactions accompanied by acid water-leaching of coals and surrounding sediments.

The aim of this paper was to investigate the partition of heavy metals having high humic acid complex stability constants, during an appropriate sequential extraction procedure of brown coals, which is applicable for speciation of the most mobile metal fractions.

Powdered brown coal samples from the Krepoljin Bassin, Eastern Serbia, were successively extracted by four extractants: **1)** bidistilled water-model for rain interaction, **2)** 2M MgCl₂-eliberation of the sorbed and exchangeable fraction, **3)** 1M Na-acetate with acetic acid, pH 5-carbonate bound fraction, and **4)** 0.1M NH₂OH · HCl+Na-citrate, pH 5-easy reducible oxides and hydroxides.

The distribution of Cu and Zn between the fractions is almost uniform, showing that many environmental factors, as rain water, Me1, waters having high ionic strenght, Me2, acid waters, Me3, and reducing conditions, Me4, will mobilize approximately the same amounts of these metals.

It can be assumed that the humic acids co-extracted during water-leaching, Me1, and being a highly competetive ligand for metal ions, will act as a disturbing agent in metal speciation procedures in coals. This assumption is supported by the obtained significant correlation between the Me1/Me2 ratio and the humic acid complex stability constants.

Poster No. 33:

ALTERATION OF HEAVY METAL MOBILITY USING ORGANIC AND INORGANIC AMENDMENTS - IMPLICATION FOR ENHANCED PHYTOEXTRACTION OF HEAVY METALS FROM CONTAMINATED SOILS

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Enhanced phytoextraction has proved to be a perspective method for remediation of heavy metal contaminated soils. The main drawback of this method is the low bioavailability of some heavy metals (especially Pb) in polluted soils. Therefore, application of organic (chelators) and inorganic (chlorides) amendments could increase phytoextraction efficiency. Samples of agriculturally used soil (0-20 cm) were collected from two sites in the mining and smelting area of Příbram (Czech Rep.), each representing a different contamination type (mining vs. smelting). The main soil characteristics, total concentrations and fractionation of heavy metals (Pb, Cd, Zn, Cu) in studied soils were determined. In laboratory conditions the effect of dosage rate of chelating agents EDTA, EDDS (3, 6, 12 mmol·kg soil⁻¹) and chlorides NH₄Cl, KCl (10, 20, 30 mmol·kg soil⁻¹) as well as the effect of incubation time (0.5-28 days) on heavy metal desorption was studied. Water soluble heavy metal contents in soils after the incubations were determined using ICP-OES. EDTA at the highest concentration (12 mmol·kg⁻¹) was the most efficient mobilizing agent for all heavy metals removing as much as 60% of Pb and 75% of Cd (a 250-fold increase in water soluble Pb concentration compared to the control). Chlorides were only effective in mobilizing Cd and Zn (a 5-fold increase of water soluble Cd). Based on the results obtained, it would be possible to choose the optimal dosage of mobilizing agents together with the best heavy metal accumulating plant species for an environmentally safe remediation of contaminated soils by metallurgical industry.

Poster No. 34:

POLYCYCLIC AROMATIC HYDROCARBONS IN THE TOPSOIL FROM THE CITY OF NOVI SAD

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This paper reviews the contents of polycyclic aromatic hydrocarbons in the soil from Novi Sad Municipality. Studies have been conducted in the framework of two projects:

1. "Soil contamination on the territory of Novi Sad Municipality", funded in 2000 and 2001 by the Public Enterprise for City Construction and Development of Novi Sad. The project dealt with soils from the urban and suburban areas of Novi Sad.
2. "Soil fertility and contamination in Novi Sad gardens", funded in 2003 and 2004 by the Secretariat for Environmental Protection and Improvement of the City of Novi Sad. The studied locations covered the garden and field production of vegetables.

A total of 84 soil samples were analyzed. Topsoil from the locations used for the production of fruits and vegetables, i.e., which take part in the primary food chain, was analyzed for the following 16 PAHs: naphthalene, acenaphthylene, phenanthrene, acenaphthene, fluorene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2-cd)pyrene.

Twenty-nine soil samples were from the urban area itself, 55 from the suburbia.

The PAHs were extracted with a Soxhlet apparatus, using the method US EPA MT 3540C. Extract purification on silica gel was done by the method US EPA MT 3630C. The purified extracts were analyzed in a liquid chromatograph HP1100 with a DAD detector, on a C18 column. Supelco EPA 610 Polynuclear Aromatic Hydrocarbons Mix Cat. No. 4-8743 was used for quantification.

The average total PAH contents in the years 2000, 2001, 2003 and 2004 were 4.28 mg/kg, 5.48 mg/kg, 1.74 mg/kg and 0.41 mg/kg of soil on dry weight basis, respectively. In other words, we registered a reduction in the total content of PAHs over the analyzed 5-year period.

Poster No. 35:

CONTENT OF Pb, Cd, Cu AND Zn IN THE SOIL IN THE SURROUNDING AREA OF ALUMINUM FACTORY PODGORICA

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Industrial era is the period of the concentrations increase of different contaminants in every part of eco-system, including human population. The expansion and accelerated technological development, especially the area of chemical industry, cause serious problems at local as well as at global level of the environment contamination [1].

After air and water the third important environment component is soil. Soil has a specific role as an area which helps to many life forms, and the most important of them are the plants that lead to humans through the food chain.

Almost every organic substances are biodegradable, except the plastic masses. However, heavy metals do not have that characteristic. None of the metals is degradable. When released to the environment all the metals are naturally capable of accumulation in soil as well as in water eco-systems. If they get to human organism through different processes in nature, they can have serious consequences on health. It is difficult to eliminate them. People give them small attention. For that reason the investigation of heavy metals in nature is very important [2].

The characteristics of heavy metals are their different chemical, physical and physiological qualities, while they have in common their toxic reaction, even in relatively small concentrations. For this reason they are considered very dangerous environment contaminants. E.g. The content of lead in today's human organisms is 500 times higher than in the organisms of pre-industrial human beings. The toxic effect of lead used as a detonator in fuels is known to people. Cadmium is released in the environment due to the friction of car tires. Lubricants in oils often contain cadmium, copper and zinc [3].

The aim of this paper was to determine the content of lead, cadmium, copper and zinc in soil samples taken from the surrounding area of Aluminum Factory Podgorica. The samples were taken in March 2004, from twenty locations in the vicinity of the factory. The total and the migration content of above-mentioned metals were determined. The migration content of Pb, Cd and Zn in the investigated samples of soil ranged within the values allowed by the Regulations [4], and the migration content of Cu in two samples exceeded allowable limits. The total contents of metals in particular samples exceeded the values allowed by the Regulations, which is probably the consequence of the influence of Aluminum Factory, street traffic and usage of plants protection products.

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Poster No. 36:

XYLENE DEGRADATION IN THE CLAYS OF AN ALLUVIAL AQUIFER

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The Sava river alluvial aquifer of Makis plain near Belgrade, consisting from clays and sands has been contaminated by a spill of technical grade xylene. Alkyl-benzenes can be degraded in aerobic environments as well as by the much slower anaerobic mechanisms (denitrification, dissimilatory Fe(III)- or sulphate reduction and methanogenesis).

In this paper we discuss xylene degradation in the alluvial clays. Xylenes in clays are occurring in a sorbed status and therefore they could be greatly protected against microbial degradation. The xylene/substrate association patterns could be one of the factors influencing the degradation kinetics of xylene.

Xylene was determined by GC-analysis after a 36 h extraction of the native samples with CH₂Cl₂. The Xylene Oxidizing Bacteria, which utilize xylene as the single Carbon source (XOBC), were estimated on a nutritive substrate containing only the mixture of xylene isomers (1 g/l), as the C-source. There are evident differences in the percentual share of the XOBC in clays with unstable sulfate-reducing conditions (URC-clays, 0.12±0.09 μmole FeS/g) and the clays with steady sulfate-reducing conditions (SRC-clays, 10.64±3.89 μmole FeS/g). So, the percentual share of XOBC in the URC- and the SRC clays was in average 6.7±8.8% (median 6.4%), and 0.9±0.7% (median 1.0%), respectively. The substantial presence of the xylene-oxidizing bacteria which utilize xylene as the single carbon-source represents a proof for a slow degradation yet occurring. Differing xylene/substrate association patterns for the URC- and the SRC-clays were proposed.

Poster No. 37:

EVALUATION OF HEAVY METAL POLLUTION AND DISTRIBUTION IN THE TISA (TISZA) RIVER SEDIMENTS

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In this paper the concentration and chemical distribution of heavy metals (Zn, Cd, Pb and Cu) in the sediments of the Tisa River and its tributaries were studied. Among the various contaminants, heavy metals are of particular concern due to their environmental persistence and biogeochemical recycling and ecological risks. Our investigations were a part of much wider investigations which encompass ecotoxicological, biological and nautical investigation of the River Tisa, from its mouth to the Hungarian border that was performed in the period of July 2nd-17th, 2001, in form of an expedition entitled as "Tisa 2001".

Sequential extraction procedure is applied for speciation of the metal forms in the sediments. The experimental results showed that: **(1)** Zn is mostly bounded to carbonates and Fe and Mn oxides (78,18%); **(2)** Cadmium is mostly present in the mobile fractions exchangeable and Mn oxide and carbonate (70,72%); **(3)** Lead was abundantly concentrated in the Mn oxide and carbonate fraction (88,78%); **(4)** Copper is strongly related to hydrous Fe and Mn oxides (74,08%).

The sum concentrations of metals released in the five fractions for some elements were compared with the guidelines for soils and freshwater sediment. These results indicate that quality of sediments in the Tisa River is on the border line between potentially polluted and polluted.

Poster No. 38:

GAMMA DOSE RATES OF NATURAL RADIONUCLIDES IN SURFACE SOILS OF SERBIA AND MONTENEGRO

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The specific activities of primordial radionuclides (^{238}U , ^{232}Th and ^{40}K) in soil samples from twenty one different locations in Serbia and Montenegro were determined by gamma-ray spectrometry. From these activities the gamma dose rates in the air at 1 m above ground level were calculated. The mean gamma dose rate due to investigated radionuclides was found to be $66 \text{ nGy}\cdot\text{h}^{-1}$, i.e. about 1.2 times higher than the world average ($57 \text{ nGy}\cdot\text{h}^{-1}$). The contribution of the radionuclides ^{238}U , ^{232}Th and ^{40}K to the dose rate was 23.8% ($15.7 \text{ nGy}\cdot\text{h}^{-1}$), 38.3% ($25.3 \text{ nGy}\cdot\text{h}^{-1}$) and 37.9% ($25.0 \text{ nGy}\cdot\text{h}^{-1}$), respectively. The contribution of each radionuclide to the gamma dose rate varied with sampling location and reflected the geological origin of the analyzed soils. The results obtained in this work may be used for preliminary estimations of population exposure to natural radionuclides. They can also be exploited to enrich the world's data bank, which is greatly needed for evaluating worldwide average values of radiometric and dosimetric quantities. The anthropogenic radionuclide ^{137}Cs was also detected in the analyzed soil samples, but its contribution to the gamma dose rate in the air was about 1%, so this dose can be neglected in calculation of the population exposure.

Poster No. 39:

EFFECT OF SOME AGROTECHNICAL MEASURES ON THE UPTAKE OF LEAD BY MAIZE PLANTS

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Lead is neither an essential nor a beneficial element for plants or animals. It can be toxic to plants when its content in soils is high. Several soil properties have effect on the uptake of lead by plants. These properties are: pH, content of organic matter and clay minerals, cation exchange capacity (CEC), content of phosphates and redox potential. The purpose of this investigation was to determine the effect of fertilization, soil acidification and liming on the uptake of lead by maize plants grown on some alluvial soils.

A pot experiment with maize plants grown on soils having various properties (weakly alkaline to acid) and somewhat elevated content of heavy metals was set up. The experiment lasted for 6 weeks. At the end of the experiment the yield of plants was measured, and roots and aerial plant parts were analyzed for the content of lead. The uptake of Pb is expressed in $\mu\text{g}/\text{pot}$.

It can be concluded from the results of the pot experiment that the addition of mineral fertilizers (without application of other measures) mainly decreased content and uptake of Pb by roots and aerial plant part. A decrease of the content and uptake of lead also occurred due to acidification of neutral and weakly alkaline soils with sulphuric acid. Liming of acid soils caused decrease of Pb content in maize roots. Lead is present in higher amounts in roots in relation to aerial part of young maize plants. The content of Pb in roots is on average 2 times higher than its content in the aerial part. The obtained results are important from the standpoint of reducing the pollution of plants with potentially toxic heavy metals.

Poster No. 40:

HEAVY METALS IN URBANIZED FOREST SOILS OF SOFIA REGION

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Cu, Zn, Pb and Cd i.e. total contents and mobile forms (Amo-acetate extractable) was analyzed in depths: 0-5, 5-10, 10-20 cm from soils under oak stands in three plots with different urbanized level (a city park; a suburban plot and a rural plot). The total concentrations of heavy metals in top-soils are below maximum permissible loads (MPL). The Enrichment factor (EF) calculated by assuming as geochemical background concentration of natural soils in Sofia region, show contamination with Cd in top-soils of city park (EF = 1.2) and rural plot (EF = 1.08). The proportions of mobile forms of heavy metals observed in this study vary as a percentage of totals: Cu 2-3%; Zn 3-8%; Pb 4-9%; Cd 6-16%. The concentrations of Amo-acetate extractable Cu, Zn, Pb and Cd are highest in top-soils of city park in comparison with other plots, especially for Pb, Zn and Cd - heavy metals associated with automobile traffic. That demonstrates the strongest anthropogenic influence on soil in urbanized areas.

Poster No. 41:

EFFECTS OF FLOODING ON LEAD AND CADMIUM SPECIATION IN SEDIMENTS FROM A DRINKING WATER RESERVOIR

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Římov water reservoir on the river Malše is the main source of drinking water for the town of České Budějovice and for the majority of inhabitants in the South Bohemian region, Czech Republic. Changes in cadmium and lead contents in bottom sediments before and after an extensive flood on the river Malše in August, 2002 were therefore determined. A five-step sequential extraction procedure was used in order to obtain more detailed information about the influence of the flood on heavy metal retention. In order to determine the mobility of lead and cadmium the mobility factor (MF) for these heavy metals was calculated. The mobility factor of cadmium showed a significant decrease in the upper parts of the sediment profiles after the flood (e.g., from 59.4% to 49.1%) caused by a release of cadmium especially from the exchangeable fraction. There were no significant changes in the lead mobility factor after the flood, but a decrease of lead concentration in the exchangeable fraction was observed. Presented results show that the flood led to a leaching of the heavy metals present in bottom sediments into the environment.

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Poster No. 42:

THE CORRELATION OF THE LEAD AMOUNTS IN THE WATER AND IN THE SOIL

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It has been investigated correlation of the lead amount in the wastewater and total and plant-available Pb in the soil, as well as lead amount in the dry leaf and stalks of the pepper. The plant-available amount of Pb in the soil determined by different extraction solutions. The sampling took place on the parcel of the Prokuplje. Total and plant-available lead amount in the soil has been determined after soil covering with different industrial wastewater.

The obtained Pb amounts are given in the Table 1.

*Table 1: The Pb amounts in the soil (total and plant-available),
industrial wastewater and in the pepper plant parts (dry)*

	Pb amount in samples (mg/kg), wastewater (mg/dm ³)						
Wastewater		0.011	0.025	0.029	0.289	0.007	0.022
Soil, total amount	13.31	15.33	13.31	11.30	49.61	27.43	18.56
Soil, plant-available amount Extragens							
2% CH₃COOH pH=2.5	0.21	0.36	0.21	0.21	0.36	0.29	0.14
1M CH₃COONH₄ pH=4.8	1.24	2.06	1.94	1.88	1.53	1.65	1.41
1M KCl pH=7	2.46	2.58	2.46	2.52	2.58	2.52	2.58
0.5M Na₂EDTA pH=5.2	3.01	4.41	4.20	4.00	4.27	4.00	3.59
mixture 0.1M KCl and 0.05M Na₂EDTA pH=6.2	3.56	5.62	5.56	4.94	5.25	5.38	5.31
Stalk (dry)	5.38						
Leaf (dry)	9.74						

The value of lead plant-available amount in the soil depends on Pb-extragens component stability constant. The lead amounts in leaf are higher than in the stalks.

Poster No. 43:

TESTING OF POLLUTANT CONTENT IN SOIL AT CERTAIN LOCATIONS IN BELGRADE

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The tests were conducted on the soil and waste water samples at the sites covering the territory of the City of Belgrade with the aim of determining the level of contamination by hazardous and harmful substances in accordance with the national legislation.

The water and soil samples were always analyzed for the same ten elements: Cu, Zn, B, Cd, Pb, Hg, As, Cr, Ni and F. Flame and electrothermal atomic absorption spectrophotometry, spectro-photometry and ion chromatography were used for chemical determination.

The testing results show that there was no soil contamination at the tested sites, since the content of the tested parameters was within the permissible limits. However, the nickel content in soil significantly deviates from the maximum allowed concentration (50 mg Ni/kg), and ranges between the following ratios: <50 mg/kg ~30%, ~50 mg/kg ~20% and >50 mg/kg ~50%. The explanation for the presence of nickel at the examined sites should be sought, among other, in the geo-morphological origin of Belgrade. The increased nickel content in the waters tested was not noted.

Poster No. 44:

ORGANOCHLORINE INSECTICIDE RESIDUES IN SERBIAN SOILS

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NB: Nebojša Protić unfortunately died in the meantime.

The organochlorine insecticides were used worldwide for many years to control agricultural and public insects, prior to being partially banned some 30 years ago. The persistence of their residues remains an important environmental problem. To better define its magnitude and estimate the risk, data are needed on existing stocks of banned compounds and residue levels present in different environmental compartments.

With an object of getting more information on the residues, levels of DDT and lindane metabolites were monitored as part of the study on soil fertility. This study uses a sequential approach to collect information on a number of relevant soil parameters for the whole area of the Republic. Phase I was started in 1991 and completed 1993 in the Province of Vojvodina, later the study was extended to phases II-VII to cover all other regions of Serbia and should be completed by 2006. The same sampling protocol was used in each phase. It provides one composite sample (0-30 cm) from 25 predefined locations covering the area of 1000 ha each as well as information on land usage. Residue data for some 1500 samples obtained to-date indicates that the levels of the targeted insecticides are generally low. DDT and metabolites (>0.01 ppm) were detected in 10% of the 617 phase III-IV samples and 28% of the 377 samples processed from 1007 of phase V. The corresponding levels of lindane and its metabolites (α β and δ -HCH) were of the same order.

Poster No. 45:

DEVELOPMENT OF A METHODOLOGY TO EVALUATE SOIL QUALITY - A TOOL FOR URBAN RESOURCE MANAGEMENT

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Urban systems represent high turnover of resources, having an effect on the environment in an unsustainable manner. Urban soil is used during urban development and needs to be managed if it is to be preserved and maintained its role in supporting and enhancing the quality of life. Since soil can be considered both as a source and as a sink of pollution, it is important to develop and validate a methodology for the assessment of environmental quality in urban soils, as a tool for sustainable resource management.

Data about the climate, topography, geology, soil type, other environmental data (air emissions, water pollution, etc.), local planning, population (type and distribution), industry characterisation and distribution, land use, transports, energy inputs, etc, should be collected in order to have a general characterization of the study area and provide a continuous available set of basic data. The potential sampling sites are chosen based on aerial photographs, soil maps and field observation. Sampling methodologies should be continuously updated and the most suitable methodologies should be selected by careful definition of sampling regimes, sampling sites/points, sampling distances and sampling design.

Indicators should be chosen taking into account that as an useful indicator of the sustainability of land management practices, a soil parameter must respond sensitively to changes in management. They should be sensitive enough to reflect the influence of management and climate on long term changes in soil quality but not be so sensitive as to be influenced by short-term weather patterns.

Geostatistical methods are used, at a final stage, to show spatial variability of contaminants and the probability of exceeding the risk-based standards. These soil maps are important information for decision-making and can be used for regulating purposes by Local Authorities since the area resources of every city are restricted.

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Poster No. 46:

THE INFLUENCE OF A CHEMICAL COMPLEX IN POTENTIAL TOXIC METAL DISTRIBUTION OF NEARBY URBAN SOILS

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Urban areas are affected by a wide variety of anthropogenic activities, such as traffic and industry. Estarreja is one of the most important industrial areas in Northwest Portugal. This chemical complex is located at about 2 km away from the town centre of the urban area also called Estarreja. Soil contamination by heavy metals is a potential problem in residential and agricultural areas. This study aims to assess the impact of the chemical complex in heavy metal distribution of the urban area.

The survey and sampling method were based on pre-interpreted maps, aerial photographs, and directly checked in the field, in order to get an overall characterization of the urban area. Soil samples were collected at two depths (0-10 cm and 10-20 cm) from 26 sites, considering different land uses. Four land uses were chosen: Ornamental Gardens (OG), Parks (PO), Roadsides (RD) and Agricultural (AG). The samples were sieved and milled to <63 µm, and after digestion in Aqua Regia the concentrations of eight potential toxic metals (Pb, Zn, Cd, Ni, Cu, Cr, Fe, Mn) were determined using Atomic Absorption Spectrometry.

Geostatistical methods show the spatial variability of contaminants and the probability of exceeding the risk-based standards. The plots of concentration of metals on GIS can show areas where the highest elements concentrations occur and the land use associated. The main usefulness of these soil maps is the important information for decision-making, allowing a better sustainable resource management in very industrialized urban areas.

Acknowledgement: This work was developed under Project POCTI/CTA/44851/2002: Towards a methodology for the assessment of environmental quality in urban soils (SOLURB).

Poster No. 47:

CHROMIUM-RESISTANT BACTERIAL POPULATION FROM MILIĆI BAUXITE MINE SOILS

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Chromium occurs in soil as soluble and toxic metal usually in two stable oxidation states, Cr(VI) highly toxic and Cr(III) as thousand times less toxic. It is known that heavy metal contaminated soils contain more metal resistant microorganisms compared to non contaminated soils. Most resistant microorganisms have ability to reduce Cr(VI) to less toxic Cr(III) and could be used for soil detoxification. The aim of this study was to isolate such bacteria resistant to high Cr(VI) concentration, and determine its reduction capacity. The samples were collected from two different locations in bauxite mine in which total Cr content was from 10.6-209.6 mg·kg⁻¹. Bacterial populations were grown on TSA (10X diluted) agar containing Cr(VI) as K₂Cr₂O₇ ranged from 200 to 1000 mg·l⁻¹ and different pH values. From this experiment we isolated 15 resistant strains. Reduction capacity was tested with three strains using 20, 40, 80, 100 µM solution, colorimetrically (λ_{540}) by method of *s*-diphenylcarbazide and lasted 24 h. All three isolated strains were reduced 20, 40 and 80 µM Cr(VI) solution achieving 100% removal. However, two strains were reduced 100 µM Cr(VI) solution achieving 60.9% removal and third, the best was reduced the same solution achieving 80.77% removal.

Poster No. 48:

EFFECTS OF HEAVY METALS ORIGINATED FROM INDUSTRY AND MINING ON SOIL MICROORGANISMS IN KOSOVSKA MITROVICA

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Industrial air pollution is most responsible factor for environmental contamination and poses a risk both for human being, plants and microorganisms. In Kosovska Mitrovica the most adverse source of metal air pollution is RMHK "Trepča" which is situated near the center of town. To investigate the effects of air pollution on different soil types, the samples were collected from location with different distance from town. The highest concentrations of heavy metals (Zn, Pb, Ni and Cd) in soil were found near the town. Parallel with metal content we investigate number and activity of microorganisms, fungi, actinomycetes, aminoheterotrophy, azotobacterium sp. etc. The most investigated location showed higher metal content than maximal allowed concentration. The number and activity of all investigated microorganisms showed strong correlation with heavy metals content, the highest metal concentration the lowest number and activity. At soils under cultivation the effects of heavy metals were less expressed on MO number and activity compared with soils in uncultivated area (meadows etc.).

Poster No. 49:

EFFECT OF PHYSICO-CHEMICAL CHARACTERISTICS OF AGRICULTURAL SOILS ON FUNGAL BIOMASS - CASE OF MEADOW AND CROP

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The fungal biomass, FB, is used as a biomarker to assess the soil fertility and to supervise the effects of an environmental pollution. The principal membrane sterol of most fungi is the ergosterol. It is generally used to estimate the living FB. Our aim is to be able to use this biomarker like an indicator of change of the agricultural practices.

We have optimized certain techniques of extraction (Montgomery, 2000 & Gong, 2001) based on two approaches: **1**: mechanical perturbation, **2**: saponification with Micro-waves Assisted Extraction.

