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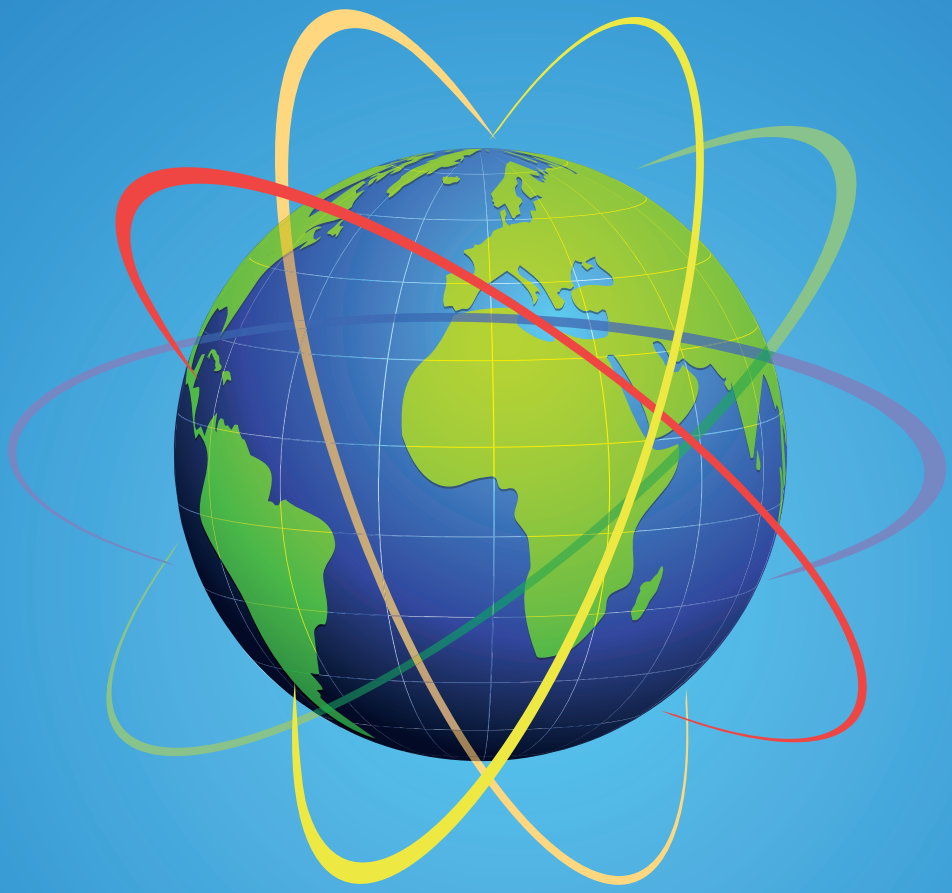

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TOPIC 1

CONCEPTUAL FRAMING

ABSTRACT NUMBER
180

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Attenuation of Escherichia coli in river water introduced in saturated zone soil

Ying Guan 10279807@qq.com Third Institute of Oceanography, SOA- China
Jinkeng Wang Wangjinkeng@tio.org.cn Third Institute of Oceanography, SOA- China
Ping Zhang Zhangping@tio.org.cn Third Institute of Oceanography, SOA- China

In the recent years, with the acceleration of urbanization and industrialization among major coastal economic zones, and the extensive and decentralized development models for marine economy, now the development of oceans is in disordered, and the coastal resources are severely wasted. Meanwhile, due to the excessive exploitation of marine resources, coastal waters are facing serious environment stress, the conflict between protection and development of marine resources is getting increasingly acute. The paper explains the concept of marine ecological red line and the situation of the marine resources and environment, analyzes the necessity of delimiting the marine ecological red line. Through studying some successful cases in the field of marine ecological management from coastal developed countries, we discuss about establishing the principles of marine ecological red line system, which will provide some practical ideas for the following delimiting marine ecological red line work

TOPIC 2

TOOLS, METRICS AND INDICATORS

ABSTRACTS NUMBERS
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Estimating clean-up costs according to site-specific conditions and technologies to be applied

Alessandra Marino a.marino@inail.it INAIL ex ISPESL, Rome - Italy
Giuseppe Buccheri g.buccheri@inail.it INAIL ex ISPESL, Rome - Italy
Mara Ciucci m.ciucci@tiscali.it CNR, IIA – Italy

This article reports about steps needed in order to develop cost estimates during feasibility studies, including aspects connected to the alternative remediation techniques, which should be applied while respecting safety criteria provided for workers (including remediation operators) and residents.
When site-specific information is available about a site to be cleaned up, costs can be estimated by using a site-specific approach, which generally provides more reliable estimates in comparison with other kinds of approaches. In spite of it, it requires at the same time the highest level of information about polluted sites. Where enough site-specific information about a polluted site is available (especially about contamination nature and extent), the latter can be directly used in order to build a defendable cost estimate.
The uncertainty of site-specific cost estimates is up to the level of project definition, including nature and extent of contamination, migration ways and targets, as well as feasibility of remediation technologies. Some uncertainty must be considered, anyway, even when site-specific information is available, because nobody is able to predict at a perfect way every technical, legal, administrative situation which can occur during a remediation process.

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Precipitation of zinc in agricultural calcareous soils as a natural attenuation mechanism to avoid groundwater contamination

Vicenç Martí vicens.marti@upc.edu Universidad Politécnica Catalunya - Spain
María Martínez rosario.martinez@upc.edu Universidad Politécnica Catalunya - Spain
Sílvia González silvia15889@gmail.com Universidad Politécnica Catalunya - Spain
Josep Olivia josep.oliva@upc.edu Universidad Politécnica Catalunya - Spain

The excess of synthetic and natural fertilizers (manures) added to agricultural soils is a well-known potential source of contamination of heavy metals such as zinc (Alloway, 2010). The present communication shows the results of equilibrium and kinetic experiments on the precipitation of zinc in a calcareous soil (24% CaCO3) from Arbeca and in calcite (97% CaCO3) from Garraf (both

from NE, Spain). Equilibrium batch experiments ranging from 25 to 2000 mg of soil or calcite and 2,5 to 60 mg•L-1 of initial concentration of zinc showed a 90%-95% of zinc elimination from solution, which could be due to sorption or precipitation. In the case of the soil, although the fitting of equilibrium data to a Freundlich isotherm was satisfactory, the high amount of zinc eliminated in comparison with previous works (Jalali and N. Ahmadi, 2012) and the alkaline pH measured (8-10) seemed to indicate that precipitation occurred. The thermodynamically stable solid phase determined by the Hydra-Medusa software (Puigdomènech, 2004) was $ZnCO_3 \cdot H_2O$, but theoretical concentrations were below the experimental values, suggesting the presence of other Zn species in solution not included in the model, such as Zn-phosphates. In the case of the calcite, the results of the model indicated the precipitation of $Zn_5(OH)_6(CO_3)_2$ and predicted solubility matched very well with experimental results.
In order to confirm that the decrease of Zn in solution was due to the precipitation with carbonate, a sequential extraction of zinc was carried out, consisting in a first extraction with sodium acetate (to evaluate the adsorbed zinc) and a subsequent full BCR sequential extraction procedure (which allowed the determination of the Zn associated to carbonates, iron and manganese oxides, organic matter and residual zinc). Results showed that the part associated to carbonates was predominant in soil and also in experiments with Zn and calcite.
In addition, a percolation test performed with the soil equilibrated with zinc showed that after 18.9 pore volumes, the breakthrough of Zn did not occur, confirming the precipitation of Zn instead of a sorption process. These results confirmed the stability of Zn-precipitated phases, which resulted in a very high capacity of calcareous soils to retain the zinc linked to fertilizers, retarding the zinc impact on groundwater. The present research work was performed under the project ATTENUATION (CGL2011-29975-C04-0) funded by Spanish Ministry of Science and Innovation.

