**Biogenic residue formation from pesticides in soil: extent and relevance for risk assessment.**

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Pesticides as anthropogenic chemicals are of high interest; since they are deliberately applied in high amounts to soils to support food crop production. Chemicals entering this complex soil system may undergo various turnover processes. They can be degraded chemically, biologically by microorganisms, immobilised in form of non-extractable residues (NER), volatilised or taken up by living organisms. Due to the difficulties in NER analytics in complex soil environments, their determination is limited mainly to quantitative analyses in 14C turnover studies. This approach, however, does not provide any information about their chemical composition. Therefore, it is speculated that these compounds of unknown structure immobilised as NER may be released from soil organic matter (SOM) and transported to all compartments of the environment posing a potential risk for the environmental and human health (Barriuso et al., 2008). However, it is generally known that microorganisms can use carbon from an organic contaminant to synthesise their biomass compounds, for instance fatty acids (FA) and amino acids (AA). After death, these biomass compounds can be incorporated into SOM forming ultimately hardly extractable biogenic residues (Nowak et al., 2011). As the biogenic residues are composed of non-toxic natural compounds, they do not pose any risk to human and environment.

Therefore, the relevance of biogenic residue formation from microbial degradation of structurally diverse groups of pesticides showing different degradation kinetics: 2,4-D (phenoxyacetic acid), glyphosate (organophosphate), metamitron (triazinone) and bentazone (benzothiadiazine) was investigated at different time scales (80 days: glyphosate and metamitron, 64 days: 2,4-D and 1 year bentazone). Compound-specific isotope analysis (13C and 15N-label) of fatty acids (FA) and amino acids (AA) extracted from the living and non-living SOM was used to quantify biogenic residue formation. The extent was balanced and compared with the hazardous xenoNER amounts, derived from parent compounds or metabolites. 13C-FA and 13C-AA in the living microbial biomass fraction initially increased, thereafter their contents decreased and a continuous incorporation of these biomolecules into the non-living SOM was observed. Three pesticides 2,4-D, glyphosate andmetamitron were mineralized rapidly and at the end labelled CO2 constituted about 58% of 13C6-2,4-D, 73% of 13C3-glyphosate and 60% of 13C6-metamitron equivalents. In line with the high mineralization, the content of 13C-biogenic residue from these herbicides was high and amounted to 44%, 20% and 30% of 13C6-2,4-D, 13C3-glyphosate and 13C6-metamitron equivalents, respectively. 13C-biogenic residues from 13C6-2,4-D, 13C3-glyphosate and 13C6-metamitron constituted nearly the total amount of NER. Analogous to the 13C-biogenic residues from 13C3-glyphosate, 15N-NER were also of biogenic origin, and at the end 15N-biogenic residues amounted to 50% of 15N-glyphosate equivalents and constituted 100% of the total 15N-NER. The residual 40% was attributed to 15N-AMPA. In contrast to 2,4-D, glyphosate and metamitron, the mineralization of 13C1015N-bentazone was very low (~9% after 1 year). However, low 13C-label incorporation from this recalcitrant pesticide into PLFA was also observed (initially into gram-negative bacteria, in the later phase also into gram-positive bacteria). Therefore, in case of more recalcitrant pesticides like bentazone, the formation of biogenic residues, although expected to be very low, cannot be completely excluded.

*Bibliography:*

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