The first technique shows weak concentrations in biomass which correspond to the free ergosterol and the MAE technique shows the most important quantities in FB which represent the total ergosterol (free and esterified).

We tried to emphasise the influence of physico-chemical characteristics on the FB content and its evolution. We are working on two types of agricultural soils: a permanent meadow and a field crop located in the same place in Normandy.

Nevertheless, the interpretation of the results obtained using these comparisons is often difficult in the case of soil micro-organisms (the main actors of soil functioning) and can be in many cases non-conclusive. It is especially true regarding cultivated soil ecosystems because of numerous pedoclimatic and environmental situations, agricultural practices... However, we can propose some trends: FB is well correlated with the carbon, apparent density and clay fraction. pH and nitrogen are two parameters important for the FB.

6. Ecotoxicology

Posters No. 50-61

Wednesday, December 7th, 19:30-20:30

Posters No. 62-73

Thursday, December 8th, 17:21-18:21

Poster No. 50:

AN EVALUATION OF RESULTS FROM MONITORING AND ECO-TOXICITY TESTING OF THE SKADAR/SHKODRA LAKE BY TRIAD APPROACH

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Lake Skadar is the largest lake of the Balkan Peninsula, located between Albania and Montenegro. Due to its unique ecosystem, the Lake was classified as a wetland site of international significance and importance. Furthermore, Lake Skadar is the largest drinking water reservoir in the area and an important region for ecotourism activities as well as fishing. The Lake is exposed to constant pollution through the Morača River and its tributaries. The pollution comes from municipal and industrial wastewater discharges, agricultural activities in the area and the aluminum processing plant near the lakeshore of the Montenegrin part. In order to evaluate the ecological and ecotoxicological condition of the lake's water ecosystem we performed a Sediment Quality Triad (SQT). Within this approach we subjected extracts of sediment samples to chemical analyses and applied several bioassays on sediment extracts as well as solid sediment samples. Furthermore, in situ researches on benthos communities were undertaken. We applied a bio-test battery on toxicity (bacteria test), mutagenicity (Ames test) and embryo toxicity (Danio rerio). Evaluation of the ecotoxicological condition of the water ecosystem based on the implemented Triad approach clearly indicated ecological and ecotoxicological effects of a chronic pollution. Sediments are contaminated by organic pollutants and heavy metals (moderately). Mutagenicity tests detected potentially mutagenic components, which can have a considerable adverse impact on the quality of this unique water ecosystem.

We acknowledge the active support of German Rector's Conference (HRK) and Stability Pact for South-East Europe helping transboundary cooperation of participating universities and institutions.

Poster No. 51:

EFFECTS OF METAL IONS ON Mg^{2+} -ATPase ACTIVITY IN PLASMA MEMBRANES ISOLATED FROM THE RAT UTERUS

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Environmental pollution by metals increases the absorption and accumulation of these in various tissues, eventually resulting in noticeable biological dysfunctions. Toxic mechanisms include interaction with cell membranes, binding to DNA and transcriptional factors, enzyme inhibition and production of reactive oxygen species. A plenitude of evidence classifies mercury, cadmium, chromium, copper and several other metals, as reproductive toxicants. The effects of these metals on reproductive organs were mostly examined under *in vivo* conditions. In this work, we investigated *in vitro* effects of metal ions on Mg^{2+} -ATPase activity in isolated membranes from rat uterus. Mg^{2+} -ATPase (ecto-ATPase, EC 3.6.1.3.) is an integral membrane protein that, in the presence of Mg^{2+} , hydrolyses extracellular nucleosides. By controlling the concentration of extracellular ATP, it influences a variety of P1 and P2 receptor mediated processes.

The effects of increasing concentrations of metal salts $CrCl_2$, $CuSO_4$, and $HgCl_2$ shows sigmoidal and complete inhibition relative to the control enzyme activity. $ZnSO_4$, exhibits up to 80% of inhibition. According to the IC_{50} , ecto-ATPase possesses greater sensibility to Zn^{2+} ($IC_{50}=2.55 \cdot 10^{-4}M$) > Cu^{2+} ($IC_{50}=5.56 \cdot 10^{-4}M$) > Cr^{3+} ($IC_{50}=6.34 \cdot 10^{-4}M$) > Hg^{2+} ($IC_{50}=7.33 \cdot 10^{-4}M$), while other metal salts exhibit the following inhibition: $CdCl_2$ 55%, $CsCl$ 64.5% and $SrCl_2$ 58%. The physico-chemical properties of these metals are of importance in defining possible mechanisms of binding and decrease of enzyme activity. By inhibiting or decreasing ecto-ATPase activity in the uterus, these metals increase extracellular ATP and P2 purinoceptor evoked intracellular events, which may disturb the proper functioning of uterine tissue.

Poster No. 52:

A QSAR STUDY OF ACUTE TOXICITY OF *N*-ARYL-SUBSTITUTED FLOUROACETAMIDES TOWARD RATS. CLASSICAL AND MOLECULAR PROPERTY SPACES APPROACH

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In our previous paper a QSAR study of acute toxicity of set of 19 *N*-alkyl-substituted flouoroacetamides toward rats was described. Main factors that influence the biological action of studied set of compounds were: atomic charges on the amide moiety, sterical bulkiness of nearest vicinity of amide N and overall lipofilicity of compounds. Possible mode of action was suggested.

In the present communication, as an extension of previous work, we study relation between acute toxicity of five *N*-aryl-substituted flouoroacetamides comparing classical and novel (literature) approach which includes range and sensitivities of chosen molecular descriptors for number of possible conformations of each compound. Assessed results are in excellent agreement with results obtained in previous work. Main factors which influence the acute toxicity of *N*-aryl-substituted flouoroacetamides toward rats are the atomic charges on an amide moiety, derived by the semiempirical MNDO-PM3 MO calculations, and range of polar surface area (PSA, which encoded polarity and H-bonding capacity). Obtained two-parameter correlations have very good statistics ($r = 0.999$ and 0.998 ; $F = 455$ and 347 ; $Q^2 = 0.998$ and 0.939 for 99% confidence interval). Consistency of data derived in previous work and in this communication are additional proof of validity of a suggested mechanism of action for studied class of compounds.

Poster No. 53:

DO LEAD - NATURAL ORGANIC MATTER COMPLEXES CONTRIBUTE TO Pb BIOAVAILABILITY TO FRESH WATER MICROALGAE?

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It is well recognised that the natural organic matter (NOM) play an important role in aquatic ecosystems, e.g. by binding trace metals and thus influencing their speciation, mobility, bioavailability and toxic effects. Nonetheless, a fundamental understanding of the relationship between trace metal speciation, biological uptake and effects is still lacking for many environmental systems. The present work focuses on the role of humic substances (HS) and extracellular polymeric substances (EPS) since they constitute the majority of the natural organic matter in freshwater systems. More specifically the emphasis is on the quantification of Pb complexation by different components of NOM and the determination of the influences (both direct and indirect) of NOM on Pb bioaccumulation by green algae *Chlorella kesslerii*. The obtained results demonstrated that polysaccharides, in particular alginic acid, had complexing properties and effects on Pb bioaccumulation that were similar to equivalent complexation capacity for humic substances. Pb uptake decreased in the presence of humic, alginic and polygalacturonic acids with respect to dissolved Pb, but accumulated Pb was higher than predicted from measured Pb²⁺ concentrations or from previous results obtained in the presence of synthetic ligands (e.g. NTA). Other effects such as a decreased surface charge and increased membrane permeability was found to be of secondary importance. The environmental implications of the results are discussed with respect to biotic ligand model application and the development of site-specific water quality criteria.

Poster No. 54:

COMPLEXES OF CHLOROPHYLL WITH COPPER, ZINC AND LEAD IN SOLUTION AND PHOTOSYNTHETIC ORGANELLES: CHLOROPHYLL FLUORESCENCE STUDIES

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Toxic heavy metals like zinc (Zn), lead (Pb) and copper (Cu), are easily absorbed by plants. Once absorbed, they penetrate to plant tissues (including leaves) and in higher concentrations, they potentially may affect photosynthesis by forming complexes with major photosynthetic pigment, chlorophyll (chlorophyll - heavy metal complexes, Chl-HMS). Chlorophyll fluorescence spectra obtained from isolated chlorophyll fractions and isolated photosynthetic organelles (chloroplasts) and sub-organelles (thylakoids) in the presence of the three metals suggested that two types of complexes have been formed in this work. Copper replaces labile bonded central magnesium (Mg) atom of chlorophyll and creates predominantly "central" or "substitutional" type of complex. On the other hand zinc rather forms 6-membered "peripheral" type of complex, fused at the edge of the Chl-macrocycle, in solution; supramolecular organization of chloroplasts and thylakoids does not allow formation of this type of complex. Lead probably forms the "central" complex, but not in the first step and with some remarkable delay. The Chl-HMS complexes, especially the "central" ones, may cause an impairment of photosynthetic function, and this, as a final consequence, may lead to plants' fatal end. Potentially, the Chl-HMS complexes may serve as *in vivo* probe to detect these heavy pollutants by using non-invasive methods, like fluorescence.

Poster No. 55:

QUALITY OF PETKA SPRING WATER IN THE VICINITY OF COAL ASH DUMP OF THE KOSTOLAC POWER PLANTS (SERBIA)

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The "Kostolac A" and "Kostolac B" power plants are located in the important agricultural region of Stig, approximately 100 km from the Serbian capital Belgrade. Coal ash from these two power plants is suspended in water from the Mlava River and at an approximate solid-to-liquid ratio of 1:10, transported to a common dump that is located at the confluence of the Mlava and Danube rivers. Near by this coal ash dump there is Petka spring.

In order to establish the influence of the neighboring surface waters (Danube, overflow and drainage waters) on the quality of the ground waters in the vicinity of the dump, in this paper we discuss the results of correlation analysis of the concentrations of the examined elements in the ground waters of the Petka spring with concentrations present in neighboring surface waters, both natural river water (the Danube) and waste waters (overflow and drainage). Also, in an attempt to establish possible delayed influence of natural and waste surface waters on the water quality of the ground water, the concentrations of examined elements in the samples of the surface waters were correlated with those found in the ground water 15, 30 and 45 days later.

It was found that the concentrations of elements in the Danube and waste waters had both immediate and delayed influence of pollution, on the quality of ground waters.

Poster No. 56:

SPECTROSCOPIC, STRUCTURAL AND QUANTITATIVE CHARACTERISTICS OF THE ARTIFICIAL FOOD DYE E124 IN SOME FOOD PRODUCTS

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Historical data suggest that people have always used additives to make food more tasteful or to preserve it for longer periods. Since introduction of additives in food manufacturing, two aims have collided: actual needs for application of additives and their misuse in "falsifying" food for economic reasons.

In the available literature in our country few studies have been performed that examine quantitative and qualitative determinations of food dyes. Control of food products has continuously been problematic. The best example includes artificial food dyes the use of which is restricted by type and quantity. During regular food control, however, neither the accurate identification of dyes nor their quantity is determined.

The paper deals with quantitative determination of food dye E124 listed as Ponceau 4R and Cochineal Red A, code C.I.16255, and chemical name trisodium-2-hydroxy-1-(4-sulphonato-1-naphthalazo)-naphthalene-6,8-disulphonate, in samples of refreshment soft drinks, soft drinks powders, and bonbons.

A quantitative analysis of the standards and samples was performed employing the UV/VIS spectrophotometric method. On the basis of the obtained absorption spectra of a series of standard solutions at various concentrations, as well as their absorbance (A), a working curve was construed. In addition, calculation of the molar absorption coefficient (ϵ) of the dye was performed which was used for determination of unknown concentration of the dye in the samples. After discussing the obtained UV/VIS spectra, the influence of other additives present in the samples was examined against bathochromic, hypsochromic, hyperchromic, and hypochromic effects. The IR spectrum of the dye was also recorded.

Poster No. 57:

HERBAL DRUGS ORIGINATING FROM MEDICINAL PLANTS OF THE FAMILY *Lamiaceae*

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In this work determination of elemental concentration, as a total analyte content (K, Ca, Mg, Fe, Mn, Al, Zn, Cu, Ni, Cd, Pb, Cr) of seven herbal drugs was performed. Investigated herbal drugs, *Salviae folium*, *Menthae pip. folium*, *Melissae folium*, *Lavandulae flos*, *Basilici herba*, *Marubii herba*, *Origani herba* (*Lamiaceae*), originating from medicinal plants of special importance in phytopharmacy and were cultivated under the strongly controlled conditions on the plantation near the Belgrade in Serbia. Additionally, rhizosphere soil samples were also collected and analyzed.

Acid assisted microwave digestion, according the official procedures (US EPA 3051 and US EPA 3052), preceded the measurements with flame atomic absorption spectrometry (FAAS), electro-thermal atomic absorption spectrometry (ETAAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES).

Obtained results were used for calculating bioconcentration factors (BCF) in order to predict the bioavailability of investigated elements and possibilities of accumulation of toxic elements in the plants tissue as well.

Poster No. 58:

MONITORING OF THE LAKE SKADAR BY TRIAD APPROACH AND MICROBIAL DIVERSITY PROFILING

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Lake Skadar/Shkodra is the biggest karstic lake in the Balkans. The most pollution that load northern sector of the lake (receives mostly via the river Morača) comes from municipal and industrial wastewater discharges and aluminium processing plant near the lakeshore of the Montenegrin part and agricultural activities in the area. Monitoring the state of the environment is therefore crucial for the protection of the lake. For the assessment of the ecotoxicological state of Lake Skadar/Shkodra we used a triad approach (chemical analysis, bioassays and in situ investigations of the benthic community structure) and Temporal Temperature Gel Electrophoresis (TTGE) profiling of the bacterial community. Samples were taken from five locations of Skadar/Shkodra Lake: Raduš, mouth of the river Morača, Plavnica, Kamenik and the middle of the lake as a reference location. In the context of bioassays for the TRIAD approach we used biotests for embryo toxicity and genotoxicity. Bioassays with embryos of *Danio rerio* were conducted and mutagenic compounds were evaluated with the Ames test on *Salmonella typhimurium*. The study of bacterial community was realized by TTGE profiling, where isolated DNA was used as a template for bacterial 16S rRNA genes in PCR. The amplified gene fragments were separated by TTGE. The TRIAD approach revealed that the most polluted location is the mouth of the river Moraca. It holds true for the results of TTGE profiling, suggesting the applicability of the bacterial community profiling as a biomonitoring tool.

Poster No. 59:

ACUTE TOXICITY EVALUATION FOR SOME CHEMICALS WITH SMALL MOLECULAR WEIGHT

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T Loomis claims: the single test that is conducted on essential all chemicals that are of any biological interest is the acute toxicity test. It is also statuated that the small and slow to react-molecules shold in priciple, be harmless or, at least, toxic only in large amounts. More differentiate rules of ecotoxicology taking in to account the particular characteristics of the single chemicals oder classes of chemicals is necessary, especially when those occuring in foods and drinks.

In this work we calculate accute toxicity (CL_{50}) for a series of chemicals with small molecular weigt: CH_3OH , C_2H_5OH , $(C_2H_5)_2O$ and $CH_2=CH-CO-NH_2$. We used relationships based on corresponding physical-chemical data: molecular weight, boiling point, melting point, density and log P (where P is calculated partition coefficient between octanol and water). Obtained values are compared with accute toxicity test data and with some properties calculated in frame of MM+ method.

Poster No. 60:

INFLUENCE OF NEW DITHIOCARBAMATE, (NH₄)₃ IDADTC, ON DEVELOPMENT OF *Phomopsis viticola* Sacc. FUNGI

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Dithiocarbamates (DTCs) are widely used in agriculture as pesticides and fungicides as well as in a manufacture of rubber products as accelerating agents.

This work is set with the intention to research influence of new synthesized dithiocarbamate, triammonium-N-dithiocarboxyiminodiacetate ((NH₄)₃IDADTC) [1] on the development of *Phomopsis viticola* Sacc. fungi. Obtained ((NH₄)₃IDADTC) has deprotonated dithiocarbamate group with potential antifungal activity. *Phomopsis viticola* Sacc. was chosen for our investigation as a pathogenic fungi which is the cause of the *dead arm disease* of grapevine. *P. viticola* have been isolated from Montenegro grapevines where *dead arm disease* appears every year [2]. The efficacy of the ((NH₄)₃IDADTC) against isolated *Phomopsis viticola* was tested on mycelial growth, and compared with the frequently used fungicide - merchantile mancozeb. Mycelial growth was recorded after 11 days.

Effective concentration at which mycelial growth was inhibited at 50% (EC₅₀ value) was calculated for both ((NH₄)₃IDADTC) and the merchantile mancozeb. The value of EC₅₀ obtained for the new synthesized dithiocarbamate ((NH₄)₃IDADTC) was 9733, which is noticeably higher comparing to the value of EC₅₀ for the merchantile mancozeb (3806).

Obtained results indicated that the triammonium-N-dithiocarboxyiminodiacetate ((NH₄)₃IDADTC) shows relatively weak inhibition against investigated fungi comparing to mercantile mancozeb.

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Poster No. 61:

CHEMICAL ANALYSIS OF SEDIMENTS AND CORRESPONDING PORE WATER AND ELUTRIATES AS A BASE FOR CORRELATION OF CHEMICAL COMPOSITION AND ECOTOXICOLOGICAL EFFECTS

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Since surface water systems are important environmental compartments, comprehensive investigations and monitoring activities have been performed for decades using analytical and ecotoxicological tools in order to assess the state of pollution and to predict the environmental risk of the contamination. With respect to the particulate matter ecotoxicological evaluation of sediments is based on tests applied to the corresponding pore water and elutriate. However, very often measured ecotoxicological effects can not be attributed directly to distinct harmful or toxic substances in particular with respect to organic contaminants. Therefore, our investigation focused on the chemical quality of different sediment compartments in order to correlate the results with ecotoxicological effects.

6 sediment samples from different locations along the rivers Rhine, Elbe and Odra were separated into pore-water, elutriate and sediment by centrifugation. These compartments were analysed for organic contaminants, both quantitatively and qualitatively, despite trace metals and nutrients. Distinct differences in the molecular composition were observed and provided insight into the mobility and bioavailability of numerous anthropogenic compounds. Selected compounds can act as candidates for an ecotoxicological based risk assessment and will be further addressed in a set of different acute and chronic toxicological tests. However, the special focus of the presented study laid on the exchange of these compounds between the lipophilic and hydrophilic compartments and their individual contribution to the total toxicity of sediment samples.

Poster No. 62:

BIOLOGICAL ACTIVITY OF COPPER(II) COMPLEXES WITH SOME BENZIMIDAZOLE DERIVATIVES

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Benzimidazole and its derivatives have a long history as antimicrobial agents. This class of compounds with methyl and amino substituents in different positions have been found to possess inhibitory effect on the development of several yeasts and bacteria. Synthesis of benzimidazoles fused to another heterocyclic ring has attracted wide spread attention due to their diverse application as antiviral-, antitumorial- and anti-inflammatory agents. It was found that the complexes of transition metal salts with benzimidazole derivatives showed a larger antimicrobial activity than only ligands.

The purpose of this paper is to examine the antimicrobial activities of the ligands (2-methyl and 2-aminosubstituted benzimidazoles) and their copper(II) complexes. Copper(II) chloride reacts with two series of benzimidazole to give complexes of the formula $\text{CuL}_2\text{Cl}_2 \cdot n\text{H}_2\text{O}$; $n=0.5$ or 1 . The first serie contained 2-methylbenzimidazole (1-benzyl-2-methylbenzimidazole and 1-(4-methylbenzyl)-2-methylbenzimidazole), as well as the second one was based on 2-aminobenzimidazole (1-benzyl-2-aminobenzimidazole and 1-(4-methylbenzyl)-2-aminobenzimidazole).

All the ligands and their copper(II) complexes were evaluated for their in vitro antimicrobial activity against *Pseudomonas aeruginosa*, *Bacillus sp.*, *Staphylococcus aureus*, *Sarcina lutea* and *Saccharomyces cerevisiae*. The majority of the investigated compounds displayed in vitro antimicrobial activity against very persistent microorganisms. None of the compounds were significantly effective against yeast *Saccharomyces cerevisiae*. MIC was determined for all ligands and their complexes. The effect of ligand and complex structure on the antimicrobial activity was discussed.

Poster No. 63:

CHEMICAL BEHAVIOR OF NITROGEN AND PHOSPHORUS IN THE VELIKA MORAVA CATCHMENT

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The concentrations of biologically available nitrogen (N) and phosphorus (P) play a key role in determining the ecological status of aquatic systems as well as the ratio in which these elements occur. Agricultural and urban activities are considered as being major sources of P and N to aquatic ecosystems. Non-point inputs of nutrients are difficult to measure and regulate because they derive from activities dispersed over wide areas and vary significantly with time due to effects of weather conditions.

The aim of this study was to compile existing data on nutrients on the Velika Morava catchment and quantify the regional distribution of nutrient influx entering into the Danube. The results of a national data bases concerning the quality of surface waters, nitrogen (NO_3^- , NH_4^+ , total N) and phosphorus species (orthophosphates, total P) collected in the time period between 1998 and 2004 at 18 locations are reported. The data were subjected to multivariate analytical techniques such as factor and correlation analysis. The principal component analysis (PCA) showed a clear separation between monitoring sites in 3 groups originating mainly to sub-basins of the Velika Morava, the Zapadna Morava and the Južna Morava. The annually nutrient loads discharged into the Danube ranged from 6386 to 31237 tn-year⁻¹ for total N and from 844 to 2111 tn-year⁻¹ for total P exhibiting the effects of heavy runoff year and dry year.

Poster No. 64:

PESTICIDES IN WORKING AND HUMAN ENVIRONMENTS AND FACTORS AFFECTING HUMAN HEALTH

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Introduction: Last years in our contry, we had some new disease, some of them reactivated, and we donknow much about it. Pesticides have resulted from a need for producing larger quantities of healthy food and eliminating diseases carried by pests. In contrast to many pollutants introduced into the environments without a proper goal, pesticides are used to help increase the food yield and fight the harmful microorganisms and pests.

Goal: The impact of pesticides on the biocenoses and human health is a multifaceted process and requires scientific and expert approach in finding adequate measures of prevention, chemical protection and removing the consequences. The effects of pesticides on biocenoses and the environments on the whole call for a very complex and diverse course of action, and this paper deals with the factors affecting the human health. Major disorders of biocenoses have been registered upon consistent use of highly toxic pesticides, mainly the organochloric compounds.

Method: We have sorted the pesticides according to the objects of their action; the way of their entering the organism; their action inside the organism; their toxicity, and their chemical composition. Examining the epidemiological and toxicological implication of pesticides, we noticed particularly the problem of intoxication by organophosphoric pesticides, carbamates and halogen derivatives of hydrocarbons. The effect of pesticides on humans has been studied as the intoxication of workers involved in the application of pesticides, as well as those getting into contact with pesticides due to their ignorance and lack of care. This research has been based on 54 scientific researches and its main purpose is to make the scientific and scilled audience acquainted with the accomplishment of the metodology in that area.

Findings: Major disorders in biocenosis have been registered due to consistent use of highly toxic pesticides. Epidemiological and toxicological meaning of intoxication by substances for plant protection is particularly manifest in the manufacture process and even more during their application. This is also significant from the aspect of population health protection due to the contamination of foodstuff and its cumulative effects. The intoxication by organophosphoric substances is especially well known for grave outcomes ranging from recover, to serious damages and to exitus. Lethal outcomes have been most often registered in cases of accidental ingestion, and rarely resulting from inhalation. Increased usage of pesticides has resulted in increased number of intoxicated people and called for a need to establish their working ability. In acute phases of disease, during convalescence and acute phase of complications, there occurs a working inability (sick leave) lasting for relatively short time. Professional inability lasts for a longer period of time depending on turning into chronic state or on intoxication consequences. In larger factories there is a labor medical service, performing the measurements of work environment pollution, early diagnostics and therapy within the manufacture process. Chronic intoxications are more often found than the acute ones, resulting from

disasters, negligence and improper application of labor protection measures and chemical protection measures.

Conclusion: The risk is defined as a product of a failure probability and its consequences. Pollution by pesticides is one of the consequences of striving to enlarge the production of food and to suppress harmful impact of various organisms that decrease the yield. Toxicologically and epidemiologically, the pesticide manufacture, transport, storage and application are getting ever larger significance. For the sake of early diagnosis, and timely and proper treatment, it is necessary that in addition to labor medicine physicians and toxicologists, other experts too get familiar with details of the chemism and pathophysiological actions of these compounds as well as with the clinical picture, first aid and general principles of treatment. The jobs on which people are exposed to pesticides should be marked as jobs of special labor conditions, which entails strict observation of legal regulations. In the pesticide manufacture process, it is necessary to organize and enforce the prescribed labor protection measures and proper chemical protection. Apart from the skilled personnel and modern technology, it is necessary to establish the hermetization of the manufacture process and top-quality filterventilation, and to use the personal and collective protection aids.

