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Rein, Arno; Smith, K. E. C.; Karlson, U. G.; Mayer, P.; Trapp, Stefan

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sorption behaviour of four different PAHs (pyrene, phenanthrene, fluoranthene and fluorene) with solid-phase NOM and BC and the effect of rhamnolipid biosurfactants on sorption equilibrium. Biosurfactants sorption was also determined. Biodegradation of sorbed PAHs in the absence and presence of biosurfactants was also followed using a representative PAH-degrading soil bacterium (*Mycobacterium gilvum* VM552). Experimental conditions included different sources of NOM and BC and different solid-aqueous phase ratios. The results showed that biosurfactants, especially when they were present at levels above CMC, often promoted desorption and biodegradation of PAHs.

WE 214

Modeling experimental findings on sorption and biodegradation of PAHs

A Rein¹, KEC Smith², UG Karlson², P Mayer², S Trapp¹

¹Technical University of Denmark, KGS, LYNGBY, Denmark

²Aarhus University / National Environmental Research Institute, ROSKILDE, Denmark

Polycyclic aromatic hydrocarbons (PAHs) in the environment are to a major degree bound to organic matter or soot particles. It is disputed whether and to which extent the adsorbed fraction of PAH in soil and sediment can be attacked by microbial enzymes, or whether dissolution in aqueous media is required. In that case, the degradation depends critically on the bioavailability, or better the bioaccessibility of PAH for microbes. The increasing non-accessibility of PAH with time ('aging') may explain the formation of a residual fraction, which has been observed in remediation projects.

A unified model for sorption, sequestration and degradation of neutral organic compounds in soils and sediments has been developed and tested (see also Trapp et al. session J01). Adsorption was considered as a two-phase process, with rapid and slow adsorption rates. Calculated or experimental sorption rates and kinetic data for growth and metabolism of PAH-degrading bacteria were obtained as input parameters. The model simulations were compared to existing solutions (such as the Best equation) and to experimental results. With this new model approach, a range of experimental observations available in literature could be simulated, encompassing various soil types and PAHs, and different bacterial strains. Own experiments are currently performed on phenanthrene, fluoranthene and other PAHs and on ad/desorption as well as on biodegradation. The results shall be used to calibrate and verify the new model approach. The model was also used to simulate typical scenarios of adsorption (aging) and microbial degradation, in order to identify sensitive parameters and processes. Furthermore, the impact of dissolved organic matter and various types of amendments was studied, which potentially enhance diffusive mass transfer and biodegradation performance. The final goal is to optimize remediation options.

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Sorption and desorption characteristics of two insecticides (chlordecone and cadusafos) previously used in banana plantations of the French West Indies

JD Fernandez-Bayo¹, C Saison¹, C Geniez¹, AE Berns²

¹Laboratoire d'étude des Interactions Sol - Agrosystème - Hydrosystème, MONTPELLIER, France

²Forschungszentrum Juelich GmbH, Inst Bio- and Geosciences, IBG 3: Agrosphere, JUELICH, Germany

Chlordecone (CLD) is a highly persistent organochlorine pesticide that was used for a wide range of pests around the world, among them, the banana weevil *Cosmopolites sordidus* in plantations of the French West Indies. It was banned in France in 1993. One of the molecules that replaced it was cadusafos, an organophosphate that has since then been removed from the market in the European Union in 2008. Nearly 20 years after its prohibition, CLD is still detected in every compartment of the environment, i.e. in soils, surface and groundwaters and some agricultural products and it is suspected to increase the prevalence of prostate cancers in exposed populations. The physico-chemical characteristics of this molecule along with its high stability due to the numerous chlorinated groups that protect the molecule from degradation, make sorption one of the most important processes that govern the fate of chlordecone in soils. However, the literature in the environmental fate of this molecule is scarce and mainly from the 80's or earlier. The aim of this work is to improve the knowledge in the sorption and desorption of CLD and cadusafos in tropical volcanic soils of the French West Indies. Sorption-desorption isotherms were carried out in batch experiments in 7 different soils and fitted to the Freundlich model. Additionally, the nature of the soil organic matter, known to be one of the determinants of the adsorption of pesticides, was examined by ¹³C-CP MAS NMR. Sorption of CLD in soils was very high ($26 < K_f < 102 \text{ L kg}^{-1}$) with a high hysteresis effect in 5 of the soils studied and no desorption at all in the two remaining soils. Freundlich's K_f parameter of cadusafos was ranging between 0.8 and 21 L kg^{-1} and contrarily to CLD, desorption was not showing a high degree of hysteresis. The K_f values were correlated to the OC content ($P < 0.01$) for both molecules and derived K_{oc} were ranging between 1200 and 2500 L kg^{-1} for CLD and between 67 and 135 L kg^{-1} for cadusafos. Despite the different nature of the soils, NMR spectra for soil organic matter were very similar between the 7 studied soils. Thus, the Koc heterogeneity is not only influenced by the chemistry of the organic matter, but must also be attributed to other soil properties. In the literature, values on the K_{oc} of CLD were missing, they were sparse for cadusafos and they represent a necessary piece of information for the use of models to predict the transfer of these molecules in surface and groundwaters.