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Use of soil respirometry in sustainable hydrocarbon bioremediation; from site investigation to endpoint evaluation

Thomas Aspray t.j.aspray@hw.ac.uk Heriot Watt University –UK

Ex situ bioremediation of hydrocarbon contaminated soils involving the addition of inorganic or organic nutrients (biostimulation) is a sustainable and cost effective alternative to landfill disposal. However, largely driven by natural processes, the application of bioremediation is not without risk for the stakeholders involved (i.e. clients, consultants and remediation contractors). Therefore, methods that can be used to monitor microbial activity in soil, highlighting nutrient limitation or

toxicity issues, and helping to predict the rate of biodegradation (alongside contaminant analysis) are of real interest.

A wide variety of methods are available to monitor microbial activity in soils including for example those based on traditional enzyme assays, as well as, more modern molecular biology techniques. However, their contribution to supporting decision making for bioremediation in a commercial context is limited. As such there has been limited take up of these methods by industry. In the case of molecular biology, there is need for industry education on the breadth of techniques, as well as, further method development before this can change.

Metabolic gas respirometry involving the measurement of either O2 consumption and/or CO2 production from soil to assess soil microbial activity is a method already showing promise but with potential for further application. Specifically the ability to measure community and population level activity, nutrient limitation, chemical toxicity, and assess catabolic diversity through a single method is unparalleled. Most respiration assays generally requires inexpensive reagents and can be carried out with basic laboratory components. To reduce labor demand, which is often in short supply, automated respirometers can be used. Here we demonstrate the benefit of respirometry for full scale commercial bioremediation projects. In addition, we highlight the potential further benefits of soil respirometry from site investigation to endpoint evaluation.

TOPIC 3

"GREENING" REMEDIATION ECO - EFFICIENT TECHNOLOGIES AND OPPORTUNITIES FROM SYNERGY

ABSTRACTS NUMBERS
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Dagmawi Degefu dagmawimulugeta@gmail.com - Addis Ababa University - Ethiopia
Mekibib Dawit mekibib1@hotmail.com - Addis Ababa University – Ethiopia

Finding an environmentally safe, cost effective method which is efficient enough to meet the regulatory standards of potable and industrial wastewater presents unique challenges. In this work, Moringa stenopetala seed powder which had particle size of 300 µm was characterized; ash content 4.7%, bulk density 0.531/cm3, particle density 0.88 g/cm3, color yellowish and pH 4.5. FT-IR (Fourier Transform Infrared Spectroscopy) analysis showed the multi-functionality of the Moringa stenopetala seed powder. Moringa stenopetala seed powder was assessed for percentage chromium removal and mg/g chromium uptake as a function of contact time, pH, and dose of the adsorbent and initial concentration. The maximum percent removal was 99.74%. Sorption kinetics of chromium adsorption by Moringa stenopetala seed powder was predicted reliably using a pseudo-second order model. An intra-particle diffusion model revealed that the bio-sorption of metals proceeds via through various processes. Equilibrium uptakes were evaluated using Langmuir, Freundlich, Temkin and the Dubinin-Radushkevich (D-R) adsorption isotherm models. Even though the correlation coefficient was not as high as the Langmuir and Ferendulich models for Temkin adsorption isotherm model, the metal uptake which was predicted by the model is comparable with the experimental value. Generally, the seed powder of Moringa stenopetala was found to be effective in the removal of chromium from tannery wastewater.

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Functionalized SBA-15 silica as sorbent for the slow release of the pesticide pentachlorophenol in soil

Paul Diagboya pauldn2@yahoo.com University of Ibadan - Nigeria
Bamidele Olu-Owolabi iromidayobamidele@yahoo.co.uk University of Ibadan - Nigeria
Kayode Abedowale adebowale2003@yahoo.com University of Ibadan – Nigeria

The need for prolonging the biological efficacy of agricultural pesticides as well as reducing their adverse environmental effects has stimulated the search for pesticide-slow-release formulations in soils. Synthesized amine and tripolyphosphate functionalized mesoporous silica SBA-15 (SA and ST, respectively) were studied as sorbents and supports for slow release of a pesticide (pentachlorophenol - PCP) in a soil (MG) with low sorption and low hysteresis for PCP. Results revealed that PCP sorptions were higher (>80 %) in SA and ST than in pristine SBA-15.

Adsorptive pore-filling and electrostatic interactions were implicated in the removal of PCP from solution, and the processes were controlled by two mechanisms: intra-particle and equilibrium diffusion. Electrostatic interaction (within and outside SBA-15 mesopores) led to ≥75 % increase in sorption upon functionalization. Desorption hysteresis was low (high release) for SBA-15 but very high (slow release) for SA and ST. MG soil amendment using 1.0 % SA or ST caused ≥80 % PCP sorption and higher hysteresis (slow release) in MG soil, and resulted in retarded release of PCP into aqueous solution and reduced pesticide leaching. These results showed potential usefulness of amine and tripolyphosphate functionalized mesoporous silica SBA-15 as suitable supports in the design of pesticide-slow-release formulations that can reduce the adverse environmental effects of agricultural pesticides applied to soils.

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Mechanisms of benzene and lead removal from groundwater by permeable barriers with selected reactive materials

Franklin Obiri - Nyarko franklin.obiri.nyarko@hydrogeotechnika.pl Hydrogeotechnika sp zo.o - Poland
Jolanta Kwiatkowska - Malina j.kwiatkowska@gik.pw.edu Warsaw University of Technology - Poland
Grzegorz Malina gmalina@agh.edu.pl Agh University of Science and Technology
Tomasz Kasela tomasz.kasela@hydrogeotechnika.pl Hydrogeotechnika sp zo.o - Poland

Permeable reactive barriers (PRBs) have shown great promise in attenuating a variety of contaminants. The removal of contaminants is achieved by placing a reactive medium across the flow trajectory of the contaminant plume to sequester or breakdown the contaminants to less hazardous compounds using one or more mechanisms such as adsorption, precipitation and biodegradation. Understanding the removal mechanism(s), together with other factors such as the groundwater geochemistry enable the selection of the suitable media and the design of an efficient PRB system for contaminant removal. Laboratory studies were conducted to investigate the mechanisms utilized by selected materials intended to be applied in a PBR for the simultaneous removal of heavy metals and BTEX (benzene, toluene, ethylbenzene, and xylene) from groundwater. The reactive materials were: zeolite, brown coal and their mixtures with municipal derived compost in different ratios. In the experiments, we focused on lead and benzene because of their ubiquity, mobility in groundwater and toxicity effects on humans and other life forms. The results indicated that benzene and lead were removed by the materials mainly via sorption and ion-exchange, respectively. Other mechanisms such as biodegradation and precipitation were also observed, but their contributions varied depending on the reactive materials used.