Poster No. 65:

COMPARATION OF DIFFERENT METHODS FOR DETERMINING BIOAVIABILITY AND BIOACCESIABILITY FACTORS FOR PAH SUBSTANCES

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The majority of parameters which are used for describing quality of polluted soil and estimation of cleaning up procedures are based upon oral intake of soluble substances which might come to gastro interstitial tract due to food or water.

Also it is interesting to explore possible harmful effects which might be observed when they are absorbed by living organisms.

PAH (polyaromatic hydrocarbons) forms unique class of substances. They reach atmosphere according to nature or anthropogenic activities (fires, vulcan activity or traffic for example).

From air they reach soil and sediments depose themselves and stay for long period.

Literature data, experiments and epidemiological studies shows that some of them have toxic, carcinogenic or mutagen characteristics, so modern laboratorial studies should supply special target analyses which might provide adequate toxicological problem estimation on time.

These result should be used for protect program development and possible risk estimation.

Quality and type of contaminants which reach organisms are responsible for possible harmful damage.

This paper compares different methods for determining basic risk factors (bioavailability and bioaccessibility) for adequate method defining.

In future this method should be used for analytical method validation and for identification of unknown substances in present laboratory conditions.

Poster No. 66:

ANTIBACTERIAL ACTIVITY OF 4-ARYL-4-OXO-2-BUTENOIC ACIDS AGAINST *Escherichia coli*. A QSAR STUDY

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Diverse groups of biological active, natural and synthetic molecules comprise common structural fragment: 4-aryl-4-oxo-2-buten. In our previous articles quantitative structure-activity and structure-reactivity relationships of alkyl, alkoxy, nitro and halo-phenyl substituted 4-phenyl-4-oxo-2-butenic acids were reported.

Present study describes the antibacterial assay and quantitative correlation between structure and antibacterial activity of nineteen 4-aryl-4-oxo-2-butenic acids against *Escherichia coli* (ATCC 35210), a bacterial species widespread in the nature. Studied compounds exert activities in a range of concentrations $1.32 \cdot 10^{-3}$ to $3.8 \cdot 10^{-5}$ M/L. Four compounds act in markedly lower concentrations than the control (streptomycin hydrochloride). Main factors influencing the antibacterial activity of studied set of compounds are virtual log *P* (conformation dependent property), and an indicator variable that describes steric demand in position 4 of the phenyl ring. One parabolic, one bilinear and one two-parameter equation were obtained for sixteen compounds, having good statistics. The reason for exclusion of the three compounds (outliners) from correlations was offered.

Poster No. 67:

PHOTOCHEMICAL BEHAVIOR OF METHOMYL

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Methomyl belongs to a class of compounds known as oxime carbamates and used as insecticide and nematocide. Like other related carbamates it acts by inhibiting the enzyme acetylcholinesterase.

This study describes behavior of methomyl under different types of light, photodegradation of methomyl with or without catalysts, photolysis of methomyl in different aqueous solutions and in organic solvents.

Initial concentration of methomyl were about $1 \cdot 10^{-4}$ M and methomyl was exposed to light during the different time interval.

Photolytic reaction of methomyl and photodecomposition of methomyl were studied by UV/VIS spectrophotometer, HPLC, ION chromatography, TOC analyzer, GC-MS and HPLC-MS.

Poster No. 68:

EVALUATION OF TOXICITY FOR ORGANIC ARSENICAL COMPOUNDS USING *Vibrio fischeri* BACTERIA AND MICROCALORIMETRIC BUTYRYLCHOLINESTERASE INHIBITION

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Arsenic is a ubiquitous element found everywhere in the environment, mainly as inorganic species which can produce various toxicities [1]. Organic arsenic can also exist in different methylated forms (dimethylarsinic (DMA) or monomethylarsonic (MMA) acids, arsenobetaine (AB), arseno-choline bromide (AC)) or as pharmaceutical compounds like 4-hydroxy-3-nitrobenzene arsonic acid (AA). However their differential toxicity has not been extensively studied. Because the mobility (and bioavailability), toxicity and reactivity of arsenic are greatly influenced by chemical speciation [1], its knowledge and the factors (e.g. pH) that can influence on it, are of crucial importance for evaluating the toxicity of arsenic in the environment. To gain a further insight on the behaviour of these organo-arsenic compounds towards *Vibrio fischeri*, both Microtox (acute toxicity test) and growth inhibition assays (chronic toxicity test) were used. The tests performed using the Microtox assay showed that light inhibition increases when solution pH decreases (from pH 8 to 4) in the case of DMA, MMA and AA, whereas no significant light inhibition was noted when bacteria were exposed to AC or AB in the same conditions. In contrast, results obtained from growth inhibition assay at pH 7.0 showed a low toxicity for DMA, MMA and AA and even a hormesis effect was detected for AC and AB. Microcalorimetric study [2] of *Butyrylcholinesterase* inhibition indicated a net increase of activity for AB and AC relative to the homologous nitrogen compounds. Although neither MMA, DMA or arsenate present any inhibiting activity, arsenite was found a strong irreversible inhibitor.

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Poster No. 69:

COPPER ACCUMULATION AND DISTRIBUTION IN VINEYARD SOILS OF SERBIA

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The intensive use for over 100 years of copper sulphate (Bordeaux mixture) to fight mildew in vineyards has led to a substantial accumulation of copper in surface soils. The focus of this work was to measure the accumulation and distribution of copper in contaminated and uncontaminated soils in Serbia as a step towards understanding copper existence in soils and its potential availability to flora and fauna.

Eight soils samples were collected at various locations within five vineyard plots and covered a large range of total Cu content. The 0-2, 2-20 and 20-30 cm layers were sampled to assess the distribution of Cu with depth. Soil samples were air-dried and sieved at 2 mm prior to being used for subsequent analysis. Physical and chemical properties and total copper concentrations were measured in soil samples including vineyard soils and adjacent background soils. Several single extractions were performed in parallel to the determination of total copper content (after aqua regia digestion). The following reagents for single extractions have been used: EDTA, ammonium acetate and calcium chloride.

This study showed that examined vineyards are contaminated by Cu as a consequence of the long-term use of Cu salts as fungicides, which resulted in an accumulation of copper to concentrations of up to approximately 430 mg·kg⁻¹. The naturally occurring concentration of copper is approximately 10-14 times lower. In the examined soil samples copper is highly plant available leading to problems when crops other than vineyard should be grown on these fields. Also vertical copper translocation was observed in the ground.

Poster No. 70:

THE PHYSICO-CHEMICAL AND BIOLOGICAL MONITORING OF THE RIVER SAVA POLLUTION

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Physico-chemical and biological monitoring of the Sava River pollution are investigated on three locations of sampling stations industrial and urban settlements (Šabac, Obrenovac, Beograd). During 2001-2002 total coliforms and fecal coliforms were tested to compare their effectiveness in detecting pollution through bacterial contamination in surface waters. That methods were use for regular monitoring Sava River provided a good urban model because a sewage river has degraded the water quality downstream. At each site dissolved oxygen, (DO), BOD₅, COD, heavy metals, total coliforms, *E. coli* were measured. *E. coli* levels increased from of 2100 MPN at site 1 upstream from the rive to 10,000 MPN at site 3. The content of dissolved oxygen (DO), BOD₅, COD, heavy metals were also found to be effective on-site indicators, but may not be exclusively caused by pollution. It was shown that the pollution minimum during last ten years period was recorded in 1994-95 years because of drop in industrial activity in region of military actions. In 2001-2002 years intervals the quality of water become worse in respect to physico-chemical and biological indicators from non point sources of pollution. The bacterial analysis as excellent indicator with measuring dissolved oxygen (DO), BOD₅, COD, heavy metals is recommended to efficiently monitor an urban and industrial places for pollution. The observed recovery distance indicates that monitoring sites of Sava River should be one kilometer or less in spacing to ensure that point source pollution is detected.

Poster No. 71:

THE INFLUENCE OF DETERGENT, ETHOXYLED OLEYL-CETYL ALCOHOL AND SODIUM TRIPOLYPHOSPHATE ON THE BIOPRODUCTION OF SOME ORGANIC SUBSTANCES OF THE FUNGI SPECIES *Penicillium verrucosum* PEYRONEL

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Detergent (MERIX, "Merima", Krusevac), and its components (ethoxylated oleyl-cetyl alcohol and sodiumtripolyphosphate) in 0,1% concentration showed the different influence on the bioproduction of organic substances: proteins, amino acids, organic acids, total biomass of fungi species *Penicillium verrocolum* PEYRONEL.

All the mentioned pollutants of applied concentration influenced the change of pH value, redox potential, and showed the influence on the proteolytic activity of the same fungi species.

The quantity of free and total amino acids stimulated by the presence of detergent, ethoxylated oleyl-cetyl alcohol and sodium tripolyphosphate in concentration of 0,1% vol. but the bioproduction of 13 different amino acids (15 different amino acids were analyzed) inhibited partially or significantly by detergent in concentration of 0,1% vol., except the production of amino acids: leucine and isoleucine, which were stimulated insignificantly, while the production of proteins inhibited significantly by the presence of detergent, ethoxylated oleyl-cetyl alcohol and sodium tripolyphosphate on the same concentration.

Poster No. 72:

ADSORPTION OF CADMIUM ON THE MEDITERRANEAN SEAGRASS *Posidonia oceanica*

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Removal of heavy metal ions from potable and industrial wastewaters is a significant issue of current interest. Of the many techniques and methods applied, adsorption yet preserves its popularity which may be attributed to low cost, variety and availability of adsorbents and operation simplicity. Although activated carbon is one of the most popular and widely used adsorbent in wastewater treatment applications, the urge to increase cost efficiency focused the research interest on utilising alternative lower cost adsorbents such as chitosan, clay, zeolites and wastes from certain industries such as orange peel, fly ash, papaya wood and red mud.

In this study, the Mediterranean seagrass *Posidonia oceanica*, collected from Gokova region in Turkey, was used as a biosorbent in cadmium(II) removal. The effects of adsorbent dosage, adsorbate concentration and solution pH on adsorption capacity were determined. When initial cadmium concentration was 200 ppm, removal was attained up to 91.88% at pH 4.5 with 6 g/l adsorbent dosage. Adsorption data was characterized in terms of isotherms and equilibrium isotherm studies indicated that the cadmium adsorption capacity of *Posidonia oceanica* was comparable to that of other low cost adsorbents. Spent adsorbent was regenerated for 0.5-2 hours in 0.1M HCl. Regenerated *Posidonia oceanica* performed quite well, retaining 67% of its adsorption capacity despite the weight loss caused by the strong acidic media.

Poster No. 73:

ECOTOXICOLOGICAL EVALUATION OF POLYURETHANE FOAMS

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Ecotoxicity tests are very important for evaluation of influence of chemicals on environment. Their role in both evaluation of newly developed preparations and classification of wastes for dumping is unique. Dumping of polymer preparations, especially those that undergo hydrolysis, has also become a quite common procedure. Polyurethane foams that are comprised in municipal refuse rank among the above preparations. Ecotoxicological evaluation of the above substances was implemented by the means of alternative toxicity tests THAMNOTOXKIT FTM and DAPHTOXKIT FTM MAGMA (Crustacean Toxicity Screening Test for Freshwater).

THAMNOTOXKIT FTM was found more suitable for evaluation of polyurethane foam extracts. The TOXKITS are aquatic toxicity tests in kits containing all materials as well as the test animals to perform simple rapid, sensitive and cost-effective acute toxicity tests on chemicals, solid waste elutriates or effluents released in water.

Both polyurethane foams without fillers and with biologically degradable fillers were tested for ecotoxicity. Freshwater crustaceans *Thamnocephalus platyurus* were subjected to the above tests. The leach was enriched with salts in the same way like diluting water. Several ways of conversion of polyurethane foam into leach, that was tested later, were examined. The highest mortality was found when foam and distilled water were refluxed for 8 hours; "standard freshwater" (SFW) was used for dilution. The lowest mortality occurred for reflux in pure ethanol.

Acknowledgement: Financial support from Ministry of Education, Youth and Sports under MSM 021630501 is greatly appreciated.

7. Water treatment, reuse

Posters No. 74-99
Thursday, December 8th
17:21-18:21

Poster No. 74:

PHOTOCATALYTIC DEGRADATION OF HUMIC ACIDS IN WATER BY UV LIGHT

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Humic substances are ubiquitous in water environment. Due to production of toxic and carcinogenic byproducts during chlorination, UV disinfection of water is much safer and healthier. Thus, the effects of UV light at humic acids (HA) in water were investigated in this study. Water model-solutions of HA were irradiated by low pressure mercury UV lamps ($\lambda = 254$ nm) in two manners: with aeration by air and without aeration. The change of HA concentration in water was monitored by UV/VIS spectrophotometry. The HA structure alteration and degradation products formation were investigated by UV/VIS spectrophotometry, gas chromatography (GC) and potentiometric titration. Results show a rather low decrease of HA concentration (only about 5%), after 10 hours of UV treatment without aeration. Aeration significantly increased effects of UV light, whereby after 10 hours of treatment concentration of HA decreased for about 30%. Obtained potentiometric titration data were treated by the modified Gran function, and results show increasing of number of hydroxyl and carboxyl groups in HA molecules. GC analysis shows the presence of low molecular mass degradation products, mainly carboxylic acids, in the water solution. Also, during the treatment certain decline of pH was noticed. Presence of oxygen in water multiple intensify efficacy of UV treatment, considering that oxygen produces very reactive oxy radicals (O_2^{\cdot} , HO_2^{\cdot} etc.) by action of UV light. Shown results indicate that UV light performs in aqueous environment oxidative photocatalytic degradation of HA.

Poster No. 75:

EFFECT OF SOME INORGANIC ANIONS ON THE FENTON DEGRADATION OF PHENOL

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The Fenton reaction is one of the processes that can be applied to the removal of dissolved pollutants in water. It consists of reaction between Fe(II) and H₂O₂ to yield the hydroxyl radical, •OH, although there is debate in the literature as to the exact nature of the oxidizing species [1]. As a process intended for water and wastewater treatment, the interaction between the Fenton reaction and the inorganic compounds present in natural waters, and the anions in particular, is of foremost importance. This work studies the effect of ClO₄⁻, NO₃⁻, Cl⁻, and SO₄²⁻ on the degradation of phenol in the presence of the Fenton reagent, starting from both Fe(II) + H₂O₂ and Fe(III) + H₂O₂. In the latter case, Fe(III) reduction to Fe(II) by H₂O₂/HO₂[•]/O₂^{•-} is required for the Fenton process to be operational. For this same reason, the Fenton reaction does not stop in the presence of Fe(II) + H₂O₂ after all Fe(II) has been oxidized to Fe(III), since the recycling of Fe(III) to Fe(II) is possible until H₂O₂ is available. No effect of the anions on the stoichiometry of the very fast first stage (Fe(II) + H₂O₂) of phenol degradation was observed, although sulfate is known to enhance the reaction rate between Fe(II) and H₂O₂ via formation of the sulfato complex [2]. On the contrary, a marked effect of the anions was observed on the slower second stage of the reaction (Fe(III) + H₂O₂), where phenol degradation rate follows the order ClO₄⁻ > NO₃⁻ > Cl⁻ > SO₄²⁻. This is most likely attributed to the different reaction rates of Fe(III) complexes with H₂O₂ [3,4].

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Poster No. 76:

DECOLORIZATION OF TEXTILE WASTEWATER BY UV-TREATMENT AND COAGULATION PROCESSES

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The aim of this work is to evaluate and compare the performance of ferrous compounds coagulations and UV treatment techniques. The optimum conditions and efficiency of the methods were determined, taking as an example four types of wastewater produced while dyeing wool. The effect of the type and dose of coagulant was investigated. Two types of iron (II) salt were used: sulphate (FeSO_4) and chloride (FeCl_2), to adjust the pH of the wastewater, a solution of calcium oxide (CaO) was used.

It was found that the tested dyeing wastewater revealed high susceptibility to treatment using an action of ferrous salts, but small susceptibility when UV used. These coagulations strongly influence the decolourisation and degradation. The increase of initial dye concentration decreases the removal rate. Four dyes were decolorised using these coagulation processes. The efficiency of decolorisation was measured by decolorisation time, dye exhaustion and concentration by colorimetric method. Additional application of hydrogen peroxide solution has a significant effect on the increase in efficiency of colored pollutant removal during coagulation in the presence of ferrous salts.

Poster No. 77:

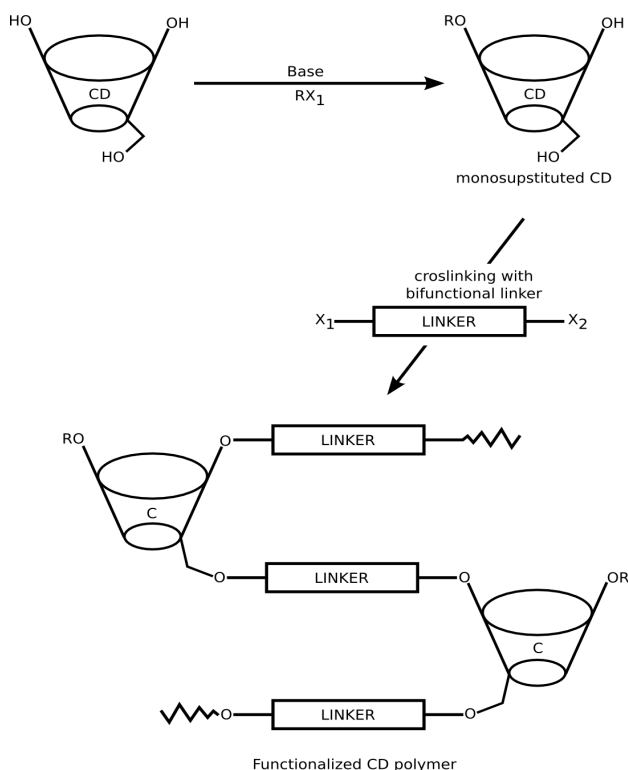
SYNTHESIS OF MONOFUNCTIONALIZED CYCLODEXTRIN POLYMERS FOR THE REMOVAL OF ORGANIC POLLUTANTS FROM WATER

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Cyclodextrins (CDs), basically starch derivatives, are biosynthetic cyclic oligomers consisting of anhydrous glucopyranosyl units linked together through α -1,4-glycosidic linkages [1]. They behave as molecular hosts capable of interacting with a range of guest molecules in a noncovalent manner within their cylindrical hydrophobic cavities [2]. These interactions are a basis for the inclusion of various organic species. However, the high solubility of cyclodextrins limits their application in the removal of organic pollutants from water. To make them insoluble, we have converted them into highly crosslinked polymers by polymerizing them with suitable difunctional linkers [3].

Under this project, several monosubstituted CD polymers or "nanosponges" (which are insoluble in water), with an enhanced ability to quench organic contaminants from water to acceptable levels, have been synthesized and successfully characterized. The process entails functionalizing the primary hydroxyls of the parent CD compound followed by crosslinking with a suitable linker to give the desired nanoporous polymer as shown in Scheme 1.



Scheme 1: A general synthetic pathway for a monofunctionalized CD polymer

The polymers obtained have demonstrated great capabilities in removing phenolic compounds from an aqueous medium. The degree of absorption was quantified and measured using UV-Visible Spectrophotometer and GC-MS analysis.

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Poster No. 78:

TOXICITY AND BIOSORPTION OF HEAVY METALS IN GREEN ALGA *Chlorella kessleri*

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Biosorption of heavy metals has attracted attention as a cost-effective means for the treatment of industrial wastewater. However, the mechanism of metal collection is not clearly understood and modeling of the biosorption performance is still raising debates. The objective of this study is to investigate toxicity and biosorption of heavy metals in the green alga *Chlorella kessleri* at various conditions. The algal cells were exposed to the growth medium containing Cr, Mn, Fe and Co in a form of either nitrate or chloride. After exposure to various metal concentrations at different pHs, absorbance at 730 nm was measured for the estimation of the growth rate. Metal content of the algal cells was analyzed using inductively coupled plasma (ICP-AES). The growth rate decreased with increasing Cr concentration and the order of pH 5.0 < 5.5 < 6.0 < 6.5 < 7.0 < 7.7. The 50% inhibitory concentration of Cr at pH 6.5 (IC₅₀ 730 µM) was especially different from that of pH 6.0 (IC₅₀ 170 µM). The accumulation of Cr could be described by two processes, an initial fast adsorption process, and a slower intracellular uptake process. These data clearly demonstrate that metal toxicity and sorption capacity of algal cells depend upon the combined factors of the metal concentration and pH condition.

Poster No. 79:

ARRHENIUS EQUATION FOR CHLOROFORM FORMATION DURING HUMIC ACID CHLORINATION: DEPENDENCE ON pH AND REACTION TIME

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Disinfection of water reduces microbial risk but can increase chemical risk associated to the ingestion of disinfection by products (DBP). Although more than 200 DBP have been detected in drinking water, nowadays, trihalomethanes (THMs) are the main DBP group. The extent at which chlorine reacts with natural organic matter (NOM) to form THMs depends on a variety of factors, such as bromide, residual chlorine level (RCL), reaction time, pH, etc. However, the nature and composition of NOM can also strongly influence reaction kinetics, and hence the overall THMs concentration.

Chloroform formation rate constants have been measured in the chlorination of aquatic humic acid solutions. First order reaction mechanism was assumed for chlorine and precursor content. Experiments were carried out under excess chlorine concentration. Resulting kinetic constant values varied significantly with reaction conditions, in the range of 0.271-5.932 [l·mmol⁻¹·h⁻¹]. The activation energy deduced from experiments carried out at different temperatures also increased notably when decreasing pH from 8 to 7. It is noteworthy the dependence observed on reaction time: higher activation energy values resulted for longest reaction periods. Preexponential factor showed similar trend where logK varied between 5.6-14.5. This effect is attributed to the existence of simultaneous reactions, each with different E_a , competing for THMs formation. The role of pH and reaction time on the effect that temperature poses on THMs formation rate should be taken into account at the time of selecting adequate disinfection conditions, especially in those regions where temperature changes from winter to summer are important.

Poster No. 80:

THE REMOVAL OF CYANIDE FROM WATER USING SYNTHETIC ACTIVATED CARBONS

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Cyanides and cyanide-containing compounds are used in numerous industry and manufacturing. The major point sources of cyanide release to water are discharges from gold mining plants, public wastewater treatment plants, iron, steel and organic chemical production. Carbon containing salts of copper, chromium and silver adsorbents are commonly used for wastewater cyanide elimination. However, this type of adsorbents has same disadvantages. Poor dispersion of impregnates in the deeper pore system, existence of large clusters of impregnants with low effective surfaces area, are some of them.

In the present work, two different types of synthetic activated carbons (SAC) doped with copper were synthesized by thermal decomposition method of macroreticular styrene/divinylbenzene sulfonic acid ion exchange resin (Amberlite 200). The influence of activated agents (water steam) as well as the active compound (copper) on CAS properties concerning cyanide removal from water was investigated. It was estimated that the equilibrium time of system CAS/cynide in water is 72 hours. The batch technique was used to define the elimination mechanism of alkaline cyanide elimination. The adsorption isotherms obey Freundlich equation. It was estimated that the capacity of cyanide adsorption is 2.06 mmol/g.

Poster No. 81:

INDUSTRIAL SCALE SOLUTION OF OIL CONCENTRATION REDUCTION FROM WASTE WATER

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There are a great number of potential environmental hazard sources of oiled waste water in industrial and thermal power generation plants, such as storage tanks for liquid fuels, lubrication oil and cooling oil storage, metal pollishing manufactory, as well as in oil refineries, oil transportation, processing, refilling and combustion. The aim of this work is to solve the environment pollution problems by reducing oil concentration in oiled waste water. Our research and further improvements in thermal power generation plant TE TO Zrenjanin showed that significant oil concentration reduction is possible by using following technological concept: collecting of oiled waste water from different sources to central storage pool, rough mechanical separation of oil, coagulation of oil residuals, mechanical separation of coagulant and finally filtration of waste water by means of oil residuals sorption.

This technological concept is applied in TE TO Zrenjanin by using unique sorbent for final filtration based on domestic materials. On the basis of industrial tests, obtained results showed that the waste water purified by this technological concept makes no harm to environment. Realized techno-economical analysis of this type of water purification unit confirm high profitability.

