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Unified model for sorption, sequestration and degradation in soils and sediments

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bolus administration by gavage of the pesticide as performed during testing. In 2005 the EFSA PPR laid out a basic framework for considering ADME processes during higher tier evaluations (EFSA Journal 2005; 240:1-21). As laid out, the approach rests on estimating two main inputs: FPM and ke. The opinion derived an estimate of FPM from a very limited number of studies and proposed a rather cumbersome approach for estimating ke. I have collected information from field and experimental studies to validate assumptions about FPM that may be used in these assessments. Data from small passerines demonstrate that birds precisely control the rate and timing of food consumption during the day to balance the need to secure adequate reserves for surviving during the night, and avoiding excess body mass during the day to facilitate take off and reduce predation risk. Field and laboratory studies have consistently reported that birds feed preferentially in the early morning and before dusk, with over 80% of mass gain occurring before noon. In addition, insectivorous birds experimentally forced to increase food intake through exposure to low temperatures and forced flying, showed an increase in meal size, but did not reduce time between feeding bouts (11-12 min). This demonstrates that birds are constrained by a digestive bottleneck, where feeding bouts are dictated by a fixed stomach and gizzard capacity. The increased food ingestion that occurs during periods of increased demand happens as a result of feeding over a larger proportion of available light hours. I also demonstrate, through nonlinear equation modeling, that ke should preferentially be derived from hen metabolism studies rather than as proposed, from the long-term NOEL and acute oral LOEL in the same species. The approach will be demonstrated with case studies using different birds and pesticides.

PE02-6
Measurement of pesticide intake rates and avoidance thresholds for small mammals

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Behaviour e.g. food avoidance, can influence risk by preventing body burdens from exceeding harmful thresholds and is a measurable response that may be included in PBPK models. Standard avoidance tests only measure the response of wildlife to treated food items over a fixed period, e.g. how much does an animal consume over a 4 hr period compared with untreated food. Far more information can be generated from studies if the response of the animal to treated food is monitored continuously over the exposure period. Such data can be used to measure not just the intake rate but also the avoidance threshold and recovery period. The objective of this work was to develop a laboratory based method which could be used with small mammals to determine the highest ingestion rate of different pesticide active ingredients and formulations in food that may be tolerated and to determine if avoidance influenced the response. Two species of small mammal were used, the laboratory rat (Rattus norvegicus) and the woodmouse (Apodemus sylvaticus). The laboratory rat was chosen as LD50 data are routinely available and the wood mouse was chosen as a focal species of the small mammal likely to feed on treated seeds. Specific measures included an avoidance response time (feeding time before animals stop feeding) and the avoidance threshold (AVT) expressed as both the dose ingested and dose rate to the point at which feeding stopped. Dietary concentrations were prepared as a block made from ground diet and a binding agent into which the pesticide was incorporated. As data were required on the uptake of the treated diet over time, a remote method of monitoring uptake was used by videoing the output from a balance on which the diet was placed on the first day of exposure to treated food. Food consumption was measured to estimate the ingested dose and the avoidance threshold (AVT). The time from when individuals started to feed to when they first avoided food (avoidance response time) was determined with reference to controls.

RA01 - (Non-)Extractability and bioavailability of organic chemicals in relation to analytical and regulatory issues

RA01-1
Unified model for sorption, sequestration and degradation in soils and sediments

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The objective of this study is to combine ad/desorption models for organic compounds with the growth and degradation kinetics of microbes in a mathematical simulation model. The goal is to interpret and predict observed effects, such as increasing persistence with time, decreasing degradation rates with concentration, and effects of amendments on sorption and degradation. A second objective is the mathematical definition of the terms "persistence", "bioavailability"and "bioaccessibility".

A numerical model was set up that combines ad/desorption, microbial metabolism and the formation of non-extractable residues (NER). It contains the compartments non-aqueous phase liquids or solids (N), dissolved compound (D), adsorbed (A) and sequestered (S) compound, bacterial mass (X) and biotic as well as abiotic NER. The exchange between these compartments is expressed by rates. Bacterial growth follows Monod kinetics minus decay (maintenance) rate, degradation is due to bacterial maintenance or growth. The evolving non-linear differential equations are solved numerically. The model is formulated in activity notation and implemented in Matlab. Comparison to the analytical Best equation gave (for suitable scenarios) full agreement, which is a verification of the model structure, mathematics and implementation of the numerical model. Validation by comparison to experimental studies is underway (see Rein et al., this session).

The unified model allows the simulation of sorption, sequestration, bacterial growth and degradation processes simultaneously and coupled together. By this, we hope to get a better understanding of aging and persistence in soil and of the formation of bound residues (better: non-extractable residues), but the goal is also the optimization of amendments, such as DOC, compost or charcoal.

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RA01-2
Microbial contribution to the bound residue formation in soils

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During degradation of organic pollutants in soil, a significant amount of the carbon remaining in soil is transformed to so-called bound or non-extractable residues. These residues can only be detected by use of isotope labeled compounds and are considered to consist of the parent compound and metabolites sorbed to the soil matrix. However, biomolecules such as fatty acids and amino acids were also found in the residue fraction indicating that C from the pollutant has been assimilated by microbial biomass. In order to estimate the extent of biogenic residue formation after incorporation of the carbon into microbial biomass, we investigated the fate of microbial biomass in soil using 13C-labeled bacteria. Even after one year of incubation, the remaining C was about equally distributed between microbial biomass different from E. coli and non-living soil organic matter. Hence, the latter fraction contributes to the 'bound residue' formation from pollutants in soil. The significant contribution of biogenic residue formation was confirmed for the microbial degradation of TNT, PAH´s, some pesticides and pharmaceuticals.