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Removal of metals from aqueous solution using bentonite modified with carica papaya seeds and pine cone

Bamidele Olu-Owolabi iromidayobamidele@yahoo.co.uk University of Ibadan, Nigeria -Nigeria
Leonard Boehm Leonard.Boehm@umwelt.uni-giessen.de Justus Liebig University, Giessen-

Germany
Emmanuel Unuabonah iyaemma@yahoo.com Redeemer's University, Ogun State-Nigeria
Paul Diagboya pauldn2@yahoo.com University of Ibadan- Nigeria

Recent studies have shown that clays modified with biosorbents are promising adsorbents for the removal of metals from aqueous solution. In this study, bentonite (B) clay was modified using carica papaya seeds and pine cone to obtain carica papaya modified bentonite (BP) and pine cone modified bentonite (BPI). The efficiency of these adsorbents for the removal of Pb(II), Cu(II), and Cd(II) ions from aqueous solutions was studied as a function of pH, time, sorbate concentration, and temperature. X-ray diffraction results showed that the modification did not cause any change in the lattice structure of the bentonite clay, but a reduction in the surface areas of the modified clays was observed. Adsorption results showed that pH did not significantly affect removal of metal species from solution between pH 3 and 7. Kinetics studies indicated that the adsorption followed the pseudo-second order model and the mechanisms were mainly surface phenomena involving sharing of electrons between the adsorbent surfaces and the metal ion species as shown by the intra-particle diffusion model. The equilibrium data fitted the Freundlich isotherm model and the n values (<1.5) showed the heterogeneity of the adsorption sites. Thermodynamic studies revealed that the adsorption process was spontaneous and exothermic characterized by reduced metals' adsorption with increase in temperature. Bio-modification of bentonite did not significantly enhance removal of Pb(II), Cu(II), and Cd(II) ions from aqueous solution.

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Modeling mass transfer coefficients at laboratory scale for in situ SMARTSTRIPPING® upscaling

Irene Jubany irene.jubany@ctm.com.es CTM, Technological Centre Foundation - Spain
Montse Calderer montse.calderer@ctm.com.es CTM, Technological Centre Foundation - Spain
Roberto Verri rv@ecosurvey.it Ecosurvey - Italy
Vincens Martì vicens.marti@upc.eduUniversitat Politécnica Catalunya - Spain

The technology called SmartStripping® is an innovative process for groundwater in-situ remediation that reduces concentrations of Chlorinated Aliphatic Hydrocarbons (CAHs) dissolved in groundwater. The process can be defined as an innovative combination of Air Sparging (AS) and Soil Vapour Extraction (SVE): groundwater remediation occurs by enabling a transfer of contaminants from a saturated zone (groundwater) to an unsaturated zone (vadose) by blowing heated air from existing wells, which then enables groundwater stripping from the aquifer. The stripping allows the separation of CAHs from groundwater that vent up to the unsaturated zone which is under a continuous vacuum status, whereby the soil vapour is extracted. Vapours are treated with granular activated carbon (GAC) adsorption filters before being re-injected into the groundwater to start the stripping process again, through a continuous closed air-cycle system. (Smartstripping 2014).
The application of this technology in each specific site needs the use of a comprehensive modelling and lab scale experiments for an optimal design of removal of volatiles as a function of operational parameters, from which air flow is the most relevant. In the present work, a combination of hydrodynamic and mass transfer model is developed and calibrated with specific laboratory tests.

The hydrodynamic model allows to obtain a region of air bubbling considered continuously stirred that defines a perfectly mixed volume (Vr) where an exchange between liquid and air phases due to an overall mass transfer is assumed (Perry & Green, 2008). Inside this volume, a gas flow extracts the contaminant (stripping). Furthermore, there exists a lateral input due to the gradient between the initial concentration of contaminant in aquifer (Co) and the concentration of the bubbling zone (C). Under steady-state conditions the lateral flux is equal to the flux of extracted volatile through the gas flow.
By using these elements, three mass balances of volatile contaminant have been performed in the bubble-water interface, in the water and in the air. From these balances, the rate of removal of volatile contaminant, the concentration (C) and the partial pressure (p) of volatile contaminant in the exit flow gas could be obtained as a function of time. The developed model was calibrated by using an in-situ stripping lab experiment consisting in a plastic vessel filled with sand and an aqueous solution of ethanol 1.2•10-3 mol.L-1 in which air was bubbled at 1.3 L•min-1. The dissolved organic carbon was measured at different times for 25 days. The volume Vr was calculated assuming a conical bubbling shape. Experimental data was fitted to the model by using the Polymath Software 6.20 to solve the differential equations and obtain values for mass transfer coefficients. Calibrated model can be used to improve the knowledge of the whole system and , thus, the design of the remediation strategy for different volatiles.

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Restoration of the lakeshore wetland ecosystem with strong wind wave and ferroconcrete wall bank

Weiping Hu wphu@niglas.ac.cn Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences-China
Jinge Zhu jgzhu@niglas.ac.cn Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences-China
Weiwei Xu wphu@niglas.ac.cn Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences - China
Jiancai Deng jcdeng@niglas.ac.cn Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences- China

Lake shore wetlands play extremely important roles such as water purification, nutrients transformation, and ecosystem biodiversity, recognized as an important part of aquatic ecosystems in a lake. As the development of economy and society, large amounts of pollutant have been discharged to lakes.

Lacustrine ecosystem and water quality have been suffering from deterioration. It has been of great interest to researchers to restore lake side wetlands ecosystem and enhance its capacity of water purification. For construction land, agricultural land and flood control safety, ferroconcrete wall banks have been constructed along the original coast line or the place near it in many lakes in the world, inducing relative strong wind wave, sediment scouring and the deep water in littoral zone in the past decades. Therefore the ecosystem and water quality have degraded even more badly in the littoral zone with strong wind wave and ferroconcrete wall bank because of superimposed metamorphism of ferroconcrete wall banks and pollutant discharge. Due to the strong wind wave and relative deep water in lakeside wetlands with ferroconcrete wall bank, the successful restorations of the lake shore wetlands have rarely been reported at present.
Aim to restore lake shore wetlands ecosystem with strong wind wave and ferroconcrete wall bank, a series of experiments have been carried out for developing suitable technologies of habitat restoration such as wave attenuation, basement repair, lake bed erosion control, as well as plant cultivation, community stabilization. Submerged breakwater, latent island, emerged plant breakwater composed of ferroconcrete ecological bowls which can dissipate wave and prevent the bed erosion have been developed. And the seed- cultivation with gabion box for the recovery of leaf-floating plant Trapa bispinosa and membrane-cover cultivation for planting Zizania latifolia and Phragmites communis Trin (PCT) have been impoldered also.
For the application demonstration, the above technologies have been integrated to a lake shore wetlands ecosystem restoration of an area with length of 650 meters and width of 100 meters without any aquatic plant in Zhushan Bay of Lake Taihu, China, which is one of the largest fresh water lakes. The results show submerged breakwater, latent island, emerged plant breakwater composed of ecological bowls significantly reduced wave intensity by 60.0% and increased 20 cm ~ 30 cm sedimentation. While the sedimentation in the control area was less than 10cm in a year. Those means a suitable lake bed and habitat conditions for aquatic plants to grow have been recovered in the area. Therefore, there grows potamogeton crispus Lour and Trapa bispinosa with coverage more than 30% in the littoral zone of the area and Phragmites communis Trin community with coverage more than 90% in the eulittoral zone. Simultaneously, more plant species such as Ctratophyllum demersum Lour, Cabomba caroliniana, Jussiaea stipulacea Ohwi, Alternanthera philoxeroides, Sparganium racemosum Huds, Vallisneria spiralis L., Hemarthria cornpressa, Scirpus validus Vahl., Acorus calamus et ac. were observed in the demonstrative area, indicating that biological diversity increased dramatically.