Poster No. 82:

ADSORPTION OF PESTICIDES ON FUNCTIONALIZED SYNTHETIC ZEOLITES

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The extent of pesticide contamination of the water environment has recently raised much concern because of the entry of these compounds into the food chain of humans and animals. A number of different methods for the removal of pesticides from waste water have been used including membrane technology, solid phase extraction, ozone and chemical oxidation, photocatalysis and adsorption on different solid substrates. Particularly, the adsorption techniques have been studied on various substrates such as soil and organic adsorbents, inorganic adsorbents, sediment fractions, silica gel, dissolved organic carbon organoclays and zeolites.

In this work, we have studied the effective behavior of synthetic zeolites (FAU and ZSM) functionalized by cationic surfactant (distearyl-dimethyl-ammonium chloride) for the removal of organophosphorus insecticides (malathion and fenitrothion), pyrethroid ester insecticides (delta-methrin) and herbicides (glyphosate) from water solutions. Comparison with natural zeolite (Clinoptilolite) functionalized by the same cationic surfactant has been made. The batchwise adsorption method was applied to obtain the adsorption isotherms. When equilibrium is attained, the mixtures, containing fixed amounts of zeolites and aqueous solution with varying amounts of pesticides, were measured by GC-MS chromatograph after separation of the supernatant. Obtained results have shown that the adsorption efficiency of pesticides depends on the zeolite type and hydrophobicity of these molecules.

In addition, the optimized structures of the pesticide molecules have been obtained at B3LYP/6-31+G (d, p) level of theory. The calculated values of molecular sizes and dipole moments are relevant for achieving better understanding of the adsorption mechanism.

Poster No. 83:

EXAMINATION OF THE ACTIVATED CARBON ANTIMICROBAL ACTIVITY

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Unsafe water has become a world problem, since even sources of drinking water, including municipal water systems, wells, lakes, rivers, and even glaciers, contain some level of contamination. A good water filter is maybe the best solution to ensure a safe drinking water. Activated carbon is most commonly used in water purification treatment as the adsorbent for the removal of inorganic and organic pollutants. However, activated carbon can not remove contamination by microorganisms. Silver in various forms has been used to inhibit the growth of microorganisms. Therefore, it is assumed that activated carbon supporting silver has antimicrobial effects.

The aim of this work was preparation of the activated carbon material with silver coating and examination of their antimicrobial behavior. Silver was spontaneously deposited at the surface of activated carbon emerged into AgNO₃ solution. Metal deposition was studied by atomic absorption spectrometry (AAS). Surface morphology of obtained material was characterized using scanning electron microscopy (SEM), and structural changes in the carbon material were determined by X-ray diffraction.

Activity of activated carbon material against bacteria, *E. coli* ATCC 25922 and *S. aureus* ATCC 25923, together with fungi, *C. albicans*, was determined using standard microbiological methods. It was found that AC/Ag inhibited *E. coli*, as well as *S. aureus* growth, with no outcome on *C. albicans*.

Poster No. 84:

THE USE OF ADVANCED OXIDATION PROCESSES AS A CONTRIBUTION TO THE DETOXIFICATION OF WATER

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During the past three decades, many different technologies used for prevention and control of pollution as well as degradation of pollutants already present in the environment, unfortunately proved more and more damaging effects on living and unliving creature. Methods based on photolysis and chemical catalysis have been included in a group of new technologies denominated Advanced Oxidation Processes (AOP), that are useful and attractive alternative for detoxification contaminated wastewaters, groundwaters and watercourse, as well as for the purification and disinfection of drinking water containing hardly biodegradable and toxic organic substances.

The subject of this research contributes to the study and development of a new environmental in everyone respect acceptable and sustainable physico-chemical, energy efficient and cost effective technique and technology for the detoxification of biorecalcitrant, non-biodegradable and toxic organic pollutants present in the aqueous medium. In this study we investigated the effects of several parts of spectrum of concentrated solar radiation simulated with different artificial lights in laboratory measurements on degradation of methyl-tertiary-butyl-ether (MTBE), in the both reactors: slurry catalyst reactor and supported catalyst reactor. The photocatalytic degradation was achieved with diferent concentrations of titanium catalysts (conventional and sol-gel obtained titanium) and hydrogen peroxide in water suspension. The results of MTBE degradation in these reactors are analyzed and their efficiencies compared. The degradation process was completed producing carbon dioxide and water, as well as some other compounds, but of non-toxic nature. Our research and theoretical conclusions could be a powerful model system for testing the degradation of other toxic organic chemicals collected from the real polluted areas.

Poster No. 85:

DEPOLLUTION OF PHENOL AND 4-CHLOROPHENOL CONTAMINATED WATER BY AN ACTIVATED CARBON PREPARED FROM OLIVE STONES

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Rising production costs and increasing needs for efficient adsorbents have directed research towards the valorisation of natural wastes to remove pollutants and contaminants. The removal of polluting organic compounds from liquid wastes is becoming very important throughout the world. The improvement of organics uptake may be achieved through chemical activation with phosphoric acid. This work deals with phenol and 4-chlorophenol removal from aqueous solutions by chemically activated olive stones. Activation was achieved by soaking the olive wastes in 50% phosphoric acid for three hours at 170°C. After washing, the product was activated under inert atmosphere for three hours at 750°C. Phenol and chlorophenol uptake by the activated carbon prepared this way was found to be largely influenced by the solution pH. Adsorption capacity for both pollutants was determined by fitting the Langmuir model to the adsorption isotherms. A maximum adsorption capacity of 212 mg/g was obtained for phenol whereas for chlorophenol this was 416 mg/g. Comparatively, the results for the commercial powdered activated carbon (Merck) were lower with 151 mg/g for phenol and 256 mg/g for chlorophenol. These results show that the activated carbon prepared from olive stones may prove to be very useful to remove and clean toxic substances from wastewaters.

Poster No. 86:

TREATMENT OF THE FECAL WASTEWATER ON THE PLANT IN PODGORICA

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One of three most important municipal problems in Podgorica is the plant for the treatment of fecal wastewater and their release in the recipient the river Morača.

The objective of this was to realize the complete treatment of the wastewater feces by their ingression into the plant till their release of the Public Company "Water supply and Wastewater" will serve to define advantages and disadvantages of the plant operating and they will point out its present deficiency. This paper represents influence of released wastewater from the plant into recipient from bacteriological as well as chemical aspect of pollution.

This research is very interesting because the plant has been constructed in 1978 for the capacity of 55000 of population equivalent.

The inventory from 2003 showed that Podgorica has 169000 of citizens and it is three times more than projected.

It is expected to increase the content of phosphate after the wastewater ingression from the public collector. It will have a bad influence on the quality of the river Morača during the low water level because it enables growth of sea-plants.

The content of ammonia, BPK₅ and the total number of coliform bacteria in the water of the river Morača under the public collector has influence on classification of the water into the quality which is lower than average of A₁ or A₂.

Poster No. 87:

STUDY OF REMOVAL OF PHENOL AND NICOTINE FROM WASTE WATERS BY THE USE OF VARIOUS SOLID ADSORBENTS

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Waste waters containing high amounts of organic pollutant materials, which are persistent and bio accumulative, are often produced in many different industries. Due to environmental considerations and legislative procedures, there is a need for their elimination. Therefore, appropriate procedures for the abatement of pollutants in waste waters have to be established. Among others, adsorption has been recognized as one of the possible methods for removal of organic pollutants from waste waters.

In this work, we investigated the adsorption possibilities of many different solid materials known as good adsorbents or catalysts towards two very common and important pollutants which, being soluble in water, are known to come easily in water streams: phenol and nicotine. The adsorptions of both pollutants on zeolites (FAU, MOR and ZSM-5 type; modified with transition metal cations or cationic surfactants), clays (bentonite and montmorillonite), layered silicates (magadiite, kenyaite), mesoporous materials (MCM-41), boron nitrides and activated carbons have been investigated. The adsorption isotherms were collected using microcalorimetry (Titrys, from Setaram); the amounts of adsorbed pollutants were determined applying UV-VIS spectrophotometer, coupled through optic fiber with a microcalorimeter.

From all the results found in this investigation, we can infer that hydrophobic materials, such as β -zeolite, boron nitrides or carbons can be good adsorbents for phenol or nicotine aqueous solutions. These results indicate the possibility of the usage of previously mentioned materials in the wastewater treatments allowing their reuse. Importantly, the possibility of regeneration of these particular materials was also tested.

Poster No. 88:

DETERMINATION OF THE ADSORPTIVE PROPERTIES OF ACTIVATED CARBON AND ITS PVA COMPOSITE

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Existence of heavy metal ions, such as As, in potable and waste waters in concentrations exceeding the tolerance limits is a potential threat to environment and human health. Adsorption is a favourable method of lowering the concentrations below the maximum permissible levels. One of the most preferred and advantageous adsorbent used for removal of heavy metals is activated carbon mainly due to its high surface area and well developed porosity. Besides, the distribution and variety of heteroatoms and functional groups in its structure makes activated carbon a good scavenger for metal ions.

In this study, activated carbon was utilised in arsenic removal from wastewaters by adsorption. Operation conditions, namely pH, adsorbent dosage, contact time and temperature, for attaining efficacious removal have been determined for arsenite and arsenate. Kinetic and thermodynamic analysis were run at these conditions. Adsorption was characterized by Langmuir and Freundlich isotherms. Optimal conditions were determined using synthetic solutions involving only arsenic species. At these conditions, removal was tested using an effluent taken from a galvanization facility, involving other metals such as copper and nickel besides arsenic.

Activated carbon was modified chemically by the production of carbon-polymer composites. The composite was prepared by sedimentation polymerization using polyvinylalcohol crosslinked with glutaraldehyde. With the modified adsorbent, the extent of removal was substantially improved both from synthetic and real media. The adsorptive capacity of modified activated carbon was calculated to be 14% and 3.5% higher in the case of arsenate and arsenite adsorption, respectively.

Poster No. 89:

MACROPOROUS FUNCTIONAL POLYMERS FOR THE COPPER REMOVAL FROM WASTE WATERS

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Functional polymers are very attractive as the selective sorbents for heavy metal ions removal and/or recovery from waste-water streams of hydro-metallurgical and other industries. They consist of crosslinked copolymer as a solid support and functional group (ligand) containing O, N, S and P donor atoms capable for coordinating of different metal ions. During the relatively simple process, functional polymer is contacted with the contaminated solution, loaded with metal ions, and stripped with appropriate eluent. Some of the advantages are simplicity of the process which is in many cases reduced only to filtration as the regeneration step, and the ability of the polymer to be recovered after the reaction, regenerated and reused, which reduces costs.

In this study we compare the using of two types of functional macroporous copolymers for the selective copper removal from waste waters. The first one is based on poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate), additionally functionalized via ring-opening reaction of the pendant epoxy groups with ethylene diamine and diethylene triamine. The second one, poly(4-vinylpyridine-*co*-glycidyl methacrylate), was prepared by copolymerization of functional macroporous monomers which already carry the required functional group. The influence of pH, the type of ligand and porosity parameters of functional macroporous copolymers on the copper was discussed. The rapid sorption rates, high selectivity for copper, the possibility of regeneration and reusing in several sorption/desorption cycles, as well as high capacities of both types of functional macroporous copolymers make them very advantageous for the copper removal from waste-water streams.

Poster No. 90:

INFLUENCE OF VARIOUS NUTRIENT MEDIUM ON CELLULASE PRODUCTION IN CMC DEGRADING FUNGI

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Cellulase production has attracted a world-wide attention due to the possibility of using this enzyme complex for conversion of abundantly available renewable lignocellulosic biomass for production or degradation of carbohydrates polymers. Different fungi and bacteria have used for production of cellulases using different substrates.

Carboxymethyl cellulose (CMC) occurs as regulary present pollutant in the waste water of printing industry. CMC is commercial product, solubility of whichin water or organic solvent is dependent upon the degree of substitution of the methyl- or methylenecarboxy for the number of protons in the hydroxyl groups.

Large number of microorganisms, especially fungi, are capable of decomposing CMC polymer through the action of their hydrolases on β -glycoside bonds inside the polymer. There are numerous ways for this versatile product to end up in the waste water of print works, since for a number of good features CMC is widely used for paper conservation. It is also included in water-based paints, detergents and a variety of paper products to name byt a few.

Monosporic cultures of fungi *Fusarium oxysporum* (Schlecht) and *Trichoderma harzianum* (Riffai) were isolated from the waste water of the "Tetrapak" print works after stagnating in basins for about 90 days.

Fungi *Aspergillus niger* (Van Tieghem) and *Alternaria alternata* (Keissler) were obtained from the mycological collection of the Science Faculty of the University of Kragujevac.

Previously we examined total cellulases activity of *Fusarium oxysporum*, *Trichoderma harzianum*, *Aspergillus niger* and *Alternaria alternata* following the amount of reducing sugar formed from carboxymethyl cellulose. Reaction were conducted for 60 min at 50°C. One unit of total cellulase activity correspond to the amount of reducing sugar produced in one minute.

The ability of the fungi to utilize glucose, saccharose and proteins as sole carbon source was examined in Czapek and protein medium containing 2% CMC.

A screening of potential cellulase inducers showed that when *A. alternata* and *T. harzianum* were cultured on media containing proteins have more enzyme activity and produced about 0.35-0.43 mg/mL reducing sugar. Contrary, fungi *F. oxysporum* and *A. niger* produced more active cellulase when grown in mineral Czapek nutrient medium (0.51-0.70 mg/mL reducing sugar).

Poster No. 91:

TESTING OF GROUND WATERS IN THE VICINITY OF THE PANČEVO INDUSTRIAL ZONE

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The town of Pančevo is located next to the industrial zone where Pančevo Refinery and Petrochemical complex are located. The by-products of the above industry are many harmful substances which through soil reach ground waters.

In order to monitor the impact of industry on the quality of ground waters, a monitoring system was established at four locations, 2 in the vicinity of Pančevo Refinery, and two in the vicinity of the Petrochemical complex. At each location there is a set of piezometers at the depths of: 45 m, 25 m, 15 m and 7 m. The depths were determined according to plan, since the water at the depths of 7 m and 15 m is used for agricultural purposes, while the water at 25 m and 45 m is the stock. The sampling was performed in October 2004 and January and April 2005. The samples of all three cycles were tested for 26 parameters: electrical conductivity, nitrates, ammonia, heavy metals, mineral oils and organic substances characteristic for the above industry. Standard analytical methods EPA and ASTM were used, and following analytical techniques: spectrophotometry, flame and electrothermal atomic absorption spectrophotometry, spectrophotometry, ion chromatography, gas and liquid chromatography.

The results of the performed tests indicate that in the majority of samples electrical conductivity exceeds the acceptable value for ground waters (1600 μ S). The most contaminated location, both in terms of the number of pollutants and in terms of concentrations, is the location No. 3. At this site, the concentration of chlorides, mineral oils, arsenic, zinc, nickel, cadmium and 1,2-dichlor-ethane increases with depth, whereas at all the sites the concentrations of benzo(a)pyren, toluen, xilene, ethilbenzene and PCBs were below the detection level.

Poster No. 92:

CARBONATE RADICAL REACTIVITY IN AQUEOUS SOLUTION

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The involvement of hydroxyl radical, a very powerful oxidant is often mentioned for the degradation of organics. However, hydroxyl radical efficiency may be affected by water constituents. Among them, hydrogenocarbonate ions scavenge hydroxyl radicals, leading to an inhibition of pollutant degradation. The reaction of hydroxyl radicals with hydrogenocarbonate/carbonate ions leads to the formation of the carbonate radical, $\text{CO}_3^{\cdot-}$, the reactivity of which is only partly understood.

In our study, carbonate radical is generated by the photolysis of a carbonatoammine complex of cobalt (III). In order to characterise the reactivity of carbonate radical, model pollutants (phenol, atrazine...) were chosen.

The first investigated system is $\text{CO}_3^{\cdot-}$ /phenol. Under continuous irradiation, phenol is transformed in benzoquinone and dihydroxybenzene by carbonate radicals. Benzoquinone is the major by-product formed in the early stages of the reaction. The second order rate constant of reaction between phenol and carbonate radical was determined equal to $3.0 \cdot 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$.

The results arising from reaction between $\text{CO}_3^{\cdot-}$ and phenol allow the use of phenol as a competitor in further experiments with other organic pollutants. The reaction of $\text{CO}_3^{\cdot-}$ with carbendazim and atrazine, two pesticides, was then investigated. The second order rate constants obtained by competitive kinetics with phenol are evaluated to be equal to $9.5 \cdot 10^6$ and $1.4 \cdot 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$, respectively.

Numerous by-products, evidenced by LC-MS, are stemmed from the reaction between atrazine and carbonate radical. The structures will be presented and compared to those observed in atrazine degradation promoted by hydroxyl radicals.

Poster No. 93:

COPING WITH MILITARY PAST POLLUTION IN ESTONIA

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The pollution caused by Soviet troops during five decades in Baltic States still remains. The leaving army left behind a large amount of different waste and polluted ground. There were 1565 military objects in Estonia with the total area approximately 2 per cent of Estonian territory. In several military missile bases the soil was polluted with rocket fuel with subsequent high concentrations of carcinogenic compounds in groundwater in the areas. Whilst the rocket fuel polluted soil has been treated with different bioremediation methods the groundwater remains polluted. There is a high risk for exposure of the groundwater to the drinking water wells, with resultant impacts on human health. To treat such groundwater, many authors have developed purification processes for rocket fuel contaminated water. These include advanced oxidation processes with UV photolysis, UV/hydrogen peroxide, photo-Fenton's reaction, and dark Fenton's reaction. The authors of this work report a successful treatment of groundwater contaminated with residual rocket fuel by ozonation and catalytic wet oxidation. Both chemical processes are feasible and could be used as a pre-treatment unit before biological treatment. The study also compares the treatment of rocket fuel-polluted water with different physical-chemical processes.

Poster No. 94:

THE INFLUENCE OF IRON IONS ON THE EFFICIENCY OF AQUEOUS PHOTOCATALYTIC OXIDATION OF ORGANIC POLLUTANTS

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An experimental research into aqueous photocatalytic oxidation (PCO) of different organic groundwater pollutants was undertaken. The complex influence of iron ions on the efficiency of aqueous PCO of 2-ethoxyethanol (2-EE), methyl *tert*-butyl ether (MTBE) and humic substances (HS) was established: a drastic PCO efficiency increase for 2-EE and MTBE at lower concentrations of iron ions (up to 0.09 mM and 1 mM respectively) changed to its sharp decrease, whereas in case of MTBE a smaller increase of the efficiency was observed at even higher iron ion concentrations (10 mM and higher). For HS, only inhibitive effect of iron ions on the PCO efficiency was noticed. The authors proposed that the explanation for the observed phenomena is based on different sensitivity of pollutants towards radical-initiated oxidation reactions and the competitive adsorption of metallic ions and the pollutants on TiO₂ surface.

Photocatalytic oxidation of 2-EE proceeds via surface reactions with positively charged holes, as determined reaction by-products suggest, thus smaller amounts of iron ions enhance PCO performance, obstructing electron-hole recombination, whereas higher concentrations of iron ions diminish absorption of 2-EE and thus the PCO efficiency. Molecules of radical-scavenging HS chelate iron ions, what obstructs their adsorption on TiO₂ surface. Methyl *tert*-butyl ether is oxidised by both radicals and holes. The increase in PCO efficiency of MTBE at higher iron ion concentrations can be explained by development of a different oxidation mechanism, where radical species are formed by UV-irradiated iron ions.

Poster No. 95:

DEFINITION OF TOXICITY OF SAMPLES OBTAINED BY NEUTRALIZATION METHOD FROM METALLURGICAL WASTE WATER

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This paper presents the results of chemical analysis of samples obtained by neutralization method of metallurgical waste water from Copper Refinery Plant. Neutralization is carried out by 1M solution $\text{Ca}(\text{OH})_2$, with or without coagulants (FeCl_3 and AlCl_3).

In the aim of determination toxicity of obtained materials is done toxic characteristic leaching procedure (TCLP) of each sample.

Atomic absorption spectrophotometry method is used for analysis of leachates obtained by used TCLP test. This method is used for determination of copper, nickel, lead, iron and zinc content.

Results of TCLP standard test show that the samples obtained by neutralization with $\text{Ca}(\text{OH})_2$, with or without coagulants, are toxic.

Extraction degree of all elements is high, especially for nickel (99.77%).

Poster No. 96:

DETERMINATION OF ARSENIC, ANTIMONY AND BISMUTH IN SLUDGE ACHIEVED FROM METALLURGICAL WASTE WATER BY ICP-AES

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This work represents the simple procedure for rapid, accurate and precise determination of arsenic, antimony and bismuth in sludge achieved from metallurgical waste water by ICP-AES.

Those elements are chosen for the analysis in order to determine the toxicity of initial sludge samples.

Extraction degree of bismuth is high and almost the same in all samples (about 50%). The situation with antimony is almost the same, the only exception is that extraction degree is lower (about 15%). The obtained results for arsenic show the highest value in sample without coagulants (about 65%). In sample obtained with added coagulants the value of extraction degree for arsenic is lower (minimum 15%).

Poster No. 97:

USE OF NEW OZONE GENERATOR FOR TREATMENT OF WATER WITH HIGH CONCENTRATIONS OF PHENOLS

D. Manojlović¹, D. R. Ostojić^{1,2}, B. M. Obradović^{2,3}, M. M. Kuraica^{2,3}, V. D. Krsmanović¹ & J. Purić^{2,3}

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New type of ozone generator based on coaxial dielectric-barrier-discharge was used for treatment of water with high content of phenols. High efficiency of this ozonizer is the consequence that ozone is produced by direct discharge in thin layers of treated water. There is no need for dissolving of ozone in water in bubble column reactor or for the additional equipment for destruction of the excess of ozone. Furthermore, enhanced efficiency is the result of the exposition of treated water to direct UV radiation which is the consequence of electric discharge. Construction of the ozonizer enables recirculation of treated water which also contributes to the efficiency.

The capability of new ozonizer in removal of various phenols was tested with several samples. They were prepared by dissolving of analytical grade phenol, 4-chlorophenol and 2,4-dichlorophenol in bidistilled water or water from river Danube. In all cases 5 liters of water containing 6.00 mg/L of phenol were passed once through the ozonizer. After five minutes up to 93.3% of phenol was degraded in samples with bidistilled water, while the results for Danube were up to 80.0%. After two hours the percent of removed phenol increased to 98.9% and 89.0%, respectively. Efficiency of the phenol removal could be increased by recirculation of water through the ozonizer.

Poster No. 98:

REMOVAL OF ARSENIC FROM DRINKING WATER BY DIRECT OZONIZATION AND FILTRATION

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Underground waters which are used for water supply in Vojvodina contain high concentrations of arsenic. Due to the high toxicity of arsenic it is necessary to remove it from raw water before distribution. For the testing of the technology for arsenic removal the water from the well in Sirig, (Municipality Temerin, Serbia and Montenegro) was used. The content of total arsenic varied from 50 to 250 µg/L. The content of As(V) and As(III) was determined by differential pulse voltametry using rotating golden electrode with the instrument Metrohm 797 VA Computrace.

Several procedures for removal of arsenic were applied. The best results were obtained with combined procedure using the new type of ozone generator based on coaxial dielectric-barrier-discharge. Then the water was treated with iron(III)-chloride, filtered through quartz sand and finally with "Manganese Greensand" modified by sorption of 0.01% of circonium-oxychloride. High efficiency of this combined treatment was confirmed by low content of arsenic in the filtrate (bellow 0.5 µg/L).

Poster No. 99:

NEW METHOD OF CATALYTIC REMOVAL OF ORGANIC ACIDS (ACETIC AND FORMIC) BY MICRO ALLOYED ALUMINIUM BASED COMPOSITE

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Water is indispensable for vital biochemical processes in every organism. Besides that, it has a great significance in industries and everyday life. Number of unpolluted high-quality water sources is less than ever. The main sources of water pollution are: household wastewaters, wastewaters of cities, industrial (galvanization, cellulose, paper industry, pharmaceutical etc.) and agricultural ones. Numerous treatments exist for refining of wastewaters, such as: physical, physical-chemical, chemical and biochemical ones. A goal of some scientific studies is an invention of optimal combination of treatments for all wastewaters types.

In this paper we will discuss the results of our studies of catalytic removal of acetic and formic acids from simulated wastewaters (model watery solutions of HCOOH and CH_3COOH ; working volume 1 dm^3 , concentration $1 \text{ cm}^3/1 \text{ dm}^3$, time of catalytic treatment was 240 min) by a composite material based on steel and micro alloyed aluminium. By this catalytic treatment, organic acids were reduced to less toxic products, which elimination was easier, during relatively short time. The concentrations of alcohols were determined by GC and colorimetry. The obtained results show that alcohols concentrations were decreased below MAC values (CH_3OH , $c=0.0009 \text{ mg/cm}^3$; $\text{C}_2\text{H}_5\text{OH}$, $c=0.0006 \text{ mg/cm}^3$). Used composite wire can be applied for removal of numerous ionic and colloidal impurities. Further investigations and wastewaters refining may be improved by preparation of a new composite wire with enough spread active surfaces and using of flowing catalytic reactors that will enable more intensive removal of inorganic and organic compounds for a shorter treatment time.

