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Combined modelling of PAH biodegradation, soil sorption and dissolution from organic phases

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partitioning from the outer into the inner membrane. The model was calibrated to two data sets which were merged: uptake efficiency of environmental pollutants measured in different mammals during feeding studies, and a pharmaceutical data set with human oral absorption efficiencies. The new model estimated uptake efficiency for compounds with logKOW ranging from -10 to +8, and estimation was improved for polar compounds by accounting for the bilayer structure of the membrane. Including the inner membrane resistance improved RMSE especially for the compounds with KOW<0 from 28.3 to 18.3, while also overall performance improved from 18.4 to 14.0. Therefore, the new model provides a tool to estimate uptake efficiency for new compounds based on sound mechanistic processes.

MO 063

A standardized contact transfer method for assessing soil-to-clothing exposure to soil-sorbed chemicals

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Exposure to chemicals, including chemical warfare agents (CWA), can present a potential Contact Hazard even when the compounds are sorbed onto soil. Previous studies have investigated levels of CWA transferred from contaminated surfaces utilizing a malleable latex material (dental dam; DD) as transfer substrate; however DD is typically inconsistent in compositions, and not reliable for toxicological investigations. Measurements of CWA on standard Army Combat Uniform (ACU), plus toxicological effects of CWA, have been reliably established for some CWA and ongoing-testing continues for others; but need still existed for a reliable transfer-exposure method for assessing the exposure potential for chemicals sorbed onto soil. We have established a method for reliably determining Contact Transfer of compounds from soil directly onto clothing, utilizing standard mass (x Gravity) as a standard force to produce a standard measure of exposure potential. We initially determined the effects of contact time and applied mass (DD); then in benchmark investigations, we established the efficacy of CWA extraction from ACU (and DD), and Contact Transfer of CWA from soil onto clothing (ACU). A 4" diameter circular swatch of ACU material was selected, similar to surface areas that may contact soil at knee or elbow locations; standard contact was created by placing the ACU swatch directly onto the soil-surface one minute after CWA dissemination, then covering the swatch with a 4" diameter Plexiglass disk to distribute force from a centrally-placed standard mass. Contact Transfer of CWA was determined by solvent extraction of swatches, with subsequent analyses by GC/GC-MS or HPLC/HPLC-MS. Masses 0.250, 0.500, 1.000, 1.500 kg, resulted in significantly greater CWA transfer ($p \leq 0.05$) at ≥ 0.500 kg compared to 0.250kg; therefore the 1-kg standard mass was selected for integration into the method. Although the quantities of soil-sorbed CWA that transferred increased as a function of contact time, the rate of transfer decreased dramatically after 1h; therefore 0.25h was selected for integration into the method. The quantities of CWA transferred from soil surfaces contaminated at operationally important levels from Soil-to-Clothing (ACU) are amounts that are within the range of concern for Soldiers. The standardized Contact Transfer Method provides reliable standard predictions of exposure potential, and in conjunction with toxicity data, for predictions of Contact Hazard.

MO 064

Combined modelling of PAH biodegradation, soil sorption and dissolution from organic phases

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Despite promising microbial degradation of polyaromatic hydrocarbons (PAH) in the laboratory, pilot-scale investigations and observations at the field scale often reveal the formation of a considerable residual fraction of PAHs in soil, which is not further degraded. Non-bioavailability of PAH due to adsorption and sequestration would thus result in residual fractions resistant to microbial degradation, which may increase with time. However, residual concentrations may also be due to kinetic reasons, i.e. the concentrations may be too low to maintain microbial metabolism. For a range of biodegradation experiments, combined modelling of microbial growth and degradation, ad/desorption processes as well as dissolution from the organic phase has been carried out. The objective of the present study was to analyse and explain observed processes mathematically.

In experiments with phenanthrene added to solution as microcrystals and the degrader microbe *Novosphingobium pentaromativorans*, fast degradation took place at the beginning, corresponding to a strong initial increase in microbial mass. Experiments with higher initial concentrations revealed slower degradation. An initial set of Monod parameters could be fitted and experimental observations could be explained by a decreasing effective surface area for phenanthrene dissolution of the phenanthrene crystal phase. These effects were stronger with higher initial concentrations (assumed higher coagulation of microcrystals with time).

Other experiments considered were done with phenanthrene-spiked soil amendments (radio-labelled ¹⁴C-phenanthrene) in suspension and degrader strain *Sphingomonas* sp. 10-1 (see also Marchal et al. session C07). Biodegradation proceeded rapidly due to high cell densities of degrader bacteria. No bacterial growth, but rather a slow decline was observed. Desorption velocities could be fitted for the experiments, reflecting differences in surface areas of the soil amendments. The modelling revealed that high sorption did not have an inhibitory effect on phenanthrene biodegradation. Indeed, simulations showed that no growth of degrader bacteria was required for degradation, since the initial bacterial numbers were high enough to achieve complete mineralisation within the experiment duration. The evaluation and modelling of new experiments with different soil suspensions and added soil amendments (activated charcoal, biochar and compost) is currently under way.