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Atmospheric Pressure DBD-based Air Plasma for Soil Remediation

Christos Aggelopoulos caggelop@iceht.forth.gr Foundation for Research and Technology Hellas - Institute of Chemical Engineering Sciences (FORTH/ICE-HT)-Greece
Panagiotis Svarnas University of Patras - Electrical and Computer Engineering Department- Greece
Agamemnonas Kalaitzis University of Patras - Electrical and Computer Engineering Department- Greece
Christos Tsakiroglou Foundation for Research and Technology Hellas - Institute of Chemical Engineering Sciences (FORTH/ICE-HT) – Greece

Soil pollution by non-aqueous phase liquids (NAPLs) could affect the human health seriously. For NAPL abatement, various soil remediation methods have been proposed, such as thermal desorption, bioremediation, etc. Due to some drawbacks of the conventional remediation technologies, such as high energy requirements and secondary pollution, it is of crucial importance to develop cost-effective and highly efficient methods for soil remediation.
Recently, Advanced Oxidation Processes (AOPs) constitute promising technologies for pollution control. Non-thermal plasmas of electrical discharges are considered a highly competitive technology for the removal of organic pollutants, among the AOPs. Plasma-based technologies take advantage of the formation of highly reactive chemical agents without the need of wet chemistry and avoiding byproducts.
In this paper, a “disc-to-mesh” of cylindrical symmetry Dielectric Barrier Discharge (DBD) reactor operates at atmospheric-pressure air and is employed to remove NAPLs from soil layers. The synthetic NAPL is a mixture of three n-alkanes (n-C10, n-C12 and n-C16) at equal mass concentrations (w/w), whereas the soil is well-sorted silicate sand (grain size 125-250 μm). The soil is contaminated with NAPL by mixing pre-weighted amounts of soil samples with NAPL solutions in acetone and then it is placed into a fume hood until the acetone evaporation being completed. In this manner, an initial NAPL concentration equal to 100 g/ kg-soil is obtained.
The plasma reactor is a cylindrical vessel made of borosilicate glass having 124 mm inner diameter and 100 mm length. The stressed electrode is a stainless steel disc (Ø 50 mm, thickness 3mm) covered by quartz dielectric of 2 mm thickness. The grounded electrode is a stainless steel mesh (Ø 46 mm) playing the role of the sample holder and allowing free air flow through the mesh/sample. The air flow is vertical at a constant rate of 2 standard liters per minute and the electrode gap is fixed at about 7 mm. The contaminated soil is spread uniformly on the ground electrode with its mass (dry) ranging from 2.5 to 7.5 g and its corresponding thickness from 1.3 to 4.0 mm. The biasing voltage is provided by a custom-made AC high voltage power supply (10 kHz, 0-30 kV peak-to-peak) and its waveform is monitored on a digital oscilloscope. The plasma actual power is well approximated by considering an equivalent discharge circuit to substrate the displacement current. The concentration of NAPL compounds in the soil is measured by Gas Chromatography-Flame Ionization Detection.
For all NAPL compounds, the removal efficiency increases versus the treatment time until a plateau is reached. Complete NAPL removal is achieved within 60 sec for soil thickness 1.3 and 2.6 mm, while the corresponding treatment time for soil thickness 4.0 mm is about 120 sec, revealing that the rate of NAPL removal is decreased as soil thickness increases. The energy density required to remediate completely the NAPL from soil is about 350 J/g and independent of soil thickness, indicating that DBD plasma has the potential to be a highly cost-effective technology for the remediation of contaminated soils.

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Remediation by Enhanced Natural Attenuation (RENA): An Eco-Efficient Bioremediation Technology for Sustainable Polyaromatic Hydrocarbons Degradation

Johnson Odukoya j.o.odukoya@cranfield.ac.uk Cranfield University -UK
Ronnie Lambert rjwlambert@cranfield.ac.uk Cranfield University - UK

Land previously contaminated with crude oil and subsequently remediated is put back into agricultural use. However, only a few studies have reported the influence of crude oil remediated sites on the chemical/nutritional composition of agricultural produce. This research was aimed at addressing this knowledge gap with particular focus on the use of Remediation by Enhanced Natural Attenuation (RENA) as a bioremediation technology for sustainable polyaromatic hydrocarbons (PAHs) degradation with eco-efficient agricultural benefits. Crude oil with pristane/phytane ratio of 0.98 (confirming its petroleum origin) and higher concentrations of two USEPA's priority pollutants (phenanthrene and anthracene) was artificially mixed with soil at crude oil: soil concentration of 5,000mg/kg. The physicochemical properties of the soil-based compost and the spent Pleurotus ostreatus mushroom compost used revealed that the pH of the soil-based compost after modification (6.6 ± 0.03) as well as its moisture content (30.8 ± 1.0%) was within the acceptable level for oil degradation though the spent mushroom compost had higher values of electrical conductivity (0.20 S/m) and carbon/nitrogen ratio (74.4 ± 1.5).

Four treatments: A, B, C and D were used for the research where treatment A (without crude oil addition) served as the planting control while treatment B was used as the control for studying the degradation of the PAHs across the crude oil contaminated treatments. After 7 days of incubation, the PAHs' (phenanthrene and anthracene) concentrations decreased from treatment B to C and then increased to D. Tukey HSD post-hoc analysis showed that the decrease of the two PAHs from B to C was statistically significant ($p<0.05$) while the increase from C to D was not statistically significant ($p>0.05$). However, their concentrations after 28 and 42 days of incubation as well as after harvesting were found below the Limit of Quantification (LOQ) except in treatment B with quantifiable concentrations after day 7.

The plants heights were found to be statistically significantly different after 10 and 24 days of growth. However, after 24 days of growth, Games-Howell post-hoc analysis revealed that the increase from treatment A to B to C was not statistically significant ($p>0.05$) though the decrease from C to D was statistically significantly different. The One-way ANOVA of the dietary macro minerals (Ca, P, Na, K and Mg) present in the vegetable samples obtained after 65 days of growth showed that though there was a decrease in the metals' concentrations when compared to the control (with the exception of sodium and potassium contents), there was no statistical significant difference ($p>0.05$) between these metals' concentrations in the harvested vegetable leaves. In addition, the Ca/P ratios of these vegetables samples being greater than one showed that they serve as a good source of these minerals for bone formation and would not contribute to high blood pressure since they have a Na/K ratio less than one.

The analysis of the phytochemical composition of the leaves also revealed that there was no statistical significant difference between the concentrations of the sugars - glucose and sucrose in the samples obtained from the different pot treatments. Hence, the research findings suggest that: (1) there is a low level of carcinogenic PAHs at a remediation target value of 5,000mg/kg, (2) weekly tillage enhances the degradation of polyaromatic hydrocarbons, (3) a low concentration of crude oil (not zero) supports plant growth, and (4) RENA performs a dual-function of remediating PAHs contamination while also favouring the growth of plants without altering their nutritional compositions.

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Microbial removal of nitrate in river water introduced in saturated zone soil

Jungyong Park yahn@dau.ac.kr Dept. of Environmental Engineering, Dong-A Univ.- Korea
Yeonghee Ahn yahn@dau.ac.kr Dept. of Environmental Engineering, Dong-A Univ.- South Korea

Aquifer storage transfer and recovery (ASTR) technology is one of technologies that are used to stably supply safe water that can be used to produce drinking water. River water is injected into soil aquifer and stored in the technology. The stored water can be recovered and used to produce drinking water. It is important to understand water quality improvement while the injected water is stored in the aquifer. In this regard, microbial removal of nitrate was investigated in this study using a lab-scale column reactor that contained saturated-zone soil mimicking aquifer. Nitrate is one of major inorganic contaminants detected in the Nakdong River that is one of the major rivers in Korea. The reactor was introduced with river water that contained nitrate at concentration (approximately 6.9 mg NO3-/l) detected in downstream of the Nakdong River during recent 2 years. While the introduced water was retained in the reactor, the nitrate concentrations decreased. Effluent from the reactor contained 1.0 mg NO3-/l or less with average 0.48 NO3-/l and showed average pH 7.98 during this research regardless of the nitrate concentrations of the influent. However abiotic control reactor showed similar nitrate-concentrations in its influent and effluent. This result suggested that microorganisms in saturated-zone soil removed nitrate in river water introduced into the reactor. Results of this study will be used to better understand microbial improvement of water quality in ASTR technology.