8. Biodegradation of toxic compounds

Posters No. 100-105
Thursday, December 8th
17:21-18:21

Poster No. 100:

BIOAVAILABILITY OF SOIL-BOUND PAHs INGESTED BY DAIRY COWS

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The excretion of PAH in milk and faeces by dairy cows was studied following a chronic supply of soil contaminated by fluorine, phenanthrene, pyrene and benzo[a]pyrene. These compounds were measured in their parental form in milk and faeces using GC-MS. This technique was also used to determine their possible absorption and metabolism into their principal monohydroxylated metabolites in milk.

No significant differences of excreted PAHs were observed in milk when they were supplied via the soil. However, an significant appearance of metabolites in milk (up to 1.6% of the ingested dose) suggested the biotransformation of these compounds after extraction from the soil. In faeces, less than 4% of the daily supplied PAHs were recovered, thus confirming their previous extraction during digestive transfer. The risk of human exposure to parental PAHs in milk is therefore negligible, as is their transfer from contaminated soil into milk. However, the appearance of metabolites in milk raises questions concerning their toxicity.

Poster No. 101:

ABSORPTION AND BIOTRANSFORMATION OF PYRENE, PHENANTHRENE AND BENZOAPYRENE IN THE DAIRY GOAT

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Polycyclic Aromatic Hydrocarbons (PAHs) are widely distributed pollutants. Dairy ruminant take in these pollutants through forage and soil ingestion. Assessment of their transfer from feed to foodstuffs still remains a crucial question for food safety. The aim of this study was to identify and understand parameters to explain the PAHs transfer from feed to milk. Four goats received three PAHs (B[a]Pyrene, Phenanthrene and Pyrene) via an oral dose (100 mg of each PAH). Kinetics of these three PAHs and their principle monohydroxylated metabolite (3-OH-B[a]P, 3-OH-Phe and 1-OH-Pyr) were studied in blood, urine and milk.

B[a]P concentration in blood was significantly lower than Phe and Pyr concentration. In milk, concentration values were under the detection limit for both B[a]P and 3-OH-B[a]P. The weak appearance of 3-OH-B[a]P in blood and urine proved a very low absorption of this compound, which may interact with enterocytes. Phe and Pyr were absorbed to a higher extend but their biotransformation resulted in a reduced transfer of parent compound to milk. Hydroxylated metabolite were found as the major compounds in milk with values reaching 50 and 100 ng/mL for 3-OH-Phe and 1-OH-Pyr respectively.

Poster No. 102:

DEGRADATION OF PETROLEUM POLLUTANT BY SURFACE WATER MICROORGANISMS *Phormidium foveolarum* AND *Achanthes minutissima*

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The aim of these investigations was to show to what extent the hydrocarbons of a petroleum pollutant are degraded by *Phormidium foveolarum* and *Achanthes minutissima*, microbial cultures which were isolated as dominant microorganisms from a surface water of wastewater canal of an oil refinery and nitrogen plant (Pančevo, Serbia). Experiments of simulation of biodegradation were conducted on one paraffinic (Sir), and one naphthenic type petroleum (Ve) during a three month period under aerobic conditions in an organic (Bh) or an inorganic medium (Kp) and in the light or in the dark. In the chloroform extracts the content of fractions of saturated hydrocarbons, aromatics, alcohols and fatty acids was determined. *n*-Alkanes and isoprenoid aliphatic alkanes, pristane and phytane were analyzed using gas chromatography (GC). Isoprenoid aliphatic alkanes as well as steranes and triterpanes were analysed by GC-MS. The most intensive degradation of *n*-alkanes and isoprenoid aliphatic alkanes (in paraffinic oil) and isoprenoids (in naphthenic oil) was observed using the medium Kp in the light; the microbial conversion is somewhat lower with Kp in the dark; with medium Bh in the light the degradation is of low intensity; with the same medium in the dark the degradation is hardly obvious. Steranes and triterpanes were not affected by microbial degradation. Obviously, the petroleum biodegradation was restricted to the acyclic aliphatics. Performed experiments may as well serve as an indication for the prediction of petroleum type pollutant fate, as well as for definition of conditions for bioremediation of some environmental segments.

Poster No. 103:

BIOREMEDIATION OF REFINERY SLUDGE BY MICROBIAL POPULATION

**B. Lalević¹, V. Raičević¹, D. Dabić², Lj. Jovanović³, M. Nikšić¹, S. Antić-Mladenović¹,
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The petrochemical industry generates a series of liquide and solid effluents during the petroleum-refining process. These effluents must be treted through depuration processes. The sludges that result from this depuration process have a high content of petroleum derived hydrocarbons, mainly alkanes and paraffin of 1-40 carbon atoms, along with cycloalkanes and aromatic compounds, thus it is a potentially dangerous waste product. High level of organic C have been found (17.45%), that originate mostly from the oil. Analysis of the heavy metal content of the semisolid refinery slude indicated that total content of Pb, Ni and Cr are above permitted concentrations for unpolluted soils (301 mg/kg, 314 mg/kg and 312 mg/kg, respectively), but concentration of their available forms are very low (< 1 mg/kg).

Biodegradation of natural microbial populations represent one of the primary mechanisms by which petroleum and other hydrocarbon pollutants can be eliminated from the environment. Total number of bacteria in the sludge was estimated as $86.8 \cdot 10^6 \text{ g}^{-1}$ and fungi as $17.84 \cdot 10^3 \text{ g}^{-1}$. Bacterial and fungal population, isolated from this sludge, was aplicated in the bioremediation process. These are, in the first place, different species of bacteria that use the organic compounds as their source of food, and due to their diversity, numerousness and activity they are exceptionally efficient detoxifiers of these compounds. Thanks to such a rich structure of microflora, the secondary products of degradation are further degraded by other present species of microorganisms all the way to the final non-toxic products.

Effectiveness was followed by measuring of biological and biochemical parameters in the sludge.

Poster No. 104:

FUNGAL GROWTH IN WATER OF A PRINTWORKS

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Analysis of waste water of the "Tetrapak" printworks in the town Gornji Milanovac (Serbia) indicates the presence of three components: carboxymethylcellulose, vinyl acetate and a pigment of the phthalocyanin type. The surface of the water was covered with a green-colored layer of mycelium, several millimetres thick. Two fungi were isolated and classified from this material, namely *Fusarium oxysporum* (Schlecht) and *Trichoderma harzianum* (Rifai). The analysed water sample was 90 days old and come from open basins where it was stored for sedimentation of dispersed particles.

The fungi *Aspergillus niger* (Van Tieghem) and *A. alternata* (Fe. Keissler) were derived from material in the mycological collection of the Faculty of Science in Kragujevac. The fungi *A. niger* and *A. alternata* were isolated from different grades of paper, according to scientific references (Das et al. 1997, Kramer et al. 2004.).

The initial aim of the research was to test adaptability of the fungi raised on modified nutrient base containing 2% of CMC as a source of organic carbon. Bioproduction of the fungi and total cellulase activity were measured as relevant parameters for that purpose. The fungi were grown paralelly on standard Czapek's mineral nutrient base and modified Czapek's base with the addition of 2% CMC. The samples were developed for 25 days at room temperature of 20°C under alternating day-night light conditions, with 2 hours of aeration a day. The measurements of biomass and enzyme activity were performed every 3-5 days, starting with the inoculation date. bioproduction of the fungi was determined by measuring the mass of filtered and dried mycelium. Total cellulase activity was expressed through the reducing carbohydrates level per time unit at 37°C (Bergmeyer, 1983).

Biomass value range for the fungi raised on modified medium is between 0.12 and 0.76 g, meaning 30-50% decrease in biomass comparing to control cultures which used sucrose as carbon source. Advance in the fungi growth is much more visiable after the initial 10 days of the test period, assumably corresponding to more efficient utilization of CMC. Most intense utilisation of CMC as carbon source takes place during 25-30 days of test period.

Results for the 21st day of the test period indicate following values of reducing sugars concentration of the fungi: *Fusarium oxysporum* -0.64 mg/ml; *Trichoderma harzianum* -0.74 mg/ml; *Aspergillus niger* -0.74 mg/ml and *Alternaria alternata* -0.78 mg/ml.

These preliminary results for CMC degradation by fungi makes solid bases for further research defining optimal conditions for most efficient biotransformation of this pollutant.

Poster No. 105:

USE OF THERMOPHILIC BACTERIA TO BIODEGRADATION OF MODIFIED POLYURETHANE FOAMS

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Microorganisms are involved in the degradation of both synthetic and natural polymers. Under condition of nutrient limitation, these materials can be depolymerised and utilized as energy source. Degradability of polymeric materials is generally a function of the structure, the presence of microbial population and the environment. In this work, several types of polyurethane modified by polysaccharide component (e.g. acetyl-, hydroxyethyl- and carboxymethyl cellulose, activated starch) were prepared. Mixed culture of *Thermophilus* sp. was used to biodegradation of modified materials. Bacteria were cultivated for 4 weeks in shaking flasks at 60°C, pH 5 and 110 rpm in presence of polyurethane sample (1 g). In regular intervals biomass and chemical oxygen demand were determined and surface microscopy of polyurethane was tested. After cultivation, polyurethane degradation degree corresponded with growth of bacterial culture. The highest degree of degradation was found in polyurethane modified by 10% activated starch; about 4x lower biomass was observed in this sample, when compared with control cultivation. High degree of biodegradation exhibited also polyurethane modified by 10% hydroxyethyl cellulose. As the most stable structure was found polyurethane foam modified by 10% acetyl cellulose; minimal growth changes and degradation degree were observed in this sample. In conclusion, mixed *Thermophilus* cultures can be used to biodegradation of modified polyurethane; degree of degradation is strongly dependent on type of modification agents. Further experiments are needed for complex study of interactions between the microflora and deterioration of polymeric materials.

Acknowledgement: This work was supported by project MSM 0021630501 of Czech Ministry of Education.

13. Analytical methods for environmental science

Poster No. 106
Thursday, December 8th
17:21-18:21

Poster No. 106:

GAS SENSOR FOR VOLATILE ORGANIC COMPOUNDS USING NANOCHANNEL SILICA THIN FILMS COATED ON QUARTZ CRYSTAL MICROBALANCE

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Volatile organic compound (VOC) gases are significant concern as regards environmental health due to their toxicity and mutagenetic properties, even at ppb concentrations. The guideline value for the indoor upper concentration of VOC in Japan is ranging from 1~10 ppb. To the best of my knowledge, there are no sensing devices that can continuously monitor such a low concentration of VOC in air. In order to achieve real time monitoring of ~10 ppb of VOC, we have developed novel gas sensor based on nanochannel silica thin films (NTFs) coated on quartz crystal microbalance (QCM) device. The QCM device has been widely used to measure mass loadings in the nanogram region. The NTFs have greatly expanded the possibilities for the design of open pore structures, because of large surface area, well defined pore size and pore shape. In this study, the sensitivities of the NTFs coated on QCM device to toluene gas are examined. A preliminary result has been given that calcination process of the NTFs is crucial for the sensitivity to toluene. The removal of surfactant-templates in the NTFs by calcination drastically improves the sensitivity higher than two orders. The influence of preparation methods for the NTFs to the sensitivities will be discussed.

9. Industrial clean technologies

Posters No. 107-114a
Friday, December 9th
17:00-18:00

Poster No. 107:

CLEAN TECHNOLOGY FOR HIDE PROCESSING

C. Gaidau¹, L. Albu¹, V. Brătulescu¹, L. Miu¹, M. Giurginca² & A. Meghea²

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Hide processing is a highly polluting process because of the large water consumption, polluting chemicals (sodium chloride, lime, surfactants) being used, and release of a significant amount of organic matters in the early processing stages, like as: soluble proteins, keratin, and fats.

Hide liming is a key process for the finished leather quality and is aimed to remove hair, inter-fiber matters like as glycoprotein, and fats, as well as to give rise to reactive groups within the collagen structure, able to interact with the tanning materials.

The paper presents some alternative liming processes by taking into account the quality-environment impact balance. The comparative level of water pollution in the case of conventional processes and new liming process with hair-saving facility has been studied in different industrial conditions.

Because of the high complexity of the liming effluents the development of new methods for assessing the environment impact of various hide liming processes has been required.

To this end, the chemiluminescence method is a new method applied in assessing the anti-oxidizing effect of the hide liming effluents, thus providing aggregate information on the environment impact of various hide liming processes.

Poster No. 108:

PHOTOCATALYSED EPOXYDATION OF CYCLOOCTENE BY TBHP OR O₂, USING TiO₂ OR Ti-SBA15 CATALYSTS

L. Truong Phuoc, B. Jarry, J. Ph. Nogier & J. L. Bonardet

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Mesoporous structured Ti-SBA15 solids showed strong activity and high selectivity in epoxydation of alkenes by tertibutyl hydroperoxyde. However the low market value of the co-produced tertbutyl alcohol limits the interest of this process and leads to research better conditions and cheaper oxidant to perform alkenes epoxydation. It is the reason why we have undergone the study of such oxidation with O₂ under photocatalysis conditions in presence of TiO₂ anatase with large surface area or TiOx dispersed upon mesoporous SBA15 silica. The rate of cyclooctene epoxydation by TBHP, measured with several Ti-SBA catalysts in acetonitrile, was taken as reference.

- Oxygen used as cooxidant strongly reduces the rate of the reaction.
- UV irradiation increases epoxydation rate by TBHP but this effect is inhibited by O₂.
- Epoxydation by pure O₂ is slow and depends on traces of water and acetic acid. The best epoxydation yield (35%) is obtained after a time reaction of 10 hours at 353 K using TiO₂ PC500 as catalyst. This result leads the way for the use of O₂ as photocatalytic epoxydation reagent.

Poster No. 109:

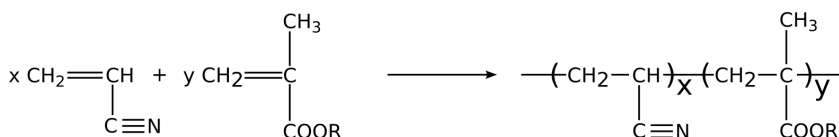
ACRYLONITRILE-BASED COPOLYMERS CONTAINING REACTIVE GROUPS: SYNTHESIS AND PREPARATION OF ULTRAFILTRATION MEMBRANES

V. B. Konsulov¹, Z. S. Grozeva¹, Tz. Godjevargova² & A. Dimov²

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Polyacrylonitrile (PAN) has been widely used as membrane material in the fields of dialysis, pervaporation and ultrafiltration. As carriers for enzyme immobilization, polymeric membranes have been used extensively since they can have various functional groups [1]. Functional reactive AN-copolymers were prepared by the copolymerization of acrylonitrile (AN) with methacrylic acid esters:



where R is: $-\text{CH}_2\text{CH}_2\text{OH}$; $-\text{CH}_2\text{CH}(\text{O})\text{CH}_2$; $-\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$; $y < 0.25$

Much attention has been paid to optimize the PAN-membrane performance through copolymerization AN with other N-vinyl monomers such N-vinylimidazole (VI), N-vinylpyridine (VP) or maleic anhydride (MA) and N-substituted maleimide.

Membranes were cast from homogeneous solution by the phase-inversion method [1]. Its use as carrier for immobilization of glucose oxidase or urease. The amount of bound protein and relative activity of urease immobilized on to membranes studied was determined (Table 1).

Table 1: Basic characteristics of immobilized on membranes of AN-copolymers

	Membrane type	Content of bound protein, mg/cm ³	Specific activity of immobilizing urease, U/mg	Relative activity, %
M ₁	Poly(AN-co-VI)	0.032	144.4	84.5
M ₂	Poly(AN-co-VP)	0.026	171.1	100
M ₃	Poly(AN-co-MA)	0.075	20.2	12.0
M ₄	Poly(AN-co-DMAEMA)	0.074	28.6	17.0

References:

1. Godjevargova T., Konsulov V., Dimov A., J. of Membrane Sci., 152, (1999) 235.

Poster No. 110:

STABILITY AND ACTIVITY OF LIPOZYME® IN SC-CO₂ - PHARMACO-LOGICAL CONVENIENT SOLVENT

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Enzymatic catalysis in organic solvents has been successfully used for the synthesis of variety of chemical compounds. However, the use of solvents in bulk quantities requires proper handling due to their environmentally incompatible effect, unless solvent recycling is practiced. SC-CO₂ exhibits properties similar to organic solvents, but with the additional capacity of encouraging transport phenomena (due to their high diffusivities) and facilitating reaction products separation by tuning solvent power, which makes it more attractive for using as green solvent.

SC-CO₂ has been used for extraction of oil from blackcurrant seeds, and as a solvent for enzymic hydrolysis of triacylglycerols of blackcurrant oil. The activity and stability of lipase from *Mucor miehei* immobilized on macroporous anionic resin (Lipozyme®) in SC-CO₂ were studied. Hydrolysis of triacylglycerols of blackcurrant oil was used as a model system. The stability of the enzyme was examined during 72 days at pressure 10-25 MPa and 30-40°C. The enzyme was permanently in contact with dense CO₂ during this period time. Between the reaction runs the temperature in the reactor was reduced to room temperature and therefore the pressure decreased to 5-16 MPa, due to the reaction conditions in the previous run. The enzyme stability was found to be excellent, chemical yields of the reaction were without decrease. Increased relative activity of the lipase after using in the system was observed under atmospheric pressure by two or three times. The finding could be contributed to modification in the active site of the enzyme.

Acknowledgement: The authors thank Grant Agency of Czech Republic for financial support of this research through the GA CR 203/04/0120 project.

Poster No. 111:

WOOD LIQUEFACTION: CONVENTIONAL VS. MICROWAVE HEATING

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Due to its complex composite structure made of saccharides, phenolic compounds and a number of other components wood is not very suitable as a renewable chemical feedstock. A method to obtain a useful feedstock is wood liquefaction where wood is reacted with a suitable reagent (phenol, glycol etc) in the presence of a catalyst. During liquefaction polymeric wood components are depolymerized and derivatized to yield a liquid material.

The purpose of our research was to investigate liquefaction using simple glycols in combination with dibasic organic acids or anhydrides in order to obtain liquid wood appropriately derivatized to allow further polyester chemistry. The liquefaction was carried out using conventional heating at atmospheric pressure as well as microwave heating in pressurized vessels.

Under conventional heating conditions with minor additions of ortho-phosphoric acid 15 to 56% of the original wood was liquefied in 3-11 hours at approx. 190°C. The unliquefied wood remains were mainly composed of cellulose fibers while liquid wood was confirmed to consist of low oligomeric polyesters with wood degradation components incorporated in the structures.

Identical reactions were carried out under microwave irradiation with powers between 300 and 700 W. The reaction temperatures easily exceeded 200°C within 10-20 minutes heating, depending on the heating power. The liquefactions under these conditions could proceed to completion within 15 or 20 minutes, depending on the amount of catalyst present. Products were characterized and showed the same chemical nature as those obtained by conventional heating with the difference that double bonds tended to saturate during the process at higher temperatures.

Poster No. 112:

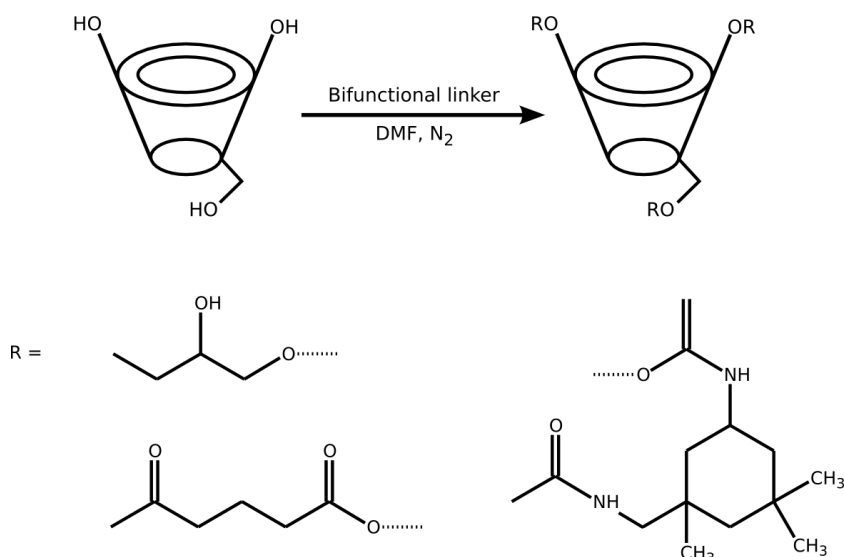
NOVEL CYCLODEXTRIN POLYMERS FOR REMOVING ORGANIC POLLUTANTS FROM WATER

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Cyclodextrins (CDs) and their corresponding derivatives have been used in a wide range of applications including pharmaceutical and pesticide removal and catalysis [1]. More recently cyclodextrin polymers have been used in water treatment for removing undesirable species found in water such as organic compounds. Cyclodextrins are cyclic oligosaccharides derived from enzyme degradation of starch. Commonly found cyclodextrins are α -, β - and γ -, which consist of 6, 7 and 8 glucose units, respectively [2].

The solubility of cyclodextrin poses a limitation to their absorption capabilities. Therefore, polymerizing a cyclodextrin monomer (Scheme 1) with an excess of the bifunctional linker produces an insoluble polymer with an added capability to form an inclusion complex with a guest molecule.



Scheme 1: Synthetic pathway for polymerization of cyclodextrin

In the poster we report on the polymerization of β -cyclodextrin with linkers, namely adipoyl chloride, epichlorohydrin, isophorone diisocyanate and poly(hexamethylene) diisocyanate. The water insoluble polymers obtained were characterized and their efficacy at removing a selected model organic pollutant, *p*-nitrophenol, was determined.

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Poster No. 113:

DESTRUCTION OF WASTE ORGANIC COMPOUNDS USING NON-THERMAL PLASMA REACTOR

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The drying treatment of coal by steam ("Fleissner") is based on transformation of colloids from coal and plastification of coal in the atmosphere of saturated steam. During the heating of coal, at the temperature of approximately 160°C, most of colloidal bonds in the capillars with high content of water are destroyed. Liberated water left coal which plasticity decreases and the density increases. Obtained dry coal is a high quality fuel.

The emission of waste vapours and gases occurs during the production of this fuel. They are usually emitted to the atmosphere through the chimney without any treatment. The content of various compounds was determined in waste gases: polyaromatic hydrocarbons, extractable organic substance, total hydrocarbons, NSO-compounds, volatile phenols and compounds containing reduced forms of sulphur. The plasma generator based on dielectric-barrier-discharge was used for the treatment. Only one pass of the waste vapours and gases through non-thermal plasma generator resulted in decrease of concentrations for several times. The greatest decrease was observed for polyaromatic hydrocarbons, volatile phenols and NSO-compounds. Results indicated possible application of this process of waste degradation during the drying of coal.

Poster No. 114:

POSSIBILITIES OF WASTE DRILLING MUD TREATMENT

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Drilling mud from oil and natural gas drilling presents a complex ecological problem. Disposal of this material temporarily postpones its treatment but creates a new problem, sanitation of formed landfills. Sanitation of existing landfills is an issue of great ecological importance. Possibilities for drilling mud treatment as an attempt to minimize landfill material are presented in this paper. Investigated techniques are separation processes based on solid/liquid phase separation with previous destabilization. Presented results are obtained through investigation of destabilization of drilling mud by coagulation, flocculation and magnetic field treatment with prior adjustment of physical characteristics.

Poster No. 114a:

NEW RUBBER PRODUCTS OBTAINED BY AN ENVIRONMENTALLY FRIENDLY PROCESS

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The investigations were aimed to obtain some new generations of thermoplastic ionic elastomers with high technical and processing characteristics intended to be processed on the injection moulding machines available in the country, resulting in high quality products complying with the internal and international market requirements.

With the view to accomplish the above objective two types of maleinized ethylene-propylene terpolymer rubber (mEPDM) with various percentages of maleic anhydride were used. The mEPDM rubbers were modified by neutralizing them with zinc oxide and stearic acid, and then the ionomer has been converted into a thermoplastic ionic elastomer by adding various percentages of ionic plasticizer to the blend. The behaviour of the thermoplastic ionic elastomers resulted by adding fillers like as precipitated silica and carbon black in various percentages was assessed. All the laboratory prepared compounds were tested for the physical-mechanical characteristics; based on the results, two thermoplastic ionic elastomers with the best characteristics were selected and the applications of these were set up.