RA01-3
Covalent binding of sulfonamide antimicrobials to organic matter and soil: the role of oxidative enzymes and metal oxides

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Rapid formation of nonextractable resiudes (NERs) of sulfonamides in soils indicates that covalent bonding is initially the dominant process of sulfonamide dissipation. As electrophilic quinone groups of organic matter, which are sufficiently reactive to undergo nucleophilic attack by sulfonamides are probably not stable for longer periods, we hypothesize that a continuous formation of these quinones by oxidative enzymes or Mn/Fe oxides is a prerequisite for NER formation. Understanding the nature and stability of the formed bonds is essential for an appropriate environmental risk assessment for these veterinary antimicrobials. Therefore, we studied the NER formation mechanisms of the radio-labelled sulfonamide sulfamethazine (SMZ) and the stronger nucleophile para-ethoxyaniline (EXA) with natural Leonardite humic acid (LHA) in solution and agricultural soil samples after selective removal or addition of oxidants. Additionally, we tested the stability of the obtained NERs against desorption and pressurized liquid extraction. Studies using dissolved LHA show that 35% of the sorbed SMZ could be desorbed in single solute SMZ system and 45% in the competition experiment with EXA. Strong covalent bonding of SMZ occurs in the presence of laccase in both single solute and competition experiment. In the control soil samples, 60% of SMZ formed NER in the presence of oxygen and only 30% under anaerobic conditions. Slower kinetics were shown for the reaction of SMZ when EXA was added few days prior to SMZ application. Addition of Mn oxide and model hydroquinones significantly decreased the extractability of SMZ and thus increased NER formation to > 85%. The study clearly shows that the action of oxidative enzymes or oxidants is involved in the formation of NER of sulfonamides in soils. But also quinone groups readily adding sulfonamides upon their entry in the soil are to certain extent present in soil organic matter which explains the NER fromation also under anaerobic conditions. After this initial phase the subsequent, slow NER formation phase might be either controlled by (i) the desorption of sulfonamides from the solid phase, which subsequently react with quinones continuously or (ii) a slow conversion of "unstable"covalent bonds into "stable"ones more resistant during the extraction procedure.

RA01-4
Instantaneously decreased extractability of sulfadiazin in soil batch experiments

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Effects of antibiotics in soil on microbial end points, leaching potential and biodegradation depend on their (bio)availability, which is generally approximated by extraction methods with mild solvents. The sulfonamide antibiotic sulfadiazine (SDZ) shows typical 'aging' in soil, i.e. decreasing extractability over time. A sequential extraction method proved to be appropriate to investigate sequestration of SDZ in batch experiments (Förster et al., 2009, ES&T). Concentration dynamics over 200 days in these extracts could be described well by a conceptual kinetic model which included a reversible sequestration process as well as an irreversible sequestration resulting in 'non-extractable residues' (Zarfl et al., 2009, Chemosphere). The experimental results along with the model simulations indicated reduced extractability of SDZ already shortly after the start of incubation. We assumed this finding to be attributed to very fast processes, being possibly of relevance for risk assessment. Therefore, we performed a set of soil batch experiments focussing on the first 24 hours of incubation and tested two hypotheses: (i) manure leads to formation of micro-aggregates or provides additional sorption places, (ii) water content of the soil before spiking SDZ and/or manure influences the observed effect. SDZ was added with water or manure to soils of different water content (dry vs. wet). We used the proved sequential extraction method (1: $CaCl_2$, 2: methanol, 3: acetonitrile/water with microwave); analysis of SDZ was performed by LC-MS/MS.

Immediately after spiking SDZ solution to soil, extractability was reduced in all setups confirming processes on a time scale of minutes. No considerable differences in the initial SDZ distribution between the different experimental treatments were observed, so none of our two hypotheses could be confirmed. However, during the following 24 hours of incubation, sequestration proceeds further, reducing extractability of SDZ with $CaCl_2$ and methanol (EAS fraction), while simultaneously increasing extractability with the high-temperature method (RES fraction). Rate constants for a sequestration process from EAS into RES appeared fairly constant in all experiments. In contrast, rate constants for an additional sink process out of EAS were clearly lower in the water compared to the manure treatments, indicating a linkage to microbial activity.

RA01-5
The influence of alternating dry-wet cycles on the water-extractability of aged 14C-pesticide residues in soils

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Due to future climate predictions, an increase in droughts, followed by heavy rain events can be estimated. Soil drying and rewetting may have a considerable impact on an increased release of pesticides present in agricultural soils, representing a potential risk by pulse inputs to deeper soil layers or aquifers after rain events. Laboratory studies using soil containing environmentally long-term aged (9-17 years) 14C-labeled residues of the herbicide ethidimuron (ETD), methabenthiazuron (MBT) and the fungicide anilazine (ANI) showed a significant increase of 14C-activity in the water-extract after soil drying. The total water-extracted 14C-activity (the amount of residual 14C-activity in the sample equals 100%) accounted for 44% (ETD), 15% (MBT), and 20% (ANI) after 20 alternating dry-wet cycles. The amount of water-extracted 14C-activity from the constantly moistened soil remained significantly lower at 16% (ETD), 5% (MBT), and 6% (ANI) after 20 cycles, respectively. LC-MS/MS analyses of the raw water extracts of the dried