MO 065

Extended dynamic range, high precision analysis of Polynuclear Aromatic Hydrocarbon compounds by GC-MS

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Polynuclear aromatic hydrocarbons (PAH) are a class of compounds used in the determination of contamination from fuels and oils and also monitored in the environment and food supply as potentially toxic compounds. The concentration range of PAHs in any given set of samples, depending on source, may be in the sub-ppb range up through the ppm range. A methodology is demonstrated which takes advantage of both GC-MS injection techniques and mass analysis techniques to extend the dynamic range of PAH analysis to encompass these concentrations. This is accomplished while maintaining the required levels of calibration, replicate and sample QA/QC (precision and accuracy), improving the productivity of the laboratory across a wide range of projects.

MO 066

Modelling PAH bioaccumulation in *Mytilus galloprovincialis* with a three-compartment model

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Polycyclic aromatic hydrocarbons (PAHs) are important organic pollutants in the aquatic environment due to their persistence and accumulation potential both in organisms and in sediment. With the entrance of PAHs into a clean ecosystem, indigenous aquatic biota may be affected due to the accumulation of PAHs in their adipose tissues. Bioaccumulation of pollutants may occur at each link in aquatic food chains, starting from primary producers to humans consuming various aquatic organisms with their diet. In this study, mussels were selected as biological indicators due to their broad geographic distribution, immobility and low enzyme activity, which cause significant bioaccumulation of pollutants in their tissues. PAH bioaccumulation and depuration in *Mytilus galloprovincialis* under dynamic environmental conditions were described using a three compartment model. First order kinetic equations were used for the description of accumulation and depuration of selected PAHs in mussel tissues. Data were obtained from experiments performed with selected PAHs under constant conditions. In the model, three compartments were defined: (1) mussels, (2) surrounding environment (seawater), and (3) algae (*Phaeodactylum tricornutum*) as food source for the mussels. During the bioaccumulation period, the mussels take up the contaminants both from seawater and with PAH exposed algae. Thus, the model considers dynamic exchange of PAHs between algae and seawater. Experimental data were used to parametrise and calibrate the proposed model for benzo(a)anthracene and phenanthrene. The observed dynamics could be described well for three different PAH concentrations. The model provides a mathematical description of bioaccumulation and depuration kinetics of PAHs in mussel species. For better agreement of simulation results with the experimental data, still a deeper understanding of the processes determining the chemical fate of PAH in the system of seawater, algae and mussels is required to be integrated into the model equations.

MO 067

Mass balance of polycyclic synthetic musks using a new dynamic segmented surface water/soil model

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Polycyclic synthetic musks (PCMs) are used as fragrances in a wide variety of personal care products. Among these compounds, the most important are galaxolide (HHCB) and tonalide (AHTN), used respectively, in Europe during the year 2000, at amounts of 1473 and 358 t. Since the removal of these substances through municipal sewage treatment has been estimated to be not higher than 60%, concentrations ranging from ng/L to µg/L of HHCB and AHTN are often measured in aquatic environments, posing a serious concern for ecosystems given the high potential for bioaccumulation of these chemicals. In this context, determining the exposure levels of ecosystems to these substances becomes a priority and environmental fate models represent an essential tool given the lack of monitoring data. In 2010, a survey along the Molgora River, flowing for about 40 km in a densely populated area in the Lombardy Region, northern Italy, was started. Samples of water and suspended solids were collected seasonally in 7 monitoring stations located up- and downstream of the 3 sewage treatment plants (STPs) present along the river. Seasonality in concentrations was observed, with the highest levels occurring in spring. Moreover, the samples collected downstream of the 3 STPs showed the highest concentrations. In order to investigate the reasons of this variability and to predict future trends, a new dynamic modelling approach (DynANet) based on an existing water-sediment model (DynA) was applied. In DynANet, the implementation of geographic information system (GIS) tools allows the subdivision of a river drainage basin in sub-basins and the resulting river links, classified according to the Strahler stream order, communicate by means of a downstream water flow. The loading data of runoff water and modelled chemical concentration coming from the different sub-basins are provided by the connection with the existing dynamic model SoilPlus, developed to evaluate the fate of organic chemicals in the air, litter and soil compartments and working in a GIS environment. The application of the DynANet model to the case study allowed to compile a preliminary mass balance for HHCB and AHTN and to predict concentration changes under environmental phenomena such as precipitations events, temperature variations, soil use, etc. The measured concentrations and simulated results were compared to the prediction of existing models such as GREATER.