



The fate of organic pollutants in soil - Emerging views on the environmental relevance of non-extractable residues

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The fate of organic chemicals in soils is determined by both physicochemical (e.g. sorption and sequestration) and biological processes (microbial degradation). As a result, C from the pollutants entering the soil partitions into the parent compound, metabolites, non-extractable residues (NER), CO₂ and microbial biomass. This distribution has to be considered for proper risk assessment. The majority of biodegradability tests have been conducted in aqueous systems (e.g. OECD 301 tests). For approval of chemicals in the new EU legislation (REACH), however, information about the fate of the tested compound in soil is required. As the necessary simulation tests in soils (e.g. OECD 307) are rather expensive and complex, it would be advantageous to use the data from aqueous systems to predict the fate of a chemical in soils. This, however, is difficult because not all processes occurring in soil are reflected in these data. In particular, NER formation cannot be simulated by tests in aqueous systems, but this is important for adequate risk assessment. The chemical nature of NER, which has not yet been sufficiently elucidated, determines the potential hazard associated with them.

In general, it is assumed that NER are mainly composed of adsorbed and sequestered parent compound or metabolites. In contrast, we could show that part of the NER is derived from the biomass of bacteria using the pollutant as carbon source. The biogenic residues are completely harmless in contrast to NER derived from the pollutant or toxic metabolites, which might be remobilized under certain conditions and thus have to be considered hazardous. We therefore compared the biodegradation of isotope labeled 2,4-D, ibuprofen and ciprofloxacin in aqueous systems and in soil. In the soil experiment, we also quantified the contribution of microbial residues to NER formation. The results revealed the processes responsible for NER formation and allowed establishing a quantitative relationship between the degradation in the two systems. Both 2,4-D and ibuprofen were mineralized fast in the aqueous system, although ibuprofen narrowly failed to meet the criteria for ready bioavailability. In soil, mineralization was lower than in the aqueous system, and significant amounts of NER were formed. High label incorporation into fatty acid and amino acids indicated that virtually all of the NER derived from microbial biomass. In contrast, ciprofloxacin was not at all mineralized in aqueous systems. In soil, we detected a small but significant mineralization of this compound but no metabolites. NER formation from ciprofloxacin was fast and independent of the microbial activity showing that NER formation from sequestration of parent compounds and from biogenic residues are competitive processes in soil. As ciprofloxacin is a potent antibiotic, it reduced the activity of both sewage sludge and soil microorganisms. This effect was weaker in soil than in the aqueous system, because sorption and spatial inaccessibility reduced the toxic effect in soil.

In conclusion, for readily degradable compounds, mineralization is lower in soil than in water. A significant part of the carbon will be incorporated into microbial biomass, which may later be stabilized in soil organic matter, resulting in biogenic residues. These may account for a large portion or even all of the NER detected by isotope mass balance. In contrast, toxic compounds are mineralized more easily in soil than in water, because NER formation and the spatial heterogeneity of soil together with the vast microbial biodiversity result in lower toxicity of the compounds. NER formation which is not accompanied by corresponding mineralization indicates formation of potentially hazardous NER derived from the parent compounds or (toxic) metabolites. In contrast, NER formation associated with significant mineralization indicates biogenic residue formation and thus a low hazard.