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Attenuation of Escherichia coli in river water introduced in saturated zone soil

Yeonghee Ahn yahn@dau.ac.kr Dept. of Environ. Eng., Dong-A Univ.- South Korea
Jungyong Park yahn@dau.ac.kr Dept. of Environ. Eng., Dong-A Univ.- Korea

Busan is the second largest city in Korea and it is located downstream of the Nakdong River that is one of 4 major rivers in Korea. Drinking water of Busan is mainly (94%) produced from the River. The Nakdong River always has potential to be contaminated due to industrial complexes and military stations located in the watershed. Besides, the river has limited amount of water in dry season. So it is necessary for Busan to develop a stable and safe source of drinking water. Aquifer storage transfer and recovery (ASTR) is one of technologies that are used to stably supply safe water that can be used to produce drinking water. River water is injected into soil aquifer and stored in the technology. The stored water can be recovered and used to produce drinking water. Five-year ASTR demonstration project has been supported by Korean government since 2013. ASTR facility will be built at an alluvial site in Busan.
It is important to understand water quality improvement while the injected water is stored in the aquifer. In this regard, E. coli CN13 (nalidixic acid resistant) was employed as a model pathogenic microorganism and its attenuation was investigated in this study using a lab-scale column reactor. The reactor contained saturated-zone soil mimicking aquifer. Coliform bacteria are one of major microbial contaminants detected in the Nakdong River. The reactor was introduced with the River

water that contained the strain CN13 at a concentration of approximately 2388 CFU/100 ml based on the concentration (average 1933 CFU/100 ml) of coliform bacteria detected in downstream of the Nakdong River during recent 23 years. While the introduced water was retained in the reactor, concentration of strain CN13 decreased. CN13 was not detected in the effluent from the reactor during 71 days of the reactor operation.
CN13 concentration in the influent decreased with time as well. This result suggested that saturated-zone soil attenuated E. coli in river water introduced into the reactor. Results of this study will be used to better understand improvement of water quality in ASTR technology

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Exploitation of cation exchange for a sustainable depollution of water channel sediments: ecotoxicological assessment, speciation of exchanged metals and water stability of treated sediments

Enrico Buscaroli enrico.buscaroli2@unibo.it Department of Agricultural Sciences, University of Bologna - Italy
Martina Bonadio Martina.bonadio@studio.unibo.it Department of Agricultural Sciences, University of Bologna - Italy
Emanuele Argese argese@unive.it Department of Molecolar Sciences and Nanosystems of Cà Foscari Venezia - Italy
Gloria Falsone gloriafalsone@unibo.it Department of Agricultural Sciences. Univesity of Bologna - Italy
Claudio Marzadori Claudio.marzadori@unibo.it Dept. Of agricultural Sciences, University of Bologna - Italy
Luigi Sciubba luigi.sciubba@unibo.it Dept.Agricultural Sciences, University of Bologna - Italy
Sebastien Lemière sebastien.lemiere@univ-lille1.fr LGCgE -Lille1-University of Lille - France
Bertrand Pourrut Bertrand.pourrutòisa-lille.fr LGCgE-Groupe ISA-University of Lille - France
Ilaria Braschi ilaria.braschi@unibo.it Dept.Agricultural Sciences, University of Bologna - Italy

In many Countries all over the world, the contamination level of soils is defined by the total content of both inorganic and organic pollutants. As far as the organic pollutants are concerned, this parameter can be considered as an acceptable index of their bioavailability due to their environmental mobility and bioaugmentation inside the leaving organisms. On the contrary, it is of general knowledge that the total content of inorganic pollutants, as heavy metals, cannot be considered responsible for the detrimental effect on soil biota for which only the bioavailable forms should be accounted [1]. A special case is represented by the sediment of water channels collecting and distributing water for agricultural purposes in lands with elevations below sea level. In case these channels are isolated from the river net, they behave like a sink for pollutants coming from the neighbouring fields and the point source pollution (e.g. waste water treatment plants and/or industrial activities) to whom they are eventually linked. The dredging up activities performed on water channel produce high amounts of sediment usually characterized by a pollution which can be considered of medium-low level but still unsafe to be recycled to build channel banks or to be distributed on the surrounding fields. In order to save soil (due to its very fine texture, water channel sediment can be potentially considered as a highly fertile soil type) and to save money (the sediment transport and disposal into waste dump is highly costly), it is of

general interest to define sustainable depollution procedures aimed at an in situ restoration of sediments dredged up from water channels. In this study, the sediment of a water channel placed into the north-eastern Italy (Emilia-Romagna Region) was sampled at different distances from the output of a municipal waste water treatment plant, chemico-physically characterized and assessed for its organic and inorganic pollutant content.
To performe an in situ restoration of sediments, an exchange with calcium ion has been applied directly on the hydrated samples in order to favour displacement kinetics. The speciation of the exchanged heavy metals through sequential extractions helped to define the speciation of the exchanged heavy metals. An ecotoxicological assessment of the treated and control sediments was performed to evaluate the potential harmful effects on the environment. Ecotoxicity and genotoxicity of both sediments and pore-water extracted from the sediments were evaluated on the three model organisms: the earthworm Eisenia fetida and the plants Lolium perene and Trifolium repens. Effects on survival, growth rate, oxidative stress and DNA degradation were determined. Finally, the stability of sediments saturated with calcium ion has been evaluated by wet sieving in order to test the resistance of treated-sediments to water abrasion and compared to the controls.
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Sorption of ionizable organic compounds to biochars for sustainable remediation

Gabriel SIGMUND, Melanie KAH, Huichao SUN, Thilo HOFMANN University of Vienna, Department of Environmental Geosciences, Althanstrasse 14 UZA II, 1090 Vienna, Austria thilo.hofmann@univie.ac.at

Biochar is a product of biomass pyrolysis and has been proposed as management strategy of organic wastes. Biochar can be a valuable soil additive as well as an environmentally friendly carbon sink. Production conditions (e.g. feedstock, temperature) influence biochar characteristics (e.g. specific surface area, ash content, polarity), which can lead to a high sorption potential for a variety of inorganic and organic compounds. The use of biochar has therefore been proposed as a particularly sustainable remediation strategy for both inorganic and organic contaminants in sediment, soil and water. While sorption of metals and hydrophobic organic compounds to biochar has received great attention, little data are available for ionizable organic compounds. Many pollutants including pesticides and pharmaceuticals, as well as hormones and infochemicals are ionizable organic compounds. Due to the influence of pH on the protonation of these compounds, conventional approaches to predict their sorption are not always suitable.
To gain a better understanding of sorption behavior and support the development of more reliable prediction approaches, we performed sorption batch experiments with a series of biochars and a series of organic acids with similar structure and covering a range of dissociation constant: 2,4-D (pKa = 2.8), MCPA (pKa = 3.7), 2,4-DB (pKa = 4.1) and triclosan (pKa = 8.1). Despite the sorbates structural similarity, sorption affinity covered a range of up to 3 orders of magnitude and generally followed the order 2,4-D < MCPA < 2,4-DB < triclosan. Sorption of 2,4-DB and triclosan decreased with increasing pH ($p < 0.05$). Differences in sorption behavior are discussed mechanistically,

based on differences in the molecular structure of the sorbates, the surface properties of the series of biochars studied, and aspects specific to the sorption behaviour of ionizable compounds.

