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Contribution of microorganisms to non-extractable residue formation from biodegradable organic contaminants in soil

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Biodegradation of organic contaminants in soil is actually understood as their transformation into various primary metabolites, microbial biomass, mineralisation products and non-extractable residues (NER). NER are generally considered to be composed of parent compounds or primary metabolites with hazardous potential. Up to date, however, their chemical composition remains still unclear. Studies on NER formation are limited to quantitative analyses in soils or to simple humic acids-contaminant systems. However, in the case of biodegradable organic compounds, NER may also contain microbial biomass components, e.g. fatty acids (FA) and amino acids (AA). After cell death, these biomolecules are incorporated into soil organic matter (SOM) and stabilised, ultimately forming biogenic residues which are not any more extractable. We investigated the incorporation of the ^{13}C-label into FA and AA and their fate during biodegradation experiments in soil with isotope-labelled 2,4-dichlorophenoxyacetic acid ($^{13}C_6$-2,4-D) and ibuprofen ($^{13}C_6$-ibu) as model organic contaminants. Our study proved for the first time that nearly all NER formed from $^{13}C_6$-2,4-D and $^{13}C_6$-ibu in soil derived from harmless microbial biomass components stabilised in SOM. ^{13}C-FA and ^{13}C-AA contents in the living microbial biomass fraction decreased over time and these components were continuously incorporated into the non-living SOM pool in biotic experiments with $^{13}C_6$-2,4-D and $^{13}C_6$-ibu. The ^{13}C-AA in the non-living SOM were surprisingly stable from day 32 ($^{13}C_6$-2,4-D) and 58 ($^{13}C_6$-ibu) until the end of incubation. We also studied the transformation of $^{13}C_6$-2,4-D and $^{13}C_6$-ibu into NER in the abiotic soil experiments. In these experiments, the total NER contents were much lower than in the corresponding biotic experiments. The absence of labelled biomolecules in the NER fraction in abiotic soils demonstrated that they consist of the potentially hazardous parent compounds and / or their metabolites.

Biogenic residue formation is relevant during biodegradation of organic contaminants, whereas abiotic NER are formed from the non-biodegraded residual contaminants. Abiotic NER and biogenic residue formation are competitive processes and do not occur in a similar extent. In the biotic treatment, the rapid mineralisation of an organic compound reduces the extent of abiotic NER formation via physico-chemical interactions between a parent compound and / or its primary metabolites with SOM. Therefore, in order to properly assess the potential risks of a target contaminant in soil to humans and the environment, it is necessary to distinguish between abiotic NER and biogenic residue formation in the mass balances of contaminants.