Geophysical Research Abstracts
Vol. 14, EGU2012-9673, 2012
EGU General Assembly 2012

Influence of alternating soil drying and wetting on the desorption and distribution of aged 14C-labeled pesticide residues in soil organic fractions

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A laboratory experiment was conducted to evaluate the effect of alternating soil drying and wetting on the release of aged ^{14}C-labeled pesticide residues and their distribution in soil organic fractions (humic acids, fulvic acids, and humin substances). The used soils (gleyic cambisol; C_{org} 1.2%, pH 7.2) were obtained from the upper soil layer of two individual outdoor lysimeter studies containing either environmentally long-term aged ^{14}C residues of the herbicide ethidimuron (ETD; 0-10 cm depth; time of aging: 9 years) or methabenzthiazuron (MBT; 0-30 cm depth; time of aging: 17 years). Triplicate soil samples (10 g dry soil equivalents) were (A=dry/wet) previously dried (45°C) or (B=wet/wet) directly mixed with pure water (1+2, w:w), shaken (150 rpm, 1 h), and centrifuged ($\sim$2000 g). The resulting supernatant was removed, filtered (0.45 μm) and subjected to ^{14}C activity analysis via liquid scintillation counter (LSC), dissolved organic carbon (DOC) analysis, and LC-MS-MS analysis. This extraction procedure was repeated 15 individual times, for both setups (A) and (B). To determine the distribution of the aged ^{14}C labelled pesticide residues in the soil organic matter fractions, the soil samples were subject to humic and fulvic acids fractionations at cycles 0, 4, 10, and 15. The residual pesticide ^{14}C activity associated with the humic, fulvic, and humin substances (organic fraction remaining in the soil) fractions was determined via LSC.

The water-extracted residual ^{14}C activity was significantly higher in the extracts of the dry/wet, compared to the wet/wet soil samples for both pesticides. The total extracted ^{14}C activity in the dry/wet soil extracts accounted for 51.0% (ETD) and 15.4% (MBT) in contrast to 19.0% (ETD) and 4.7% (MBT) in the wet/wet extracts after 15 water extractions. LC-MS-MS analysis revealed the parent compound ETD 27.9 μg kg^{-1} soil (dry/wet) and 10.7 μg kg^{-1} soil (wet/wet), accounting for 3.45 and 1.35% of total parent compound initially applied after a total of 10 water extractions, respectively. MBT was detected but not quantified, whereas its metabolite MABT (2-methylamino-benzothiazole) was detected (0.8 vs 0.3 μg kg^{-1}, in dry/wet vs wet/wet soil water extracts, respectively) after 10 water extractions. These results demonstrate the long-term persistence of ETD and MBT and metabolites and their remobilization potential facilitated by soil drying and rewetting.

For all samples, the DOC content was significantly higher for the water extracts obtained after dry/wet cycles compared to values obtained from the constantly moistened soil samples. The DOC and water extracted residual ^{14}C activity correlated positively. This result indicates that pesticide residues are associated with DOC which might function as a shuttle for the distribution of pesticide residues. This molecular association can be released into solution where it might be degraded co-metabolically.

Overall, the results suggest that intermittent soil drying and rewetting alters the disaggregation of soil aggregates, resulting in a release of entrapped organic carbon and pesticide molecules.

Furthermore, analysis of the organic fractions obtained from the ^{14}C pesticide residues containing soil revealed that ^{14}C residues were mainly associated with the humin fraction.

The analysis of the organic fractions revealed that extractable residual ^{14}C activity of ETD was more associated with the fulvic acid fraction compared to the residual pesticide ^{14}C activity of MBT, being more associated with the humic acid fraction.

For ^{14}C MBT residues, the distribution of the ^{14}C residues in the organic fractions remained rather equal throughout the water extraction cycles. This observation can be supported by the non-mobile character of MBT in soil and its higher K_{OC} value of 247–587 compared to the rather mobile pesticide ETD with a K_{OC} value of 37.1–149. However, for both pesticides a decrease of residual ^{14}C activity in the humic and fulvic acid fractions throughout the water extractions cycles was observed. This observation was more pronounced in the samples of the dry/wet setup.