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Removal of TCE by compost and brown coal in a Permeable Reactive barrier

S. Johana Grajales-Mesa jgrajales@geol.agh.edu.pl AGH University (Poland)
Grzegorz Malina gmalina@agh.edu.pl AGH University (Poland)
Tadeusz Szklarczyk tszklarc@agh.edu.pl AGH University (Poland)

Trichloroethylene (TCE) is a chlorinated solvent widely used for a variety of industries (ammunition, electronics, automotive parts, textile and dry cleaning) as cleaning and degreasing solvent. It is one of the most frequently detected contaminants in groundwater. TCE and its daughter products are considered to be of health concern and are included in the list of probably carcinogenic to humans. Moreover, due to its physical and chemical properties, TCE is not easy to remediate once it has migrated into groundwater. Permeable reactive barriers (PRBs) are passive in situ remediation technologies that may offer a low-cost and efficient treatment of groundwater contaminated with TCE. One key step in designing PRBs is the selection of appropriate reactive materials to treat the contaminants of interest. To date, zero valent iron (ZVI) is the most widely used reactive material for the removal of chlorinated solvents from groundwater. Although significant removal efficiencies of chlorinated solvents have been demonstrated, the formation of mineral precipitates may limit the long-term performance of the PRB with ZVI by decreasing its reactivity and permeability. Therefore, this work includes the selection and use of alternative materials such as compost and waste brown coal to treat groundwater contaminated with TCE to overcome the problems that ZVI possesses. Compost except for its sorption capacity serves as a source of readily degradable organic carbon in the form of cellulose to stimulate anaerobic biodegradation of TCE. Waste brown coal provides a long-term source of organic carbon as well as an improvement of physical-chemical properties, i.e. porosity and sorption capacity of the barrier. The materials were evaluated individually and in a mixture in laboratory batch and column experiments. The results have shown that both compost and waste brown coal are effective in remediating TCE contaminated groundwater reaching the removal efficiencies of up to 98%. Waste brown coal was more effective, while compost ability to remove TCE was exhausted earlier. The ongoing studies include the pilot installation for a field demonstration of TCE removal from groundwater using the PRB technology with compost and waste brown coal as reactive materials.

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Humics-based sorbents for heavy metals and radionuclides

Kamila Kydralieva kamila.kydralieva@gmail.com Institute of Chemistry and Chemical Technology, Chui ave, 267, Bishkek, Kyrgyzstan
Elvira Kasymova, Viktor Prokhorenko, Institute of Chemistry and Chemical Technology, Chui ave, 267, Bishkek, Kyrgyzstan
Vladimir Muratov, Institute of Applied Biochemistry and Machine-Building, Moscow

Sharipa Jorobekova, Institute of Chemistry and Chemical Technology, Chui ave, 267, Bishkek, Kyrgyzstan

In the Kyrgyzstan contaminated sites include the former uranium-producing provinces of Republic. During the Soviet period, discharges of radioactive elements resulting from uranium and complex ores (mercury, antimony, lead, cadmium and etc) mining industry in the environment were a common practice and, as a result, more than 100 contaminated sites are accounted for in the Republic. Those tailing dumps and tips contend 70 million m3 of wastes posing huge environmental threat. These radioactive contaminated sites are located mainly in the districts of Ak-Tyuz, Kadzhi-Say and Maily-Suu. Although uranium processing is no longer practiced in Kyrgyzstan, a large number of open landfills and uranium ore storages still remain abandoned at the vicinity of these settlements.
A set of functional hybrid compositional materials based on magnetite nanoparticles and humic substances (Fe3O4-HS) were formulated and the feasibility studies on their production were developed. These nanocomposites have the characteristics as well high-efficacy sorbents as specific characteristics of magnetic materials. In other words, they are the controlled magnetoactive nanocomposite materials. The Fe3O4-HS was able to remove over 95% of UO22+, Zn2+, Pb2+ in soil water. The Fe3O4/HS loaded with sorbed heavy metals and uranium can be simply recovered from water with magnetic separation at low magnetic field gradients, which can hopefully reduce water treatment expenses.
The cross-linked porous copolymers of Cu2+, Zn2+, Ni2+, Pb2+ humate and their macromolecular templates, having selective sorption properties with respect to corresponding metal ions ions, were obtained. The macromolecular complexes reveal the high specific surface area and micro- and mesoporosity. The strength of the metal-template bond can be easily modulated by adjusting the experimental conditions. Sorptive capacity decreases, as a rule, with an increase in the cross-linking degree. So, there is an optimal area of compositions when sorption properties are revealed most efficiently for the copolymers of Cu2+ humate with aminophenol: the factor of selectivity is 20–27 at the content of a crosslinking agent 42–53 mol%. Probably, at higher content of metal in a copolymer, decrease of selectivity occurs because of change of the mechanism of ions sorption which is carried out not only by the “prearranged” centers, but also by others, in particular, ester groups by the coordination mechanism.

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Polymer-based technology for detoxication of technogenic environments

Alexandr Yaroslavov, Andrey Sybachin, Lomonosov Moscow State University, Moscow
Kamila Kydralieva kamila.kydralieva@gmail.com Institute of Chemistry and Chemical Technology, Chui ave, 267, Bishkek, Kyrgyzstan
Vladimir Muratov Institute of Applied Biochemistry and Machine-Building, Moscow
Sharipa Jorobekova Institute of Chemistry and Chemical Technology, Chui ave, 267, Bishkek, Kyrgyzstan
Alexandr Zezin Lomonosov Moscow State University, Moscow

The goal of this study is to develop and demonstrate the technology for fabrication and practical use of polymeric materials for remediation in anthropogenic areas.

In order to clean up contaminated soil by high toxic metals/elements (chrome, cobalt, arsenic), radionuclides the non-stoichimetric interpolyelectrolyte complexes (NIPEC) with an excess of either component, cationic or anionic polymer including natural one - humic acids are proposed. A polymer, taken in excess, is usually referred to as the lyophilizing, and taken in shortage as the blocking. NIPECs are formed in the presence of minimum salt concentration, in the order of 10-3 M, that practically has no effect on the water-salt balance of soil. Depending on chemical nature of polymers and linear charge densities in macromolecules, water-soluble NIPECs can be prepared with long sequences of interpolymer salt bridges (hydrophobic blocks) in which up to 50 mol% of the lyophilizing polymer units can be involved. Due to hydrophobic blocks and residual non-compensated charges, NIPECs are effectively bound to soil particles and cannot be washed away with rainfall, or artificial irrigation, or water from melted snow. NIPEC solutions with low salt concentrations are actually “one-solution” formulations without producing a negative effect on the water-salt balance of soil.