The resulted thermoplastic ionic elastomers are a novelty in the world. They can be processed by processes specific to thermoplastic materials by removal of the curing operation with high power consumption and releasing noxious substances. The new elastomers also can be used in making materials with particular characteristics such as: increased elasticity, ageing resistance, abrasive resistance, alkali and acid fastness etc.

The potential users of the new rubber materials will be economic operators processing rubber and plastics, footwear and car component manufactures etc.

10. Waste valorization

Poster No. 115
Friday, December 9th
17:00-18:00

Poster No. 115:

HYDROMETALLURGICAL TREATMENT OF COPPER SLUDGE FROM BLUE VITRIOL PRODUCTION

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At blue vitriol production ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in Chemical Industry in Šabac, copper of various grades and origin is used when waste sludge is produced containing: 25% of copper, 10% of lead, 0,2% of silver, 0,1% of iron, 0,0025% of gold and 20% of moisture on average 12 t of copper, 5 t of lead, 100 kg of silver and 1 kg of gold are obtained out of sludge per year. By the valorization of these metals the economy of blue vitriol manufacture can be improved and, at the same time, ecological problem of sludge disposition can be solved.

It has been developed, in laboratory and pilot-scale, a method of waste sludge processing from the blue vitriol manufacture where by leaching procedure a predominant copper quantity is separated, while silver, gold and lead are concentrated in leaching residue from which they can be valorized by known metallurgical methods.

11. Atmospheric chemistry, air pollution, modeling of pollutants diffusion

Posters No. 116-132
Friday, December 9th
17:00-18:00

Poster No. 116:

INFLUENCE OF THE PRIMARY AND SECONDARY AEROSOL ON THE CONTENT OF IONS IN THE PRECIPITATION

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The sampling site, which is located in the town of Herceg Novi (18°33' N, 42°27' E), about 10 meters from the coast of the South Adriatic Sea, is a part of the MED POL program for monitoring of airborne pollutants along the Mediterranean coast. The average annual precipitation sum at Herceg Novi is 2016 mm. The samples of the precipitation were collected in the period 1995-2000. The precipitation samples were analysed for conductivity, pH, SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cd, Pb, Zn, Cu. The dominant ions are: Na^+ , Ca^{2+} , Cl^- and SO_4^{2-} , with the following overall order: $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{K}^+$; $\text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$.

Correlation coefficients with high statistical significance ($p < 0.001$) were obtained for the following pairs of elements: SO_4^{2-} - NH_4^+ ($r=0.531$), SO_4^{2-} - K^+ ($r=0.532$), Na^+ - Mg^{2+} ($r=0.688$), Na^+ - Cl^- ($r=0.676$), Na^+ - K^+ ($r=0.517$) and Mg^{2+} - Cl^- ($r=0.633$).

The principal component analysis (PCA) was applied to the database in order to differentiate the influence of the primary and secondary aerosol on the investigated chemical species content in the precipitation and 5 significant components were extracted. Component 1 has high eigenvalues of the varimax-rotated eigenvector for Na^+ , Mg^{2+} and Cl^- , which are major constituents of seawater. Component 2 is characterised by high eigenvalues for NH_4^+ and SO_4^{2-} , representatives of the continental secondary aerosol contribution. Component 3 shows high eigenvalues for Pb, Cu and Zn, which are representatives of the anthropogenic influence. Component 4 is characterised by high eigenvalues for H^+ and NO_3^- and can be marked as acidity component. Component 5 has high eigenvalue for Cd.

Poster No. 117:

GAS-PHASE PHOTOCATALYTIC OXIDATION OF ETHANETHIOL IN SIMPLE TUBULAR CONTINUOUS-FLOW REACTOR

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Volatile organic sulphur containing compounds, released mostly from biological activities and a number of manufacture processes (paper making, petroleum refining), are toxic, malodorous and contribute to acid rain formations. Adsorption currently employed for the removal of mercaptans, results in secondary safe transportation and utilisation problems with the used adsorbents. Incineration presents an option of choice where appropriate, however, resulting sulphur dioxide still ends up in acid rains. Therefore, the search for a safe reliable method of sulphur transformation to its harmless forms is under consideration. Photocatalytic oxidation (PCO) over titanium dioxide takes place at the ambient conditions, although higher temperatures may be also applied. The temperature influence to the reaction pathways and kinetics of gas-phase PCO and thermal catalytic reaction of ethanethiol (ET) over TiO_2 (Degussa P25) was studied by a continuous flow method in a simple tubular reactor at temperatures from 373 to 483 K.

Water and carbon dioxide were identified as PCO products at low ET conversion degree at short contact times. Acetic acid formed as an intermediate by-product. Sulphur dioxide was seen as sulphur containing oxidation product. Long-term operation of the reactor resulted in accumulation of sulphate on TiO_2 , which was observed in water after rinsing of the reactor. Sulphuric acid partially converted titanium dioxide to titanium sulphate: titanium was observed in rinsing water samples. The pH of rinsing water was as low as 3.0 and no organic constituents were observed in rinsing water: COD was close to zero. Thermal catalytic decomposition of ET resulted in formation of products similar to PCO, although with much smaller rate. Both reactions have their concentration limits for the stable work of the reactor, above which the deactivation of the catalyst was observed rather quickly. The increase of temperature resulted in overall reduction of PCO rate, which may be explained by deterioration of adsorption.

Poster No. 118:

MICROBIAL POPULATION IN CLOUDS: IMPLICATION ON CLOUD CHEMISTRY

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Although micro-organisms are ubiquitous in the atmosphere, very few investigations have been carried out in this field. In this study, the structure of the microbial community present in atmospheric water samples from clouds at the puy de Dôme (alt. 1465 m, Massif Central, France) is described and the metabolic potential of some bacteria is investigated. The total microflora was quantified by epifluorescence microscopy and ATP concentration was measured by an enzymatic method, while the cultivable aerobic micro-organisms were isolated. Bacteria were identified by 16S rDNA sequencing and fungi by morphological criteria. Most of the isolated cultivable micro-organisms, including 90 bacterial strains and more than 40 fungal and yeasts, are described here for the first time in atmospheric water. Many bacterial strains seem to be adapted to the extreme conditions found in cloud water through several points: **(1)** most of them are psychophylics, as seen by their good growth at 15°C, or even at 5°C for some of them; **(2)** they generally present pigments (or at least are spore-forming bacteria), which are well-known to protect against cold and light exposure; **(3)** some bacterial strains are closely related to polar ones. We have also shown, using *in situ* ¹H NMR, that most of the isolated bacteria are able to degrade various organic substrates such as formate, acetate, lactate and succinate which represent the major organic acids present in cloud water. Our results suggest that bacteria could play a role in cloud chemistry.

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Poster No. 119:

CONTRIBUTION OF VARIOUS EMISSION SOURCES ON CONCENTRATIONS OF SURFACE AIR POLLUTANTS OF INDUSTRIAL AREA

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Pančevo (20°45' N, 44°55' E) is one of the main industrial towns in Serbia and Montenegro, having developed oil, petrochemical, fertilizer industry etc. Specific pollutants are continuously measured at two sampling sites as receptor models.

At the same meteorological conditions, low level concentration of pollutants in ambient air can be significantly different, depending not only on the meteorological parameters but also on the number and the height of emission sources.

GC/FID technique was used to detect organic pollutants from characteristic low level emission sources, which are constituents of oil and its derivatives, in ambient air. Gas are noticeable presence of peaks as a "fingerprint" of low level emission sources.

The cluster analysis technique is the most appropriate method to evidence correlations between variables. The clustering features of the other pollutants and the values of the obtained Pearson-correlation coefficients for data base of Vatrogasni dom receptor the existence of three additional associations was assessed: association II (Me-Me), association III (SO₂, NH₃) and association IV (NO₂). Results of cluster analysis of data base of Vojlovica receptor revealed the existence of the same three additional associations: association II (TRS), association III (PM₁₀) and association IV (SO₂).

There are various emission sources that variously contribute on concentration of pollutant in the ambient air. The strongest associations are between variables consisting of data of pollutants' concentrations from low-level emission sources.

Poster No. 120:

CLOUD WATER SENSITIVITY TO PHOTOCHEMISTRY

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Formaldehyde and hydrogen peroxide are important constituents of atmospheric photochemistry, closely linked to the HO_x and NO_x cycles. Moreover organic substances are considered to be the most affected by photochemical reactions (direct oxidation and radicals/oxidants action). We compare the results from monitoring of the day-night variations through continuous in situ sampling and the results from laboratory experiments irradiating real cloud samples and simulated cloud (artificial solution) in order to evaluate which role has the light in aqueous-phase chemistry and in interstitial gaseous-phase chemistry.

A significant seasonal dependence of H₂O₂ concentration in cloud droplets is evident from the in-situ measurements, as well as a pronounced diurnal. It is clear that solar radiation is one of the most important factors that drive the hydrogen peroxide concentration. Also the major carboxylic acids shows the same augmentation during the central hours of the day, with a delay of 3-4 hour with respect to H₂O₂, probably due to more complex reaction chains that bring to organic degradation. The cloud water irradiations in laboratory show results not always in agreement with the direct observation in-situ. H₂O₂ concentration during the irradiations shows a decrease of about 15%·h⁻¹; DOC is not varying, while carboxylic acids and formaldehyde has not a reproducible behaviour (the concentration can undergo both rise or decrease in different irradiation experiments).

These results lead to conclusion that photochemical production of hydrogen peroxide has priority in gas phase in a continental free tropospheric site. The photo-degradation of organic matter (that leads to formation of little molecules, like the measured carboxylic acids or formaldehyde) happens in both gas and liquid phase, but it has priority in gas phase.

Poster No. 121:

REDUCING BENZENE VAPOR EMISSION FROM STORAGE TANKS TO ENVIRONMENT

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Earlier researches regarding causes and level of air pollution, on Pančevo town territory confirmed high concentration of benzene, toluene and xylene in air of south industrial zone of Pančevo, which influence on air pollution in Pančevo. These air pollutants are produced by evaporation, insufficient combustion of oil derivatives in industrial and other furnaces, as well as in self combustion motor cars.

The aim of this article is to resolve the problem of benzene emission from storage tanks in Oil refinery Pančevo and Petrohemija Pančevo. This method can be applied for reducing vapor emission of pyrolytic benzene, and some other oil derivatives. Causes of benzene vapor emission from storage tanks are non-adequate thermic insulation, which implies on benzene evaporation at high environmental temperature, as well as at refilling tanks. Solving of these complex problems must include following steps: **1.** antirust (protective) coating and thermal insulation coating system, which results in lowering benzene temperature in tanks, **2.** mounting of heat exchanger (condenser) on the roof of tank, and **3.** condensate return to tank, which eliminate high loss of benzene and improves process profitability.

Poster No. 122:

CARBON ISOTOPE COMPOSITION OF ANTHROPOGENIC METHANE FLUX FROM THE UPPER SILESIAN COAL BASIN, SOUTHERN POLAND

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The main objectives of the present study are to (1) compare the stable carbon isotope composition of coalbed methane from Upper Carboniferous strata of the Upper Silesian coal basin (USCB) with atmospheric methane, (2) evaluate the quantity of methane flux in specific areas of the basin and assess the importance of various natural (geological, as faults and outcrops), and human (coal mining and ventilation) factors that influence the flux. Comparison of the stable carbon isotope composition of methane from Upper Carboniferous coalbed methane from the USCB and atmospheric methane reveals the influence of coalbed methane on stable carbon isotope composition of atmospheric methane. Upper Carboniferous coalbed gases in the southern part of the USCB are variable both in their molecular and stable isotope compositions. Hydrocarbon index [$\text{CH}_4/(\text{C}_2\text{H}_6+\text{C}_3\text{H}_8)$] varies from 14 to more than 980,000, $\delta^{13}\text{C}(\text{CH}_4)$ from -79.9 to -47.1‰ and $\delta\text{D}(\text{CH}_4)$ from -202 to -157‰. The $\delta^{13}\text{C}(\text{CH}_4)$ and hydrocarbon index of gases from ventilation shafts varying in a similar manner from -71.6 to -48.8‰ and from 270 to more than 10^5 , respectively. Isotopic studies also indicate the presence of two genetic types of coalbed gases: thermogenic (methane and higher gaseous hydrocarbons), and microbial methane. Methane emission to the atmosphere through the ventilation shafts decreased from 977 Gg in 1984 to 504 Gg in 2002, with a simultaneous drop of coal output from 192 Tg to 104 Tg. The $\delta^{13}\text{C}$ -values of atmospheric methane in Upper Silesia vary from -59.5 to -48.8‰, lower than the average value for the atmosphere (-47‰). This isotopic shift is caused by the flux of coalbed methane to atmosphere. Recent studies indicate that coal mining and natural gas ventilation are significant components of total annual global flux from all methane sources. This work is partly supported by national grant No. KBN 4 T12B 059 26.

Poster No. 123:

MOSSES AS BIOMONITORS OF AIR POLLUTION IN THE CITY OF BELGRADE

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The accumulation abilities of two moss species: *Brachythecium* sp. (*B. rutabulum* & *B. salebrosum*) and *Eurhynchium* sp. (*E. hians* & *E. striatum*), as a biomonitors of atmospheric trace elements pollution, was evaluated in this study. The mosses were sampled at two locations of Belgrade in the autumn of 2004. A concentrations of 36 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Sm, Tb, Dy, Hf, Ta, W, Hg, Th, U) were determined by instrumental neutron activation analysis. It was shown that both moss species, have almost the same abilities to accumulate elements and they could be used for biomonitoring purposes. Two different techniques of preparing moss samples prior further analysis (washing/unwashing) were used. A difference in accumulation of elements in washed and unwashed samples is within analytical error of INAA for the majority of analyzed elements.

The comparison of the most elements concentration obtained in this experiment, to the previous data for the year 2000 from the area of Belgrade (after the NATO military action in Serbia and Montenegro in spring 1999) indicates a decreasing trend. As typical for all countries in the region, the concentrations of V, Cr, Ni, and As in our investigations are several times higher as compared to some other European countries.

Poster No. 124:

TRANSFER FROM WATER TO ATMOSPHERE: BUBBLING THROUGH CO-ADSORBED LAYERS OF IONIC AND ORGANIC POLLUTANTS

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Bubbling is a well known mechanism of passing of adsorbable pollutants from the water surface to the atmosphere, under the form of aerosols. It occurs under the influence of wind agitation and wave breaking. In this poster, we collect several sets of data concerning the adsorption of heavy metal salts at the surface of aqueous solutions, by a mechanism of coadsorption with organic molecules. Salts do not adsorb when they are the only solutes. But in the presence of another solute as organic molecules, they exhibit a positive adsorption, even in the absence of any complex formation.

Organic components examined here are other potential pollutants: hydrocarbons and an insecticide, carbofuran. Studies have been made in dilute solutions, between 10^{-5} and 10^{-2} mol·L⁻¹, for both components of each salt/organic species solution. Adsorption was calculated from surface tension measurements.

The measured adsorption parameter is the relative adsorption of Gibbs, which is a mixture of salt surface excess, organic molecule excess and water excess. Rough modelling of ionic adsorption through Onsager-Samaras' model shows that water is very perturbed in the surface layer, but does not give any clue onto the ionic arrangement. As this aspect is very topical, given the observations on aerosol ionic charges, we propose some views about these arrangements on the base of quantum mechanical modelling.

Poster No. 125:

ANALYSIS OF PM₁₀ AND PM_{2.5} AIR POLLUTION EPISODES IN BELGRADE

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The measurements of average daily concentrations of airborne particles PM₁₀ and PM_{2.5} have started at three representative points in the urban area of Belgrade in June 2002. Suspended particles were collected on Pure Teflon filters by using a Mini-Vol air sampler. Particle mass was determined gravimetrically after 48 h of conditioning in a Class 100 clean room.

We have analysed in detail several selected episodes involving substantially high concentrations of PM₁₀ that occurred in Belgrade during 2002-2004.

The model used for simulation and trajectory calculation of this study is a limited area primitive equation model with step-mountain coordinate, the so-called Eta model. It is a regional weather prediction primitive equation model for synoptic and meso-scale processes.

For this study 60-h air-back trajectories are calculated by specifying final parcel locations and time, and then tracing the parcels with decreasing time to determine the air mass origins.

All cases observed during measuring period were characterized by very slow flow field caused by small gradient of the pressure field. The prevalence of stagnant or weak flow regimes favors the suspension and accumulation of particles produced locally, resulting at the elevation of PM levels.

The main sources of particulate matter were traffic emission, and, in winter, individual heating emissions. When the air masses were coming from the SW direction, the contribution from the Obrenovac thermal power plants was evident.

Poster No. 126:

REPETITION OF THE REGIONAL MAGNETIC FIELDS ON THE SUN AND THEIR IMPORTANCE FOR THE DEVELOPMENT OF THE WEATHER CIRCUMSTANCES ON EARTH

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Behavior of the air polluters, their transformations, time of stay, transport and effect are in a close connection with the meteorological conditions from the local to global scale. The same could be said, although to a less extent, for the marine and soil polluters. Any modeling of the polluters' dispersion is not possible without complete knowledge of the meteorological phenomena and possibilities of their forecast and prognosis. Relying on the previous researches, we have noticed a possible connection between energy changes on the Sun and meteorological phenomena on Earth that broadens the possibility for the long term weather forecast.

According to approximate estimates, the protons of high energy could cause important disturbances in a zone of upper troposphere and stratosphere by stimulating the development of cyclones and anticyclones. The obtained results are in accordance with the data of numerous researches of the solar activity - atmospheric circulation connection (Sazonov, Loginov, according to Vitinskih, Olj, Sazonov, 1976). However, one could get an impression that there are still no satisfying results in this field. *"Karen Labitske in Germany has done a lot of research in this area. The physics is still highly speculative at this point though"* [1].

Our weather electromagnetic and meteorological parameters that could have been used as indices of the repetition for making the long - term forecast were related to: active surface of energetic region on the Sun, intensity of the Solar flux on 2800 MHz, the number of spots on the visible side of the Sun and the repetition of the Solar wind energies in the function of the Sun and Earth rotation. Under energies of the Solar wind it is meant on electrical, magnetic, thermal and kinetic energy.

On the basis of researches of causality of electromagnetic activity on the Sun and atmospheric processes, we have come to knowledge that some energetic regions, depending on their characteristics, when they are in geo - effective position, cause, as a rule, certain disturbances in the atmosphere (Radovanović, Stevančević et al, 2003). Under the term of energetic region we mean on the location on the Sun that contains a certain number of spots of different magnetic structures. NOAA (National Oceanic and Atmospheric Administration) [2] in its scale of the cosmic weather gives criteria and units for description and effects that occurred by the magnetic storms, solar radio storms and cuts of the Earth radio connections.

References:

1. <http://www.sec.noaa.gov/info/FAQ.html>
2. <http://www.noaa.gov/>

Poster No. 127:

^{210}Pb IN GROUND LEVEL AIR IN BELGRADE CENTRAL AREA

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The paper presents the results of ^{210}Pb activity monitoring in ground level air in urban area (Belgrade city parks), from 2002-2005. Daily samples of aerosols were collected on filter paper (F/W, relative efficiency 80%, rate 600 m³/day) ashed at 400°C and formed as a composite monthly sample (average volume 15·10³ m³). The sampling sites (three city parks) differ strongly in microclimate conditions (ventilation, vegetation, buildings, vicinity of large traffic avenues, etc). The concentrations of ^{210}Pb were determined on HPGe detector (ORTEC, relative efficiency 23%) by standard gamma spectrometry (geometric calibration performed by IAEA-083/AIR-4 simulated air filter standard). Total standard error of the method was estimated below 25% and minimum detectable concentrations of ^{210}Pb were 20 µBq/m³. Average ^{210}Pb concentrations in ground level air in the very centre of the city were in the range of the values obtained in the long-term study of contents of natural and man made radionuclides in ground level air in the non-urban areas (0.1-5.4·10⁻⁴ Bq/m³) exhibiting similar seasonal variations pattern, with a maximum in fall-winter period and a minimum in early spring. There was no correlation between the ^{210}Pb concentrations in air and the amount of precipitations.

Poster No. 128:

CONCENTRATION OF NANOMETRIC FAST AIR-IONS MEASURED IN SOKOBANJA SPA IN SEPTEMBER 2005

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Concentration of both positive and negative nanometric fast air-ions have been measured in Sokobanja (Serbia), well known as an "radioactive" spa because of radon-222 in the air and mineral springs. The radon is the heaviest noble gas 100% α -emitter, half-life 3.825 days, a decay product of radium-226. Energy of the α -particles of 5.59 MeV is enough to produce 10^5 ion pairs in the air. As a result of this ionization process, approximately 5 ion-pairs/cm³ appear near the ground every second.

We used the Gerdien type air-ion detector designed and built in our laboratories [1,2] to measure the ion concentrations at places where the radon exhales from the ground more probable. Evolution of positive nitrogen (N_2^+) and negative oxygen (O_2^-) primary molecular ions is characterized by appearance of many molecular species and their ions in collision processes on the 1-100 eV energy scale. This low-energy region and enormous multiplication factor of 10^5 mentioned above served us to consider Sokobanja as the atomic rather than "radioactive" spa. To prove this hypothesis we also performed geological observations and simultaneous measuring of ozone concentration, aerosols (PM_{2.5}), radon in the air and some of the other physical parameters in September 2005. We have found the level of negative air-ion concentration of $n=500$ ions/cm³. The unipolarity coefficient (n/n^+) grater than 1 during this measurements is an indication of healthy conditions based on the atmospheric ions.

Continuous 9-day measurements of the ozone concentration (in 1 h steps) show characteristic diurnal variation, without any behavior that indicates pollution of the atmosphere [3]. The mean value of the concentration was approximately 40 ppb, without significant long-range pollution transport to the measuring place.

Numerous epidemiological studies have demonstrated the strong negative health effect of exposure to the inhalable aerosols. Suspended particulates were collected on pure Teflon filters by using a Mini-Vol low volume air sampler and mass concentrations were determined gravimetrically. Very low 24 h mass concentrations for PM_{2.5} were obtained with average value of 3.5 $\mu\text{g}\cdot\text{m}^{-3}$.

References:

1. P. Kolarž, B. P. Marinković and D. M. Filipović, *Rev. Sci.Instrum.* **76** (2005) 046107.
2. P. Kolarž, J. Šekarić, B. P. Marinković and D. M. Filipović, *J. Atm. Solar-Terr. Phys.*, **67** (2005) 1357-1364.
3. D. M. Marković and D. A. Marković, *J. Serb. Chem. Soc.* **12** (2005). In press.

Poster No. 129:

CHARACTERISTICS OF PM₁₀, NO₂, SO₂ AND CO IN AMBIENT AIR DURING POLLUTION EPISODE IN WINTER SEASON IN BELGRADE CENTRAL ZONE

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In this study, the hourly variation of the mass concentrations of NO₂ and SO₂ (at three) as well as PM₁₀ and CO (per one sampling site) were observed in Belgrade central zone during air pollution episode occurrence period in February 2005. By comparing the hourly and daily pollutant concentrations before, during and after pollution episode happened the variations characteristics of PM₁₀, NO₂, SO₂ and CO are presented. The results show that maximum daily average concentrations were recorded on February 11 at all sites for all observed pollutants. Before February 11 it was observed 10 successive days with daily average temperature below 0°C and atmospheric pressure under 1000 mbar. Before that daily average wind speed were less than 0.6 m/s in the period of 6 days. The highest concentration of PM₁₀ was 494 µg/m³ what is 9 times greater than limit value according to EU legislative. PM₁₀ daily average concentrations exceeded limit value 18 times. There is better ratio between hourly average concentration of PM₁₀/CO (R²=0.73) than between PM₁₀/NO₂ and PM₁₀/SO₂ (R² are 0.61 and 0.58, respectively). At location at Ohridska street SO₂ was extremely higher than at other sites. At February 11 SO₂ daily average was 450 µg/m³ what is 3 times greater from limited value. SO₂ concentration once reached 900 µg/m³ per hour that is 2.5 times greater in comparison to EU and Serbian limit value. There was not notified great difference in concentration variation as well as in number of cases above limit value of NO₂ in Belgrade central zone.

Poster No. 130:

CHARACTERIZATION OF POLLUTION MEASUREMENT PLACES IN URBAN AREA OF BELGRADE

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Urban air is complex physical and chemical system in which many processes are occurring due to presence of pollutants. These processes have a huge influence on the pollutants and health effects. That is why it is very important to spot these processes and pollutants in air, which change its primary form and way of work very often.