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On the challenge to remediate a soil contaminated with crystalline DDT by activated charcoal

A Younas¹, I Hilber², M Khwaja³, JD Bucheli²

¹Environmental Science Department, PESHAWAR, Pakistan

²Agroscope Reckenholz Tanikon Research Station ART, ZURICH, Switzerland

³Sustainable Policy Development Institute, ISLAMABAD, Pakistan

The production and distribution of the insecticide dichlorodiphenyltrichloroethane (DDT) resulted in a polluted area of about 85 hectares at Nowshera, Khyber Pakhtunkhwa (KPK), Pakistan. At the factory's place the contamination is up to 800 g/kg DDT in dry soil. To reduce DDT exposure of the environment and humans, this contaminated site has to be remediated. Therefore, the aim of this joint research project is to test a remediation strategy with activated charcoal (AC) added to substantially reduce the bioavailable fraction of the aged DDT in the soil. To the best of our knowledge, AC has been used for remediation purposes in a concentration range of ppb to ppm in soils and sediments, but never in the percent range. Under these circumstances, limitations are set at extremes and are manifold. Results from this study will give important information on the performance of AC materials in a naturally contaminated soil and reveal the influence of soil treatment on the immobilization of DDT.

Pots with five kg of field soil were placed in the laboratory. Then, 2% and 10% GAC and 0.1% and 2% PAC were added. To test the influence of different soil treatments on the binding quality

of the AC, the amended soil was then treated in three different ways. Some pots were watered during a month to simulate monsoon season, but left untreated for the following five months (treatment 0). Others were mixed fortnightly to simulate ploughing (treatment P) and a third group was subjected to regularly watering (treatment W) and watering and ploughing (treatment PW) over the whole period of time. After certain time periods, bioavailable DDT and metabolites were assessed by six hours Tenax[®] extractions with two grams of Tenax[®] beads and one gram of dry soil.

Results from this experiment were surprising. The Tenax[®] extractable DDT decreased drastically over time not only in all AC amendments and treatments, but also in the control. After 150 days, the concentration of the DDT extracted by Tenax[®] was very low with a few per milles. Overall, two main questions arise under this situation with extremely high DDT concentrations: 1) is Tenax[®] the appropriate tool to assess the bioavailability, and 2) is AC amendment capable to substantially reduce DDT exposure. These important issues will be addressed in this presentation.

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Distribution of aged ¹⁴C-atrazine residues in soil following 22 years of environmental exposure.

Y Andreou

Cyprus University of Technology, LIMASSOL, Cyprus

Distribution and localisation of pesticide residues into the different physical fractions of soil may reveal information on processes taking place in soil. Soils amended with ¹⁴C-atrazine, were aged for 22 years under environmental conditions in a lysimeter in Germany. The soil was sampled and subjected to physical and chemical fractionation before and after incubation with the earthworm *Apporectodea caliginosa* for 7 days. No significant change in the soil physical and chemical fractionation of the ¹⁴C-atrazine residues and organic carbon was observed in this study as a consequence of the activity of the *A. caliginosa*. The low organic carbon of the soil, the absence of relatively fresh organic matter and the long ageing time might explain the limited bioavailability of the ¹⁴C-atrazine to the earthworm. Approximately 9% of the applied ¹⁴C-atrazine associated activity was found to be present in the top soil layer 0-10 cm of the lysimeter. This amount represented approximately 36% of the total amount of ¹⁴C-atrazine associated activity presented in the soil after 22 years of environmental ageing. Soil half lives calculated in this study taking into account the non-extractable ¹⁴C-atrazine residues were much greater than those reported from previous studies. This finding is of particular importance given that the soil used here was aged under natural environmental conditions compared to laboratory studies.