Additionally, NIPECs are able to bind effectively a majority of toxic heavy metals: chrome, cadmium, cobalt, copper, zinc and others, due to incorporation of metals inside hydrophobic NIPEC fragments generated by mutually neutralized cationic and anionic units. As a result, thermodynamically stable structures are formed with a central metal ion surrounded by functional groups of both polyelectrolytes. This allows the extraction of heavy metals even from extremely diluted solutions. Commercially available biodegradable polyelectrolytes (carboxymethylcellulose, sodium alginate, humic acids) are used for NIPEC formation. In such polycomplexes, both polymers or either of them can be biodegradable. These formulations ought to be used in combination with sowings of perennial herb seeds. This approach ensures formation of stable grass covering in a shortest period of time which prevents wind and water erosion and suppresses spread of heavy metals. After completing the protection function, the formulation is destructed, being affected by soil microorganisms, and transformed down to simple non-toxic substances that will improve the environment. Thus, use of NIPEC will allow to solve two interrelated problems: extraction and concentration of heavy metals and radionuclides and prevention of their spread by means of wind and water erosion. Formulations will be prepared and tested in the lab and in the field, fabricated from commercially available polymers, anionic (polyacrylic acid, carboxymethycellulose, humics) and cationic (polydimethydiallylammonium chloride, polyethyleneiminen). Anionic groups in polymers are represented by carboxylic (-COOH) and sulfo groups (–SO3H), cationic by different amino groups, from primary to quaternary. Molecular mass of polymers is varied from 2×103 до 105 кDa that approximately equal to 20-103 degree of polymerization. All the above mentioned polymers are soluble in water and water salt media at 1-10 wt% concentrations that are typical for polymer-based soil-stabilizing formulations.

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TOPIC 4

CASE STUDIES

ABSTRACTS NUMBERS
105-117-120-174-186-188

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Sustainable Closure of Two Former Uranium Mines

Lee Holder lholder@golder.com Golder Associates - USA
Frank Shuri, Golder Associates - USA
Barbara Nielsen, Freeport McMoRan Copper & Gold - USA
Russel Jonas, Barrick Gold Corporation – USA

The White King / Lucky Lass CERCLA site consists of two former uranium mines in south-central Oregon.
The remedy included consolidating two large mining overburden stockpiles that contained low levels of radioactivity and heavy metals by moving over 700,000 cubic yards of material and then capping the combined stockpile. An innovative armored cap design was used to minimize the stockpile footprint and thereby prevent disturbing existing wetlands. In addition, the stockpile was designed to merge into the surrounding topography. The remedy also included stream restoration and development of new wetlands. The stream was returned to its pre-mining channel, with the addition of hydraulic features to create new wetlands. The wetlands have greatly enhanced the ecological value of the remedy and the site.

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Pilot test : In-situ chemical reduction of chlorinated solvents by injection of micro-scale and nano-scale zero valent iron (Citychlor project ; Herk-de-stad, Belgium ; 2012)

Ward Goyens wdg@tauw.be Tauw nv - Belgium
Dirk Paulus dpa@tauw.be Tauw nv - Belgium
Art Lobs a.lobs@verhoevemw.com Verhoeve Milieu & Water - The Netherlands

Commissioned by OVAM, the joint venture Tauw Belgium nv - Verhoeve Group Belgium carried out a pilot project in which in-situ chemical reduction (ISCR) of chlorinated solvents by the injection of zero valent iron (ZVI) was investigated. The pilot project intends a treatment of the source zone by injection of micro-scale and nano-scale ZVI particles. For this purpose non-exclusive, commercially available, iron materials are tested. The pilot project is part of the CityChlor project.
Biological degradation of chlorinated solvents does not always occur and when it occurs, it is often incomplete and stagnates on intermediary products that are even more mobile and toxic than the motherproduct. ZVI can however facilitate the process of dechlorination.

This principle is already being used in permeable reactive barriers (PRB) to control groundwater contamination (plume zone). The difficulty in the remediation of source zones of pollution by using zero valent iron, is bringing the iron into contact with the pollution. A solution might be the injection of small scale (micro or nano) ZVI particles that have the potential to move through the subsoil with the natural groundwater flow and can potentially penetrate the smallest pores.

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Experimental pilot scale remediation of mine waters at abandoned Sb-deposit Poproc (Slovakia)

Peter Sotnik sottnik@fns.uniba.sk Commenius University in Bratislava, Faculty of Natural Sciences, Mlynská dolina, 842 15 Bratislava - Slowakia
Ľubomír Jurkovič jurkovic@fns.uniba.sk Commenius University in Bratislava, Faculty of Natural Sciences, Mlynská dolina, 842 15 Bratislava - Slowakia
Jaroslav Vozár vozár@elsro.sk EL Ltd., Radlinského 17/A, 052 01 Spišská Nová Ves - Slowakia
Tomáš Klimko tomas.klimko@vsb.cz Technical University of Ostrava, Faculty of Mining and Geology, 17, listopadu 15, 708 33 Ostrava-Poruba, Czech Republic - Slowakia

Proper evaluation of contamination generated by Sb mining (by a range of toxic elements such as As and Sb), migration of the contaminants, their speciation, sorption onto colloids and ability to enter food chain requires complex approach of all geological (mineralogy, hydrogeology, geochemistry) and chemical (analytical chemistry, biochemistry) specializations. Antimony as an element naturally occurring in the environment, toxic for humans, became a target of many researches in the past 10 years, but its behavior is still not completely known. The topic of ground and surface water remediation is very actual and frequently realized. There are many remediation technologies developed and used to eliminate or decrease (under appropriate limits) the level of contamination. Research dealing with development of the remediation technologies including polices for rapid and economical decontamination is still in progress at the present time.
Study area is located in SE part of Spiššsko Gemerské Rudohorie Mts. in Petrova valley. Poproč together with Betliar, Čučma, Spiššská Baňa a Zlatá Idka belogs to historically important deposits in the southern part of Spišské Rudohorie Mts. At Poproč, exploitation of Sb ores started in the 17th century and the mines were closed in 1965. The most intense mining took place between 1931 and 1965 when more than 10 000 metric tons of antimony and c. 80 kg of gold were recovered. The main minerals of the hydrothermal veins are quartz and stibnite, with less common pyrite, arsenopyrite, berthierite, tetrahedrite, sphalerite, and the Pb-Sb sulphosalts zinkenite and fülöppite.
The Poproč deposit (abandoned Sb deposit selected for this project) was integrated into the state program for environmental loads remediation (2010 - 2015; established by Ministry of Environment and Slovak Environmental Agency) and was suggested for detailed research, risk analyses and if necessary remediation. Main goals of our study supported by Slovak Research and Development Agency (project number: APVV-0344-11) are:

1) To define the reduction rate of contamination extension at selected locality after application of settling basin, or passive aerobic wetland
2) Experimental verification of controlled crystallization of secondary minerals for proposes of mine and technological water remediation

3) Verification of suggested remediation methods applicability in pilot scale experiment
4) To characterize and identify mineral phases originated during the experiments, classify them as waste or as alternative metal source
5) Design of final solution for mine water treatment.

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Model of environmental sustainable mine waste management for the Biely vrch deposit

Peter Sottnik sottnik@fns.uniba.sk Comenius University Bratislava, Faculty of Natural Sciences, Slovakia
Lubomir Jurkovic
Jana Brcekova
Peter Kodera

In the year 2006 the company EMED Slovakia, s.r.o., assisted by two of the submitters of this project, determined at the locality Biely Vrch near Detva the presence of a new type of porphyry mineralisation with a relatively high Au/Cu ratio that in the literature is marked as Au-porphyry mineralisation. This type of mineralisation was not known in Western Carpathians yet.
Low content of metals and big amount of ore in porphyric systems requires exploration by open pit methodology which produces a big volume of mining waste. In the case of Au porphyry systems it is possible to produce gold efficiently only by cyanide leaching, what increases requirements for a safe environmental management of exploration.
Slovakia has signed the agreement about implementation of DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL 2006/21/ES from 15. March 2006 on the management of waste from the mine industry. The law No. 514/2008 on management of waste from mining industry with related legislative changes is valid at the moment in Slovak republic. Mining waste is necessary to characterize when the mining waste management plan is created, especially if there is not enough information for mining waste site categorization. Mining waste testing is focused to two groups of waste properties:

- geotechnical properties
- geochemical properties and waste behavior

Definition of mining waste properties include determination of chemical and mineralogical properties of mining waste and all chemical substances and agents remained in mining waste. Main goal of environmental part of the project is the determination of composition and subsequent behaviour of mining waste after deposition on mining waste sites. These data will by used as a bases for determination of potential chemical composition of drainage waters for each kind of mining waste during the operation of mine. Main goal of this research was a characterization and qualified categorization of mining waste, which will be potentially created by exploitation of the Biely vrch deposit. This will enable to predict and prevent environmental problems related to mining and processing of ore by leached with cyanides.