During the period from 2002 to 2005, measurement of ozone concentration on several places in urban area of Belgrade show multiply exceeding of means one our concentration above 90 ppb. That is characteristic of days with high concentration of ozone (high ozone day). That is why measurements of ozone precursors (like nonmethanes hydrocarbons (NMHC) and nitrogen oxides) as well as meteorological data, are essential for better understanding of production mechanism of very high concentrations and their influence on urban area quality.

In way of ozone production, production potential of some urban area depends on NO_x concentration and ratio NMHC/NO_x. Nitrogen oxides disappear from atmosphere faster than NMHC. Production of ozone is stopped when the NO_x concentration is less than determination level. On the other hand, high concentrations of NO_x prevent ozone accumulation due to OH radicals necessity for forming peroxy radicals RO₂. That is very important, because without RO₂, the ozone accumulation in urban air is impossible. This is characteristic of urban area with high density of traffic. In those areas we do not have high ozone concentration, although we have huge concentration of ozone precursor.

This study shows the measurement results from two places chosen from measurement net of Institute of Public Health of Belgrade, during period May-June 2005. According to shown results, place near Institute represents area of emission of primary pollutants and place in Omladinskih brigada street represents area with dominant influence photochemical tropospheric reactions with secondary pollutants production.

Poster No. 131:

FACTORS WHICH DETERMINE SUMMERTIME COMPOSITIONS OF PAH ASSEMBLAGE IN MEDITERRANEAN AIR: HERCEG NOVI SAMPLING STATION AS AN EXAMPLE

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Polycyclic aromatic hydrocarbons (PAHs) were determined in total suspended particulates (TSP) samples collected during the summer months of 1998 in the ambient air of Herceg Novi (Adriatic coast of Montenegro). The sampling site is included in the network for the monitoring of airborne pollutants along the Mediterranean coast. All samplings had 24 h duration in 1-in-6 day schedule program.

Ultrasonic extraction utilize dichloromethane was used to separate non-volatile solvent-extractable organic (SEO) fraction from the samples. Twelve PAHs were identified, ranging from phenanthrene to benzo[ghi]perylene in total of 16 extracts analyzed by gas chromatography-mass spectrometry.

Concerning the relative composition in atmospheric PM, the collected samples were characterized by greater proportion of high molecular weight PAH (~64%). The potentially carcinogenic PAHs represent 28% of total PAH concentrations (on average). Statistical analysis, in particular principal component analysis (PCA) was employed to analyze this data set. Correlation studies between PAHs of the individual factors identified by (PCA) and meteorological parameters such as temperature, humidity, pressure, wind speed and direction revealed no consistent relationship, indicating a different influence of meteorological parameters on individual PAHs.

The abundance and sources of these compounds were also discussed.

Poster No. 132:

LAZAREVAC REGION AIR POLLUTION REGIMES

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Lazarevac region in Serbia hosts the Kolubara coal mines complex, which contains several air pollution emitters, but also a major one - the Kolubara thermoelectric power plant. The region within and around the complex is regularly monitored for imissions as prescribed by the law, with particulate matter emissions apparently being the main concern locally. However no study as to the local regimes of the air pollution has been carried out so far.

In this paper we discuss the results of our measurements of the pollution in two periods - summer (August) and winter (February). The chosen parameter of pollution was the SO₂ concentration, as a good representative of the general behaviour of local air pollutants. The measuring point was positioned effectively between two pollution emitters: a drying facility power plant and the Kolubara electrical power plant. The results indicate that the measuring point is obviously separately affected by the two emitters - one is dominant in summer and the other one in winter. According to meteorological data simultaneously collected with SO₂ measurements and subsequent modelling, the reason apparently lies in the difference of the frequency of wind directions in summer and winter, indicating two regimes of pollution. The modelled pollution of the whole complex and its neighbourhood is discussed in terms of these findings.

12. Marine chemistry and marine pollution

Posters No. 133-136

Friday, December 9th

17:00-18:00

Poster No. 133:

FORMATION OF HALOGENATED ORGANIC MATTER IN SEAWATER IN PRESENCE OF IRON OXIDES OR Fe(III) IONS

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Several iron oxides have been found in the surficial seawater layer, as goethite ($-\text{FeOOH}$), hematite ($-\text{Fe}_2\text{O}_3$) and akaganeite ($-\text{FeOOH}$), whose concentrations are in the range of 0.01-15 nM. The first marine layer is liable to the occurrence of photochemical reactions that, thanks to the contemporaneously presence of semiconductor oxides and high halides concentrations, may induce the halogenation of the organic matter in seawater. These oxides are largely diffused in nature, above all hematite, and the photocatalytic halogenation may represent an important natural production of halogenated compounds. The band gaps are 2.34 eV for hematite, and 2.10 eV for goethite and akaganeite, so that their photoexcitation can be obtained by using visible light. We have also studied the role of iron(III) ions, generated from the oxidation of Fe(II) by H_2O_2 , on the degradation of organic compounds. Phenol has been used as target molecule in all cases.

The phenol photodegradation has been studied in artificial seawater (pH 8) in presence of iron oxides (or iron (III) ions) at diverse concentrations in a dispositive simulating the solar light. This study has been extended to the identification of hydroxylated and halogenated intermediate compounds, coming from the phenol degradation, and at the quantification of Fe^{2+} , coming from iron oxides through a photoreductive pathway. Several chloro and dichlorophenols have been identified.

Poster No. 134:

INFLUENCE OF THE SEDIMENT EXPOSURE TO ANOXIC CONDITIONS ON EDTA EXTRACTION AND FRACTIONATION OF TRACE METALS FROM SEDIMENTS

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In estuarine system, tidal phenomenon induces a regular change between oxic and anoxic conditions for sediments of the superficial layer and have, consequently, influence on trace metals release to the water column or sediment binding. Redox conditions have not a direct effect on the mobility of trace metals as Zn, Pb, Cu or Cd, which redox state is not directly affected by the redox conditions generally found in natural environment. However, the mobility of these metals can be influenced indirectly due to the natural ligands (iron and manganese oxide and oxyhydroxide) disponibility that can be affected by variations of the redox potential.

In the present work, the influence of the oxic/anoxic state of the sediment on the EDTA kinetic extraction and fractionation of Cu, Cd and Pb has been studied with three estuarine sediments. The sediments, originally in an anoxic state, were exposed to anoxic conditions to obtain the same sediments in an anoxic state called, in the present work, "treated sediment". It appears that, when some sediment are exposed to anoxic conditions, the quantity of metal extracted by EDTA decreases. However, it happens only with certain sediments and metals. Furthermore, the fractionation of trace metals in treated and untreated sediments showed that, in treated sediments, the quantity of metal quickly extracted by EDTA decreases and that the quantity of metal slowly or not extracted increases. These decrease should be attributed to a redistribution of metals in sediments, namely from the quickly extracted fraction to the other two fractions.

Poster No. 135:

DETERMINATION OF HEAVY METALS IN SEA WATER, MARINE SEDIMENTS AND MUSSELS IN BOKA KOTOR BAY (SOUTHERN ADRIATIC)

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The aim of this research was to determine the content of heavy metals in sea water, marine sediments and the mussels *Mytilus galloprovincialis*. The content of heavy metals in sea water, marina sediments and marina organisms were monitored at three different places in the Boka Kotor bay: Kotor, Tivat and Herceg Novi. The samples were collected in spring 2005.

A heavy metals in samples of marine sediments were determined directly on the grinded sample *via* EDPXRF techniques. The experimental results of heavy metals in sea water and marina mussels are obtained by using AAS and GF-AAS methods. The traces of elements in examined marina mussels were determined after usual sample preparation by previously decomposing organic matter with mineral acids. and by direct analysis of the lyophilized samples *via* EDPXRF (Energy Dispersive Polarised X-Ray Fluorescence).

The content of heavy metals in sea water and marine mussels is higher in the samples of Tivat and Herceg Novi than in Kotor samples, but it is opposite in the samples of sediments: the sediments in Kotor have much higher concentrations of examined heavy metals than the sediment samples of Tivat and Herceg Novi.

The obtained results in the samples of sediments can be explained by high intensity water movement in Tivat and Herceg Novi bays, because of the open sea, causing bottom erosion, while in Kotor bay there is almost no water movement at all, causing fine particles sedimentation.

Higher concentrations of the examined heavy metals into Tivat and Herceg Novi water and mussels, than into Kotor samples, can be explained, beside water movement, by strong anthropogenic influence from coast, especially from shipbuilding industry in Tivat bay from some time ago.

At the same time, there is impact on the obtained results of incoming river's fresh water and spring water from the Kotor bay bottom.

Mussel are commonly employed in the monitoring of metal pollution, because they are consumed by humans and they have a broad geographical range. In the present study, the mussel *Mytilus galloprovincialis*, was chosen as a biomonitor of coastal metal pollution.

Poster No. 136:

APPLICATION OF THE EXPERIMENTAL DESIGN METHOD TO THE STUDY OF SEA WATER FLOCCULATION COAGULATION PERFORMANCE

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Many studies devoted to sea water coagulation- flocculation show that, due to high salt concentration, it behaves distinctively compared to the case of freshwater. Jar tests with Aluminium sulfates allow the determination of optimal conditions for coagulation- flocculation of sea water coming from Algiers area. A first part of the study is dedicated to the effects of some parameters on the coagulation- flocculation process. These parameters include the pH and the coagulant concentration. A non conventional experimental design method based on the second degree model with interactions of order two is used. This model presents the effect of suspension pH (factor 1) and coagulant concentration (factor 2) on organic matter elimination efficacy (answer1) and turbidity reduction efficacy (answer2) versus the value of various levels of these two factors. Results show that the influence on answer1 and answer2 is not the same. Moreover, the model allows the prediction of the experimental optimal conditions.

13. Analytical methods for environmental science

Posters No. 137-164
Friday, December 9th
17:00-18:00

Poster No. 137:

VERSATILE AND MOBILE MS SYSTEM FOR THE ENVIRONMENTAL APPLICATIONS

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A versatile and mobile MS system for environmental applications has been developed and implemented for indoor and outdoor air pollution analysis and monitoring using positive and negative ion mass spectra and the advantages of both. The electron energy dependant positive ion fragmentation as well as the electron energy selectivity of the negative ion spectra has been used to facilitate the spectra interpretation by scanning the electron energy too for the chosen mass peak, or by taking the mass spectra at different electron energies. The single ion counting detection system and the various modes of the signal averaging has provided a high sensitivity with a detection limit below 0.1 ppm.

Gaseous, liquid and solid phase complex probe inlet system enables the versatile applications of the MS system exceeding the needs of the air pollution analysis and real-time monitoring.

A homemade gaseous sampler with a multiple stage cryogenic sampler/concentrator operating at the atmospheric pressure and having a programmable temperature control has been tested on the system. This has additionally decreased the detection limit for gases condensable in the achievable temperature range. Owing to that fact the application field of the MS system has been broadened.

Poster No. 138:

EXTRACTION OF ^{137}Cs FROM LICHEN WITH SOLUTIONS SIMULATING ACID RAIN

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In this work desorption of radiocesium from the lichen *Cetraria islandica* with acid solutions by simulated acid rain of different pH values from 2.00 to 3.75 was examined. The extraction efficiency for radiocesium by acid extraction solutions (1, 2, 3, 4), after five steps, was in the range from 44.0% (solution 4, pH 3.75) to 69.4% (solution 2, pH 2.87) of the initial radioactivity. After five extraction steps with distilled water (pH 6.48) 57.2% of the initial radioactivity was extracted. The final mass of the lichens only slightly decreased after this procedure (approximately 5%), indicating that the desorption was achieved without significant destruction of plant structure.

Poster No. 139:

A NEW METHOD FOR THE FREE + INORGANIC COPPER FRACTION ASSESSMENT IN SALINE SOLUTIONS

D. Fangueiro^{1,2}, A. Bermond¹, E. Santos², H. Carapuça² & A. Duarte²

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The determination of the metal complexation capacity of natural ligands as humic acids implies the assessment of the metal fraction complexed by those ligands or the fraction of metal in a free form and complexed by inorganic ligands (free + inorganic metal). In the present work, a new method to determine the fraction of free + inorganic copper in a saline solution after equilibration with a cation exchange resin was developed. This method is based on the determination of the coefficient of metal distribution between the resin, Dowex 50W-X8, and a solution with a composition similar to the studied solution but in the absence of any organic ligands, followed by the determination of the concentration of free + inorganic copper in the studied solution (containing the studied ligand) equilibrated with the resin. This method was first validated with two saline solutions containing copper and citric acid in different ratio ($[\text{Cu}]/[\text{citric acid}] = 1/9$ or $1/3$). The concentration of free + inorganic copper was assessed using the method proposed and by calculation and results obtained never diverged more than 5%. Finally, the method was applied to two different saline solutions containing copper and humic acids and the concentration of copper complexed by humic acids in solution was calculated.

Poster No. 140:

THE INFLUENCE OF SODIUM THIOSULPHATE ON DIFFERENTIAL UV ABSORBANCE FOR MONITORING TRIHALOMETHANE FORMATION

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Chlorination of natural waters leads to trihalomethane formation. Reaction path involves the electrophilic attack of chlorine over selected functional groups of natural organic matter (NOM). This reaction reduces the intensity of absorption spectra in the ultraviolet (UV) wavelength range. Chlorination experiments with commercial humic and fulvic acid have been carried out to investigate relationships that allow estimation of generated THMs by measuring ultraviolet absorbance depletion ($-\Delta A_\lambda$). Chlorination was quenched by adding excess sodium thiosulphate. This situation allowed to investigate THM *vs* $-\Delta A_\lambda$ relationship in a high UV absorptivity matrix.

Relationship was linear for all reaction interval. Linear equations do not pass through origin indicating the existence of a threshold absorbance depletion, once it is surpassed THMs release begins. Optimum λ for $-\Delta A_\lambda$ computation varied with NOM nature and also with chlorination time. Correlations were quantitative by linear regression. Likewise, r^2 and threshold $-\Delta A_\lambda$ varied with selected wavelength. Lower wavelengths decreased threshold $-\Delta A_\lambda$ up to negative values (THMs are formed without absorbance reduction). The slope (κ) and threshold value for THMs *vs* $-\Delta A_\lambda$ relationship was calculated for different chlorination situations including: natural waters, natural waters spiked with bromide and NOM fractions isolated by DAX and DEAE resin. The presence of bromide significantly increased slope while humics extracted by resin adsorption showed lower κ values.

Poster No. 141:

METHOD DEVELOPMENT FOR THE ANALYSIS OF ACRYLAMIDE IN WATER BY LC-ESI-MS/MS

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The analysis of acrylamide in water samples and in products used for drinking water treatment became extremely important in Quality Control Laboratories. The Council Directive 98/83/EC of 3. November 1998 regarding the quality of water intended for human consumption states a parametric value of 0.1 µg/L for acrylamide. This parametric value refers to the residual monomer concentration in water as calculated according to specifications of the maximum release from polyacrylamide in contact with water. Polyacrylamide flocculants can be used during the treatment of public water supplies. The analysis of acrylamide in water, in order to control this treatment process, can be performed by HPLC with DAD detection using a wavelength of 198 nm, after concentration of the sample under nitrogen flow. However, the presence of several interferences in water matrices compromised sometimes the selectivity of this method and the confirmation of the presence of acrylamide. Multiple Reaction Monitoring (MRM) with tandem MS, coupled to HPLC, provides exceptionally clean product ion chromatograms for quantification and can solve the above interference problems. In this study we optimized several parameters influencing MS signal in order to get the best formation conditions of the precursor ion, using an electrospray ionization source. Two different precursor ion-product ion transitions were selected for acrylamide, one for quantification (MRM1 71,7 → 54,4) and another one for confirmation (71,7 → 71,5), after optimization of the collision cell energy of the triple quadrupole. Linearity range (2.38-34.7 µg/L), detection and quantification limits, precision (RSD=6,8%) and recovery studies of acrylamide in water samples (50.6% recovery with a RSD of 15.7%) were also determined, in order to obtain a full method validation.

Poster No. 142:

DETERMINATION OF Cd AND Pb BY POTENTIOMETRIC STRIPPING ANALYSIS IN THE MUSSEL *Mytilus galloprovincialis* COLLECTED IN BOKA KOTOR BAY (SOUTHERN ADRIATIC)

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Potentiometric stripping analysis (PSA) has been used to determine trace metals in fresh and sea water, food and biological fluids as: human plasma, urine, whole blood and serum [1,2,3,4]. The main advantages of this technique are its high sensitivity and specificity. However, the direct determination of metals in biological samples, using this technique, can be biased by the high level of organic matter. For this reason, most of the stripping procedures always require a preliminary removal of organic constituents to release metallic ions from ligands and to eliminate the problems associated to organic compounds adsorption on the electrode surface.

In this work a PSA technique for determination of Cd and Pb in the mussel *Mytilus galloprovincialis* and reference materials is proposed.

The samples were lyophilized for 48 hours and then digested in a closed-vessel microwave oven; 5 ml of concentrated nitric acid, 10 ml of hydrogen peroxide and 15 ml of de-ionized water were added to 1 gram of the lyophilized sample. PSA was performed utilizing a glassy carbon electrode with a mercury thin film, using dissolved oxygen as an oxidizing agent.

The results obtained in this study, were compared with the ones get using different instrumental methods (AAS and GF-AAS) or by direct analysis of the lyophilized samples *via* EDPXRF (Energy Dispersive Polarised X-Ray Fluorescence).

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2. P. Ostapczuk, Clin. Chem. 38 (1992) 1995
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Poster No. 143:

HPLC-MS SPECTRA OF SELECTED PHARMACEUTICALS USING DIFFERENT MOBILE PHASES

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Pharmaceuticals are regarded as "emerging contaminants" due to the fact that they are only partially metabolized and in this way directly released to the environment. Of all pharmaceuticals, antibiotics are probably the major problem. They seem to be responsible for the appearance of bacterial strains resistant to these drugs, important for treatment of many serious infections. High performance liquid chromatography-mass spectrometry (HPLC-MS) is the most powerful technique for determination of pharmaceuticals at trace levels. In this work it was shown that HPLC-MS spectra of some selected pharmaceuticals seem to be strongly influenced by the choice of mobile phase. The influence of water, methanol and ammonium-acetate was studied. The relative abundances of protonated molecular ions as well as adduct ions were strongly dependent on the mobile phase composition. Finally, it was determined that ammonium-acetate as the mobile phase constituent provided the best mass spectra suitable for quantitative analysis.

Poster No. 144:

CARBENDAZIM RESIDUES IN COMERCIALY AVAILABLE FRUIT JUICES

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Carbendazim is one of the most frequently detected pesticides in the monitoring of fruits and fruit products. It is primarily used to control post-harvest rots and moulds of fruit. There is a special importance in determination of pesticide residues in fruit juices, because children are their principal consumers. A survey on carbendazim residues in commercially available fruit juices, produced by four different domestic companies, was performed. The analytical procedure was based on matrix solid-phase dispersion (MSPD) with diatomaceous earth and analysis of the extracts by high performance liquid chromatography - tandem mass spectrometry, with electrospray ionization (HPLC-ESI-MS/MS). Results of the study showed that many of the investigated fruit juice samples contain carbendazim residues. This confirms that this pesticide is indeed extensively used in fruit juice production. However, the detected levels were always below the MRLs set by the EU.

Poster No. 145:

PROTON BINDING CHARACTERIZATION OF METHYLATED HUMIC ACID

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The most important ionizable sites in humic substances (HS) are carboxyl and phenol groups. Those groups control interaction of HS with heavy metal ions, radioactive metals, pesticides, xenobiotics, influencing on their transport, deposition and bioavailability in waters, soils and sediments. Due to huge environmental importance of those groups, some efforts have been made to determine the content of those functional groups contained in HS, as well as, their contribution to the overall humic proton/ metal interaction. The goal of this paper is to present a new approach in determination of contribution of those groups in the total humic acidity. In that context, proton binding to humic acid (HA) is interpreted by selective blocking of phenolic and carboxylic groups by methylation with $\text{CH}_3\text{I}/\text{Ag}_2\text{O}$, followed by potentiometric titration of underivatized and derivatized HA. Differences in underivatized and derivatized HA's acid-base properties are ascribed to carboxyl and phenol groups influence on total humic acidity. Potentiometric data were treated with the modified Henderson-Hasselbalch equation. Infra red results confirmed the selectivity of proposed derivatization method. Also, the acidic group contents and the average values of apparent pK for underivatized and derivatized HAs confirms selectivity of the applied derivatization methods. After blocking of the functional groups, the value of acidic group content decreased, while the value of apparent pK increased after derivatization. Model of humic acidity can be proposed by obtained quantification and characterization of those ionizable groups.

Poster No. 146:

VALIDATION METHOD OF VOLATILE ORGANIC COMPOUNDS IN WATER BY PT-GC/MS

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Drinking water directive 98/83/EC requires that some volatile organic compounds (VOCs) must be monitored regularly in drinking water, due to its adverse effect in human health. VOCs can appear in drinking water after surface water contamination by industrial discharges, as by-products of water disinfections or by lixiviation from materials used in contact with drinking water.

The analysis of VOCs in drinking water can be performed by gas chromatography coupled to mass spectrometry using a *purge & trap* system for sample preparation (PT-GC/MS). In this study we validated a method for the identification and quantification of the following compounds: vinyl chloride, 1,2-dichloroethane, epichlorohydrin, trichloroethene, tetrachloroethene, carbon tetrachloride, and trihalomethanes (bromoform, bromodichloromethane and dibromochloromethane).

The quantification limits of this method range from 0,01 µg/L (vinyl chloride and dibromochloromethane) to 0,33 µg/L (epichlorohydrin). Recovery studies in several water matrices were performed and results varied from 87,2 to 107,8% recovery with a RSD lower than 12,1%. The accuracy of the method was tested in an interlaboratory assay and met the requirements of 98/83/EC Directive. A detailed analysis of the uncertainty sources of this method is included, which allowed to estimate expanded uncertainties in the 11,1 - 22,6% range.

Poster No. 147:

ZIMOGENOUS STRAIN OF *Bacillus Circulans* FROM ALEKSINAC OIL SHALE: PROPERTIES AND INTERACTIONS WITH SILICEOUS SUBSTRATES

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Bacillus circulans (*B.c.*) is a typical chemoorganoheterotrophic bacterium which uses mono-, di- and polysaccharides and polyhydroxylic alcohols as source of carbon, energy and electrons. The efficiency of removing silicates and aluminosilicates is not the same with all strains of siliceous bacteria. It depends on the nature of silicates as well as on the bacterial metabolic products, primarily on organic acids and the mucous polysaccharide capsules. The activity of *B.c.* is attributed to its metabolites and their specific reactions such as acidolysis, alkalysis and complexolysis.

The siliceous bacterium *Bacillus circulans* was proposed for bacterial desilicification of the same oil shale in biogeotechnology and in agriculture as bacterial preparation.

The zymogenous culture was isolated from Aleksinac oil shale on modified Ashby's medium and tested for special characteristics of the species of genus *Bacillus*. Siliceous bacteria was used for bacterial desilicification of the Aleksinac oil shale. In order to promote aeration the experiments were carried out in central hollow Erlenmeyer flasks, on a rotary shaker at 35°C, with a solid/liquid medium ratio of 1:50 (w/v) for 30 days. Every third day fresh Ashby's medium was added to the substrate with zymogenous strain.

The zymogenous strain was identified as a strain of *Bacillus circulans*, very efficient in the bacterial desilicification of oil shale.

Poster No. 148:

METAL ACCUMULATION IN DECIDUOUS TREE LEAVES IN BELGRADE URBAN AREA

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Accumulation of heavy metals was studied on deciduous tree leaves in the urban area of Belgrade. Leaves of horse chestnut and linden species were assessed for their suitability for monitoring metal pollution. Three city parks were chosen: Studentski park, Karadordev park and Botanic garden. Sampling was conducted on trees at 2 m height in the beginning and in the end of 2002-2004. Metal concentrations were measured using the AAS and INAA techniques. Metal contents for most elements markedly increased in the end of the vegetation season as compared to the beginning. Generally, there was no significant difference in the accumulative properties between the investigated species. Concentrations for some elements (Cu, Pb, Zn, As) were in both species significantly higher at Studentski Park site. It is due to a specific position of this site. Also, a discrepancy was noted for V, being the highest for Karadordev park in both species. This site is traffic-exposed and close to the big junction with high-way. Both examined species can be applied for monitoring of metals in urban environment as clearly show differences in element concentrations depending on sampling site and

Poster No. 149:

EXAMINATION MOBILITY OF TOXIC HEAVY METALS FROM NATURAL CAOLINITE

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The content and mobility of Pb, Cd, Zn and Cu were analysed in natural clays. Leaching of these metals was studied during the different stages of caolinite demineralization with acids. High purity natural caolinite of KGa-1 type (Georgia, USA) was analysed. Potentiometric stripping analysis (PSA) with oxygen as oxidant was employed for metals determination due to its high selectivity and sensitivity. Total content of Pb, Cd and Zn was 8-10 ppm and for Cu it was about 40 ppm. About 60% of Pb and 10% of Cd were released from caolinite sample in weakly acidic solution (acetic acid, pH \approx 2.8) during the 8 hours under standard conditions. During the same period about 10% of Pb and 50% of Cd, Zn and Cu were released under more drastic conditions (cold 6M HCl).