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Use of solid-phase microextraction and toxicity tests to determine the bioavailability and toxicity of hetero-PAH with the oligochaete *Lumbricus variegatus* in sediment-pore water systems

AJ Schneider¹, TB Seiler², K Schmidt³, G Witt³, B Schmidt², A Schäffer², H Hollert²

¹RWTH Aachen University/Institute for Environmental Research, AACHEN, Germany

²RWTH Aachen University, Institute for Environmental Research, AACHEN, Germany

³Hamburg University of Applied Sciences (HAW), Faculty of Life Sciences, HAMBURG, Germany

Polyaromatic heterocycles (hetero-PAH) are N-, S-, O- substituted polyaromatic hydrocarbons (PAH). They occur together with their unsubstituted analoga e.g. at creosote-contaminated sites. Their acute, chronic and reproduction toxicity as well as their higher water solubility compared to their unsubstituted parent compounds account for their ecotoxicological relevance.

In the present study the chronic toxicity of two hetero-PAH acridine (AC) and xanthene (XA) in a sediment-pore water system of a spiked natural river sediment (Altrip, Rhein, Worms; AC 6.3-146.2 $\mu\text{g/g DW}$; XA 0.1-270 $\mu\text{g/g DW}$) on the reproduction of sediment dwelling endobenthic oligochaetes *Lumbricus variegatus* was determined according to OECD guideline 225. In parallel to chronic toxicity, the freely dissolved pore water concentrations ($c_{f, \text{free}}$) of the substances were determined by solid-phase micro extraction (SPME) and high performance liquid chromatography.

Determined effect concentrations (ECx) for the reproduction of *L. variegatus* were based on the total sediment concentration (EC₅₀ AC 37.8 $\mu\text{g/g DW}$, EC₅₀ XA 2.4 $\mu\text{g/g DW}$), the tissue concentration (EC₅₀ AC 0.0052 $\mu\text{g/mg DW tissue}$ and $c_{f, \text{free}}$ (EC₅₀ AC 0.034 $\mu\text{g/ml}$). Hormesis was observed for the reproduction of *L. variegatus* at the lowest tested concentrations of both substances. Furthermore, with the SPME technique it was possible to determine $c_{f, \text{free}}$ of both substances in sediment pore water at higher sediment concentrations (AC $\geq 30.5 \mu\text{g/g DW}$ and XA $\geq 90 \mu\text{g/g DW}$) and to prove metabolic degradation of xanthene to xanthone in the sediment. In contrary, no degradation of acridine to acridone was detected in both, the sediment and *L. variegatus*.

The results emphasize, that for sediment contact tests, i.e., testing the ecotoxicity of hydrophobic organic chemicals ($\log K_{ow} < 5.7$) on endobenthic organisms, it is important to simultaneously determine $c_{f, \text{free}}$ of the substances to be able to link the observed ecotoxic effects to the real exposure.

WE 219

Characterizing the bioavailability of cationic surfactant using passive sampler

Y Chen¹, STJ Droge², JLM Hermens¹

¹Institute for Risk Assessment Sciences, UTRECHT, The Netherlands

²Helmholtz Centre for Environmental Research-UFZ, LEIPZIG, Germany

Cationic surfactants are ubiquitous contaminants that are extensively detected in sediment, sewage sludge or surface water due to their wide applications in industrial and domestic products. However, the understanding of the impact of this class of compounds on the environment is still limited. The freely dissolved concentration of an organic compound is an important parameter for accessing the environmental fate and bioavailability of the chemical. The free concentration of cationic surfactants, are difficult to determine because of their high adsorptive capacity to lab apparatus and because the difficulty to separate the bound particles from the aqueous phase.

In the current study, a solid phase microextraction (SPME) method was optimized and applied to characterize the bioavailability of two cationic surfactants, hexadecyl trimethyl ammonium chloride (IV-16) and benzyl dimethyl dodecyl ammonium chloride (C12-BAC). The effect of solution chemistry on the sorption isotherm to SPME was first examined. Sorption experiments of the two cationics to Pahokee peat and humic acid were carried out. The influence of pH and the presence of inorganic cations on the sorption behavior were examined within the range of relevant environmental concentrations. The results suggest both ionic and nonionic interactions could play a role in the sorption process for cationic surfactants.

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Sorption of cationic organic compounds: how important is clay compared to organic mat-