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Influence of 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) ^{14}C-labeled residues of the herbicide ethidimuron (ETD), methabenthiazuron (MBT) and the fungicide anilazine (ANI) showed a significant increase of ^{14}C-activity in the water-extract after soil drying. The total water-extracted ^{14}C-activity (the amount of residual ^{14}C-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 ^{14}C-activity from the constantly moistured 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 and rewetted soils revealed the parent compound ETD and MBT in detectable amounts (15.0 μg ETD kg^{-1} and 0.23 μg MBT kg^{-1}in total, calculated per kg soil (0-10 cm ETD-soil / 0-30 cm MBT-soil), accounting for 1.83% and 0.01% of total applied parent compound per soil layer, respectively), but neither ANI nor the main ANI metabolite dihydroxy-anilazine could be detected. In comparison, the constantly moistened soil released significantly smaller amounts of residual pesticide fractions (1.87 μg ETD kg^{-1} in total, calculated per kg soil (0-10 cm ETD-soil), accounting for 0.23% of total applied parent compound, respectively, but no MBT or ANI residues were detected).

For all soils the water-extracted dissolved organic carbon (DOC) was significantly higher in the previously dried soils, compared to the constantly moistened soils (ETD-soil: 10.8 vs 4.8%; MBT-soil: 8.4% vs 3.7%; ANI-soil: 9.8% vs 4.6% of total organic carbon in the soil). In case of the previously dried soils, the DOC content correlated with the measured ^{14}C-activity in the aqueous liquids (ETD-soil: r=0.80; MBT-soil: r=0.81; ANI-soil: r=0.91).

The overall finding demonstrates a readily water-extractable pesticide residue fraction which can easily be removed from the soil, representing a potential risk for leaching. The data suggest that an increase in environmentally relevant dry-wet cycles may result in an increased remobilisation and release of aged pesticide residues in soils.