Metals studied in this work are important because they contribute to the contamination of soil and water and they could reach men through the food chain.

Poster No. 150:

β -HYDROXY- β -ARYLALKANOIC ACIDS SELECTIVELY SUPPRESS PROLIFERATION OF FOUR HUMAN TUMOR CELL LINES *IN VITRO*. A QSAR STUDY OF ANTIPROLIFERATIVE ACTIVITY TOWARD HeLa CELLS

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In our previous communication we have reported antiproliferative activity of six β -hydroxy- β -arylalkanoic acids against human cervix carcinoma (HeLa) cells. Present work describe syntheses and determination of antiproliferative activity of eight novel congeners. Compounds were synthesized by modified Reformatsky reaction, starting from aromatic or cikloalkyl aldehydes or ketones, as described previously. Antiproliferative activity were assess using Kenacid Blue R dye binding method, as described in literature. Examined compounds influence proliferation of HeLa, Fem-X, K562 and LS174 cells in concentration range 62-154 μ M/L. Seven of eight examined compounds didn't affect proliferation of healthy human peripheral mononuclear blood cells (PBMC and PBMC+PHA). A QSAR study of antiproliferative activity toward HeLa cells, against which all 14 compounds exert activity, results with two-parameter correlation ($r=0.941$, $F=42.5$, $Q^2=0.810$). The highest weight descriptor in correlation is the estimate log P , while indicator variable that describes the steric demands for the activity has a less weight. Arrangement of H-bond donor, H-bond acceptor and hydrophobic areas within receptor is discussed.

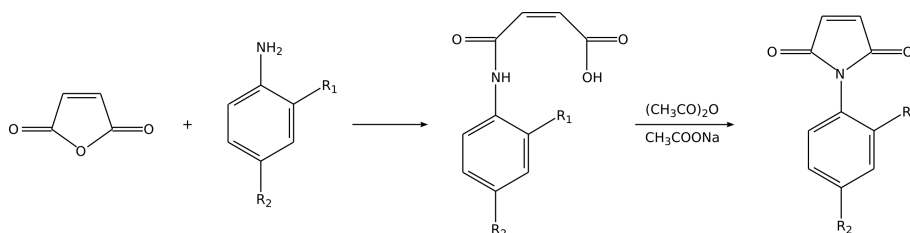
Poster No. 151:

SYNTHESIS OF NEW FUNCTIONAL N-SUBSTITUTED MALEIMIDES AND THEIR COPOLYMERS WITH STYRENE

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The new functional (N-substituted maleimides) maleimide monomers N-(2-methoxy-4-nitrophenyl)maleimide (Ia), N-(4-nitrophenyl)maleimide (Ib), N-(2-nitro-4-methylphenyl)maleimide (Ic), N-(4-carboxy-phenyl)maleimide (Id) and N-(4-N,N-dimethylaminophenyl)maleimide (Ie) were synthesized (Table 1) by the reaction:



I a-e

Table 1: Characteristic data of the obtained maleimides

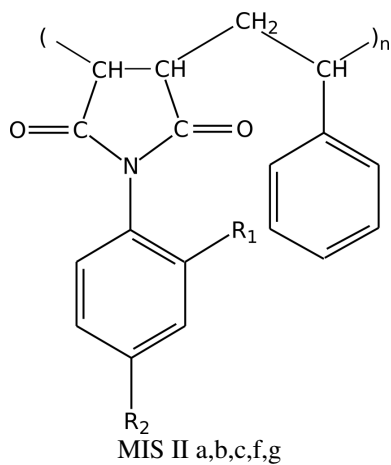
<i>N</i> -substituted maleimides			<i>Formula</i>	<i>%N found (calc.)</i>	<i>M.w.</i>	<i>m.p. °C</i>
	<i>R₁</i>	<i>R₂</i>				
I a	-OCH ₃	-NO ₂	C ₁₁ H ₈ O ₅ N ₂	11.24 (11.28)	248.2	146
I b	-H	-NO ₂	C ₁₀ H ₆ O ₄ N ₂	12.72 (12.84)	218.1	162
I c	-NO ₂	-CH ₃	C ₁₁ H ₈ O ₄ N ₂	11.96 (12.06)	232.2	98
I d	-H	-COOH	C ₁₁ H ₇ O ₄ N	6.38 (6.45)	217.2	228
I e	-H	-N(CH ₃) ₂	C ₁₂ H ₁₂ O ₂ N ₂	12.88 (12.96)	216.1	155

New kind maleimide copolymers with styrene (MIS) were synthesized by radical-initiated copolymerization in a solvent at 60-80°C (with structure MIS II).

Table 2: Copolymerization of *N*-substituted maleimides (*M*₁) with styrene (*M*₂)

MIS II	Yield, %	Copolymer composition, mol%		[η] dl/g
		<i>m</i> ₁	<i>m</i> ₂	
II a	73.5	48.2	51.8	0.42
II b	68.6	47.4	52.6	0.28
II d	81.0	48.8	51.2	0.95
II e	65.8	47.8	52.2	0.46

MIS II a,b,d,e



The characterization of the structure of the maleimide monomers and alternating copolymers was performed by IR and NMR spectroscopy. It was found that the maleimide copolymers MIS have higher stability than the polystyrene.

Poster No. 152:

INVESTIGATION OF CONTEMPORARY PROTECTIVE EQUIPMENT IN FUNCTION OF PHYSIOLOGIC COMPLIANCE

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Introduction: Heat produced during the inaction or physical activities must compensate by heat indulging and is connected with increasing of accumulation. One of the most important devices for chemical protection in the high-toxic environment is chemical protective overgarment (CPO). This suit is designated for protection of high-toxic materials. The construction of suit offers better physiologic compliance than protective equipment based on isolation materials.

Purpose: Investigation of tolerance on uncompensated stress of test people during the wearing four different models of CPO. Investigation are based on simulation of main purposes in the heat environment. For researching of physiologic compliance of NBC overgarment was realized two investigation profiles with engagement of test people: investigations at climatic chamber and cross country investigations, where they worked on primary missions (based on telemetry observing). Comparing of parameters to heat stress and making conclusions about influence of CPO to heat stress intensity and neurophysiological researching.

Methods: Investigations of anthropometric characteristics: measuring a physical height, weight, calculating skin thickness of puckers at four places, calculating area of the body, calculating scale of fattiness and calculating the composition of body mass structure. Ergometric investigations. Investigations of thermoregulation in the climatic chamber. This investigations are realized in the climatic chamber at Military medical academy and technical testing center, designed for final investigation and verification for the Army and defense.

Results: During the investigations of four CPO models are diagnosed the highest statistical differences of importance between the models, based on active carbon flour and model consists of spheres activated carbon materials. The differences are in values of skin temperature and tympanic temperature, heart frequency and sweat intensity. The great differences ascertained in the 55 minutes of experimental working, after that started normalization period. According to One-Way ANOVA statistical test, for tympanic temperature, we reached next values: squares 1,94985954, square 0,649953180, F-Value 6,22939, P-Value 0,00080. During investigations of all CPO models heart frequency was lower than 190/min and experiment were successful. CPO model based on polyurethane foam (PUF) enabled sweat intensity 0,37 L/m²/h, which is small higher from model based on active carbon flour. That difference is more significant comparing to model 2, and the highest comparing to model with "Saratoga" material (~11%).

Conclusion: Only one of the four investigated CPO models, by their characteristics of physiologic compliance, represents optimal choice of protection device and offer longer work in the contaminated area. That is model based on spheres of active charcoal "Saratoga" material, which is suitable for military equipment ABHO and civilian defence units.

Poster No. 153:

OPTIMIZATION OF LC METHOD FOR THE CHARACTERIZATION OF BIOCOMPATIBLE POLYMERS DEGRADATION PRODUCTS

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In this study the degradation behaviour of multifunctional copolymers poly(D,L-lactide-*co*-glycolide) grafted with poly(ethylene glycol) (PLGA-*g*-PEG) additionally modified by itaconic acid (ITA) was observed. These copolymers are biodegradable and biocompatible, and therefore they are widely used for biomedical applications like drug delivery systems or materials for osteosynthesis.

The degradation of the copolymer starts with the absorption of water, followed by the hydrolytic cleavage of ester bonds which generates chain fragments with the acidic groups. This process is characterized by the decrease in molecular weight of sample accompanied by the increase of low molecular chain compound concentration in the surrounding medium.

The object of this study was the optimization of GPC with RI detection for the determination of molecular weight of copolymers and their degradation products and that of RP-HPLC with UV-VIS detection for the identification of low-molecular-weight degradation products.

Acknowledgement: Financial support from Ministry of Education, Youth and Sports under project No. MSM 021630501 is greatly appreciated.

Poster No. 154:

ASSESSMENT OF MINORITY AND MAJORITY PCB CONGENERS IN TISSUES OF BUZZARD

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This pilot study evaluated the presence of both major and minor PCB congeners in birds of prey. Birds of prey were selected as a biotic material that can serve as a suitable bioindicator to monitor the levels of contamination by PCBs.

Efforts have been made to develop a reliable method to allow the processing of matrices in which organic pollutants are determined in intramuscular fat from wild animals. Basic metrological parameters were also established for this developed method.

This developed and validated method was verified by using real samples of buzzards from hunting grounds in the surroundings of Přerov, the Czech Republic. It was shown that the sources which may contribute to contamination cannot be simply identified only on the basis of the spectrum of respective congeners. It appears that this was a contaminated ecosystem since the findings in young animals did not differ too much from those in adults. Secondary contamination from old loads should therefore be considered.

Statistical evaluation could not be performed in detail because of a small number of species available in the experiment. However, this pilot study has shown that dead buzzards can serve as a suitable bioindicator to monitor the level of contamination in various ecosystems.

Acknowledgement: This work was supported by project MSM 6215712402 of Czech Ministry of Education.

Poster No. 155:

NEW ANALYTICAL PROCEDURE FOR ESTIMATION OF THE INFLUENCE OF ECOCHEMICAL TYPE OF SOIL ON THE QUALITY OF WATER IN ACCUMULATION LAKE

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After formation of accumulation lake the quality water sometimes deteriorates due to the interactions of river water and inundated soil. Therefore, it is interesting to develop the methodology for the estimate of influence of ecochemical type of soil in inundation area on the quality of water in accumulation lake.

In this paper the analytical methodology which was applied in inundation zone of the future accumulation Rovni near Valjevo would be presented. It consisted of: (i) sequential extraction of the native samples, (ii) sequential extraction of the same samples after the simulation experiment, and (iii) investigation of the water phase from simulation experiments. Identification of the influence of each ecochemical type of soil and making a prognostic model.

In all ecochemical types of soil there was a distinctive differentiation of chemical and physicochemical parameters with depth. The share of each ecochemical type of soil in the total emission of specific substances was determined. Mixed fraction of intimately bonded hydroxides and the oxides of iron, manganese and aluminum was identified as the main substrate for microelements and phosphorus in the inundation zone.

Poster No. 156:

COMPARING SCANNING ELECTRON MICROSCOPY - ENERGY DISPERSIVE X-RAY SPECTROMETRY WITH INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETRY FOR THE QUANTITATIVE ELEMENTAL DETERMINATION OF SUSPENDED PARTICULATE MATTER

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Increased understanding of the physico-chemical behaviour of estuarine suspended particulate matter is an area of scientific investigation with growing significance, due to the importance of particles in regulating the speciation and destiny of contaminants and nutrients in the aquatic environment. This study compares the use of Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES) with Scanning Electron Microscopy - Energy Dispersive X-ray Spectrometry (SEM-EDS) in determining the elements Al, Fe, Mg, Si, Zn, Mn, Ca, K and Ti in an estuarine Certified Reference Material (CRM). Initial comparisons involved the processes for preparation of samples for analysis. ICP-AES required a LiBO₂ fusion process in order to release Al. SEM-EDS required the production of polished resin stubs containing the CRM. Following analysis of fifteen scans from the ICP-AES and analysis of 100 individual particles by SEM-EDS, no significant difference was found between the medians for Al, Fe, Mg, Ca and K. Generally, good correlation was observed between instrument and reference values. Significant difference was observed between medians of Mn and Ti, while the Si value was not established as a reliable reference. Trace Zn was not determined by SEM-EDS and the instrument performed poorly on Mn and Ti, which were also present at trace levels. The ICP-AES values correlated closely with CRM values throughout, except for K, which it undervalued substantially. Investigation led to questioning aspects of the digest process, though no causal link was established. Qualitative elemental mapping techniques were performed on SEM-EDS. The results were mainly illustrative but showed potential for further development.

Poster No. 157:

ION CHROMATOGRAPHIC DETERMINATION OF ANIONS AT LOW LEVEL IN POWER PLANT WATER

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Inorganic anions (Cl^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-}) from pure water of the Nikola Tesla Thermal-Energy Plant were determined by ion chromatography (IC). Isocratic separation was performed by injecting high sample volume directly into the chromatographic system. No any pre-concentration step was used. $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ was used as an eluant and the detection was carried out with a suppressed conductivity detector, after separation on an IonPac AS14 column. Calibration graphs, for all analyzed anions, are linear in the analyzed range, with correlation coefficients, $r=0.9999$. Obtained concentrations faals in the range of 0.01 to 20 ppm. Detection limit is 0.01 ppm. The method is simple, rapid and reliable. In general, this IC method can be considered as a method of choice for anions analysis at the low ppb level.

Poster No. 158:

COMPARATIVE ANALYSIS OF ARSENIC DETERMINATION IN COAL AND COAL ASH WITH DIFFERENT SAMPLES PREPARING METHODS

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Coal is one of the most important sources of energy. Its worldwide use will continue to expand during the next several decades due to its relatively abundant reserves. Unfortunately, the pollutant emissions from coal utilization may cause serious environmental and health risks, so it becomes an important issue with respect to environment protection. The concern about the behavior of trace elements during coal combustion is a relatively new subject. Arsenic, as a very toxic element, is found in coal and coal ash in various concentrations, depending of coal origin. Determination of arsenic in coal and coal ash is connected with serious problems due to arsenic different occurrence mode in them. In coal, arsenic has a strong affinity to concentrate in sulfate minerals. The mode of occurrence of arsenic in fly ash depends upon the composition of the original coal and its derivative fly ash, and on conditions during coal combustion, particularly during cooling.

In this paper different digestion procedures (1-3) for determination of arsenic in coal and coal ash were employed with the aim to compare them. The sample of coal was collected from the coal basin "Tamnava-West field". Coal ash was prepared by coal combustion at the temperature of 815°C. The content of arsenic was determined by atomic absorption spectrometer Perkin Elmer AAnalyst 200 model with Mercury Hydride System (MHS 15). Although many facts have influence on the results, the effects they cause are not very considerable.

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Poster No. 159:

EFFECT OF SOIL COMPOSITION AND DOM ON ROTENONE SORPTION, DECOMPOSITION AND MOBILITY

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The retention and mobility of a pesticide in the soil is determined by the extent and strength of sorption reactions, which are governed by the chemical and physical properties of soils and pesticides involved. Although rotenone has been used as a commercial product for many years, there are very limited studies in the literature regarding its residues, mobility and adsorption in soils. Furthermore, additional data are needed on rotenone metabolism and derived metabolites in the soil-plant system.

In this study, rotenone application to plants grown in greenhouse will be investigated in the order to estimate: **i)** the relationship between rotenone and various soil amendments (liquid and solid ones); **ii)** the relationship between rotenone and dissolved organic matter (DOM) released by different substrates; **iii)** the potential mobility of rotenone and its two major metabolites in the soil and into the plant tissues. Thorough physical-chemical characteristic of soil and amendments will be performed by means of spectroscopic and chromatographic approach.

Poster No. 160:

GC-MS AND IR SPECTROSCOPY AS A WIDESPREAD ANALYTICAL METHODS FOR IDENTIFICATION AND QUANTIFICATION OF HYDROCARBONS IN SOIL AND WATER

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This paper presents study of water and soil contamination, focused on analysis of specific group of hydrocarbons, which are known to be a wide spread contamination in soil and water due to industrial activities or unintended spill. After the NATO destruction of the Novi Sad Oil Refinery large amount of crude oil and its derivatives (mineral oils), oil hydrocarbons and polycyclic hydrocarbons (PAH) were split out. By destroying the factory installations, 73569 tons of crude oil were lost, 90% burnt, 5600 tons were discharged into the river Danube, and the rest was spilled over the soil. This study mostly considered water and soil contamination, since the largest pollution was and still is within the Refinery area. Contaminated water and soil samples have been taken from Refinery area near destroyed tanks, from surface and deep down layers. In this work GC-MS method for PAH determination was developed, with emphasis on sample preparation procedure - Solid Phase Extraction (SPE). Gas Chromatography coupled with the Mass Spectrometry (GC-MS) was used for identification and quantification of Polycyclic Aromatic Hydrocarbons (PAH) in soil and water, as well as for identification of mineral oil (Hydrocarbon-CH) content. Infrared Spectrophotometer (IR) was used for determination of oil content in water. High concentration of hydrocarbons were measured in analyzed samples. On the basis of Environmental Protection Agency (EPA) criteria and the results of this study it can be concluded that soil and water in Refinery area are highly contaminated. This work has significant contribution in evaluating the degree of contamination in NATO bombarded area of Refinery and helps to evaluate how a contaminated material has to be sanitized.

Poster No. 161:

RADIOANALYTICAL INVESTIGATIONS AT FLNP JINR: STATE OF THE ART

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In spite of competing non-nuclear analytical techniques (AAS, ICP-ES, ICP-MS, etc), reactor **neutron activation analysis** is continuing to be the most powerful multi-element analytical technique used in geosciences, life sciences and material sciences. Radioanalytical complex REGATA at the IBR-2 reactor for more than 20 years of operation has become a source of analytical data for a considerable number of international projects carried out with JINR member and non-member states. They are supported by grants of JINR Plenipotentiaries (Bulgaria, Czech Republic, Poland, Slovakia, Romania). All together they are joined in the JINR project REGATA (2000-2004) dedicated to **air pollution studies** in the above countries and Central Russia, South Urals, Bosnia and Herzegovina, Serbia and Montenegro, Macedonia (FYROM), and Western Ukraine. The results obtained in Dubna are reported to the European Atlas of *"Atmospheric deposition of heavy metals in Europe - estimates on the basis of the analysis of mosses"* edited each 5 years under the aegis of the UNO Commission of transboundary transport of atmospheric deposition in Europe (UNECE ICP Vegetation). The next all-European moss survey will be in 2005. Several more research groups from Greece and Turkey, as well as from some Asian countries (Vietnam, Mongolia and China) expressed their desire to joint our activity in this field. This led to a suggestion to prolong the JINR project REGATA for 2005-2007 with extension to Asian countries besides Eastern Europe and Balkans. The other newly developing trend of applying NAA in life sciences is **food quality and safety**. IAEA Technical Cooperation (2003-2005) and IAEA Co-ordinated Research Programme (2002-2004) support these studies. The year of 2004 is the final for our project in 5th Frame Programme of EU: *"Workplace monitoring and health-related studies at fertilizer plants in Russia, Poland, Romania, and Uzbekistan"*. Our intense and productive cooperation since 1999 with the Georgian scientists in developing new pharmaceuticals (selenium- and chromium-contating) and sorbents of toxic elements (mercury, uranium, etc) based on blue-green micro-alga *Spirulina platensis* (**biotechnology**) resulted in two patents, the necessary prerequisites for production of *Spirulina* derivatives for food, perfume and medical needs. Non-destructive NAA is the only analytical technique for studying high-performance technology of producing **fine crystalline diamond powders** for manufacturing composite materials and abrasive disks. Together with specialists from Minsk, Belarus, we have submitted the same name project (2004) to the EURO-TECH foundation in Brussels for innovation technologies. Department of NAA serves a basis for training young specialists in nuclear analytical techniques. A special course *"NAA for studying the Environment"* and practicals at the radioanalytical complex REGATA are offered for graduate and undergraduate students from the University of Dubna and JINR member-states. Every year 5-6 Master and Bachelor diploma are prepared, one Ph.D. thesis is defended (2003), and another three are in progress.

Poster No. 162:

ION MOBILITIES THROUGH POLYMERIC EXCHANGE MEMBRANES

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Proton ion exchange membranes (PEMFC) are used as electrolytes for energy conversion devices such as fuel cells. These cationic membranes based on perfluorosulfonated polymers act like a physical barrier between anode and cathode avoiding direct contact between hydrogen and oxygen, but allowing transport of protons from anode to cathode side at a rate enough to fulfill energy requirements. In this work, diffusion of several cations through the membrane was studied in a two compartment diffusion cell own designed, which consists of two semicells of 250 mL each one. The potential drop through the membrane was fixed at desired values using two Ag/AgCl reversible electrodes. The objective of present work was to study the diffusion of proton, potassium, and barium. Effects of the presence of potassium and barium in the diffusion of protons through the membrane were also studied. Diffusion of counter-ions (proton, potassium and Barium) and co-ion (chloride) was followed measuring pH and conductivity of diluted dissolution and potential drop across membrane using an Ag/AgCl electrode to measure potential drop between reference electrode at one side of the membrane and working electrode placed at the other side. Potential drop through the membrane was calculated subtracting from total drop the contributions due to Nernst potential in working electrode and reference electrode. Several experiments were carried out using initial concentrations between 10^{-3}M to 0.1M for hydrogen, potassium and barium chloride solutions. Results were modelled using Nernst-Planck equations. Diffusion coefficients obtained were in the range 10^{-8} - $10^{-9}\text{ cm}^2/\text{s}$.

Poster No. 163:

INDUCTION OF COLOURED INTERMEDIATES WITH FENTON REAGENT

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Fenton reagent is an effective treatment to oxidise phenolic compounds down to concentrations accepted by legislation, but water oxidized shows a dark brown colour that it must be removed. This colour indicates the presence of toxic intermediates that can produce condensation compounds, difficult to degrade. Colour generated during the phenol oxidation has a multi-source origin. Here is demonstrated the contribution of different reaction species. During the first mechanism steps, phenol is degraded to dihydroxylated rings (catechol and hydroquinone). On one hand, these intermediate species can react with iron catalyst producing colour metal complexes. On the other hand they are oxidated to quinones (o-benzoquinone and p-benzoquinone), higher coloured compounds. Hydroquinone and catechol are colourless compounds but they generate a dark colour complex with quinone compounds, called quinhydrone. This kind of complex is defined as a charge transfer complex.

So colour can be a control parameter of the mineralization degree achieved with the oxidation treatment. The conditions for the complete colour removal have been studied, checking that Fenton reagent is an effective treatment to oxidise phenolic compounds and also can degrade the colour generated in the water operating under more drastic conditions. The minimum conditions required are the following, working at pH 3.0: molar ratio 10 mol H_2O_2 /mol $\text{C}_6\text{H}_6\text{O}$, ferrous ion concentrations of 20 mg/L, and reaction time around 24 hours.

Poster No. 164:

RELATIONSHIP BETWEEN THE OXIDATION DEGREE AND REDOX POTENTIAL DURING THE FENTON REACTION

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The main advantage of the advanced oxidation technologies is that they can work at low cost for usual operating conditions. But industrial application with real wastewater also requires a fast, accurate and reliable analysis method to check the depuration degree. Redox potential control requires installation and working costs lower than other alternatives. It makes that redox potential is a relevant parameter to check the state of water under oxidation treatment.

Although redox potential is a relatively simple concept, requires careful conditions to obtain real data about the process state, because measurements depend on different parameters like pH, temperature, equilibrium constant, oxygen concentration and species dissolved in water. Consequently its application in wastewaters depuration has only an empirically use, because usually poor information can be taken from data. Although redox potential have been analysed in several studies, its application for control processes is rare. Then it has been here necessary to normalize the redox measurement to obtain information with practical interest.

This work has analyzed the redox potential measurements obtained during the phenol oxidation working at low pH, and molar ratios of oxidant to phenol up to 14 mol H_2O_2 /mol $\text{C}_6\text{H}_6\text{O}$ and testing different catalyst concentrations up to 20 mg/L of ferrous iron. During the oxidation, reaction redox potential falls to minimum value that later on increases to a constant value. This minimum is related with the concentration of dihydroxylated rings and general operation conditions. When reaction intermediates are degraded to biodegradable acids, redox increases to achieve a stable value.

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