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The role of fungi and plants in metal-contaminated mine soil

Grazia Cecchi grazia.cecchi@edu.unige.it Department of Earth, Environment and Life Sciences - Polo Botanico Hanbury, University of Genoa (Italy)
Enrica Roccotiello
Simone Di Piazza
Pietro Marescotti
Mauro Giorgio Mariotti
Mirca Zotti

Metal contamination is one of the world's major environmental problems, posing significant risks to human health and ecosystems. Contamination from mining activities is the 4th source of land pollution (e.g. it represents 7% of the National Priority (Superfund) Sites in the USA) (1). In Europe the number of potentially polluting activities now stands at about 3 million (2), and around 250,000 sites may need urgent remediation (3). The physicochemical properties of the contaminated environment tend to inhibit soil-forming processes and, consequently, plant growth, affecting the area's biodiversity and exerting a strong selective pressure on native vegetation and mycobiota (4, 5, 6, 7). Therefore soil communities are strongly affected by environmental changes; in particular, microorganism communities can provide important information about soil metal bioavailability (8). The importance of below and aboveground biodiversity is increasingly considered for the cleanup of the metal-contaminated ecosystems. Care should be taken in choosing the right species for the application of bioremediation techniques, because the introduction of alien fungi and plants may alter and disrupt indigenous ecosystems (9), and because the species may be unsuitable for local climate conditions (10). This subject represents a key area of research thanks to its ecological and commercial significance in the contemporary field of green technology. The present case study consists into a 6-years-study of a sulphide-rich waste-rock dump of the derelict Libiola mine (eastern Liguria, Italy). This mine was one of Italy's most important Fe-Cu sulphide mines; it was industrially exploited from 1864 until 1962 and, during this period, produced over 1 Mt of Fe-Cu sulphides with an average grade ranging from 7 to 14 Cu 93 wt% (11). The soils of the dumps are characterised by severe edaphic condition due to their peculiar physical (steep slopes, low moisture retainability, impermeabilization due to cementification and hardpan formation) and chemical (high metal concentrations, low pH values and low availability of essential macronutrients) properties. This site presents serious environmental problems due to active Acid Mine Drainage process, which determine acidification and metals pollution of soils and waters. The soil of the studied dump is characterized by severe edaphic conditions, mainly represented by high concentration of several toxic metals (Cr, Cu, Co, Ni, and Zn) exceeding commercial and industrial limits for metals elements, paucity of nutrients (in particular P, Ca, and K) and presence of outcropping Fe-rich hardpans (12).
We evaluated the plant and fungal diversity in these contaminated soils in order to 1) identify factors that influenced the first fungi and plants to colonize this stressful environment 2) identify and select tolerant and hyperaccumulating plants and fungal strains suitable for mine remediation.
Plants, macrofungi, and their respective soils were analysed for metals content revealing Cu>1000 mg kg-1 in Thelephora terrestris Ehrh., and Ag>50000 µg kg-1 in Scleroderma polyrhizum (J.F.

Gmel.) Pers. These fungi are also able to actively absorb in their basidiomata most of the potential toxic elements occurring in the mine spoil. The recognized absorption sequence Cu>Zn>Cr>Ni>Co obtained for these macrofungi well matches with the sequences resulted from water leaching tests and EDTA extractions (12). To test the growth responses of isolated strains in copper enriched media and to evaluate their potential use in mycoremediation, soil microfungi were evaluated. The majority of isolated colonies belonged to the genus Penicillium, a common feature for copper contaminated soils, while occurrence of other genera, including Aspergillus, Clonostachys, Trichoderma, and Botrytis was significantly lower. The species most recurrent are filamentous microfungi: Trichoderma harzianum Rifai, Clonostachys rosea (Link) Schroers, Samuels, Seifert & W. Gams and Aspergillus alliaceus Thom & Church. We hypothesized that these fungi are particularly tolerant/resistant to copper. The Cu tolerance level of T. harzianum and C. rosea were tested in vitro at increasing Cu (II) concentrations. The tests have shown a Cu (II)-tolerance capability ranging from 100 to 400 mg L-1. These preliminary analyses prove that several fungal species are able to grow in Cu-contaminated media, underlying the importance to select new tolerant strain and test their potential metal uptake capability for application in mycoremediation protocols. The study area is characterised by different successional plant communities ranging from herbaceous to arboreal stage. In all the plots, species richness and vegetation cover were extremely low. The flora showed an acidophilous character (13). Despite these harsh environmental conditions, the studied waste rock dump has been progressively colonized by several plants of Pinus pinaster Aiton., already found naturally on metal-rich sites establishing ectomycorrhizal symbiosis (14). We found that this species is able to cope with some of these limiting factors by completely avoiding toxic metals from its tissues, acting as a rhyzostabilizator. The success of Pinus pinaster colonization is mainly due to the presence of Telephora terrestris and Scleroderma polyrhizum, ectomycorrhizic with pine.

A screening on native flora by ICP-MS analyses revealed Alyssoides utriculata (L.) Medik. as a new Ni hyperaccumulator, able to concentrate more than 1000 mg kg-1 Ni DW in leaves (15). Plant efficiency test were carried out on native soils to evaluate the growing ability of this promising species. Because of the complexity of soil and in-situ conditions, each site requires its own strategy and site specific designs for decontamination. The combined use of hyperaccumulator plants and fungi belonging to plant rhizosphere could provide natural assisted phytoextraction, increasing metal hyperaccumulation. The same for macrofungi. The enormous potential of native fungi and plants able to colonize metal-contaminated soils should be deeply studied to preserve the natural genetic resources of metalliferous habitats and to increase our basic knowledge about the natural adaptation mechanisms of hyperaccumulators, employing them in bioremediation purposes.

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Improving the Sustainability of Cleanups Through Conservation and Reuse of Groundwater: A SURF Initiative

Amanda McNally amanda.mcnally@aecom.com SURF/AECOM (USA)
Jake Torrens Jake.Torrens@amec.com SURF/AMEC (USA)
Paul Hadley Paul.Hadley@dtsc.ca.gov California Department of Toxic Substances Control (USA)
Dave Woodward dave.woodward@aecom.com AECOM (USA)

The Sustainable Remediation Forum (SURF) promotes the use of sustainable practices during implementation of remedial action activities with the objective of balancing economic viability, conservation of natural resources and biodiversity, and the enhancement of the quality of life in surrounding communities. In 2012 SURF undertook an initiative to improve the sustainability of remedies by encouraging a greater focus on conservation and reuse of groundwater at cleanup sites. To that end, SURF produced a document titled â□œConservation and Reuse of Groundwater at Remediation Sites. This document considers the impediments to conservation and reuse, and also provides case study examples where reuse of treated groundwater from remediation sites was accomplished. The document also highlights examples of reuse from the municipal wastewater industry, focusing on situations where concerns similar to those associated with reuse of groundwater from remediation sites w ere successfully resolved. This presentation will include an informative overview of the document and highlight the noteworthy case studies where reuse of treated groundwater has been successful in California.