Influence of dry-wet cycles on the water-extractability of aged ^{14}C-pesticide residues in soils

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INTRODUCTION & SCOPE OF THE STUDY

A growing world population and a growing demand for food and bioenergy may require an increased use of pesticides for crop protection [1]. In agriculture, a majority of approximately 80% of all pesticides are used for crop protection, exceeding 5.0 billion pounds (approximately 2.3 million metric tons) globally in 2000 and 2001 only [2]. Simultaneously, a decline in arable land for agricultural production and an increase of agricultural droughts are predicted for the future [3-5]. Droughts, increased in intensity as well as duration, supposed to impact most parts of the world, including large areas of conventional agricultural practice as predicted in numerous climate scenarios [6]. In return, precipitation models indicate "a shift toward more intense and extreme precipitation for the globe as a whole and over various regions" [67, and "intense and heavy episodic rainfall events are interspersed with longer relatively dry periods with increased evapotranspiration" [8].
The scope of this study was: 1) evaluate the influence of alternating soil drying and rewetting compared to permanently moistened soil on the water-extractability of aged ^{14}C-labeled pesticide residues; 2) analyses of the soil water extracts by means of liquid scintillation counter (LSC) to determine ^{14}C-activity, and 3) LC-MS/MS to determine the chemical nature and quantities of the water-extracted pesticide residues; and 4) the influence of dry-wet cycles on the release of dissolvable organic carbon (DOC).

RESULTS & DISCUSSION

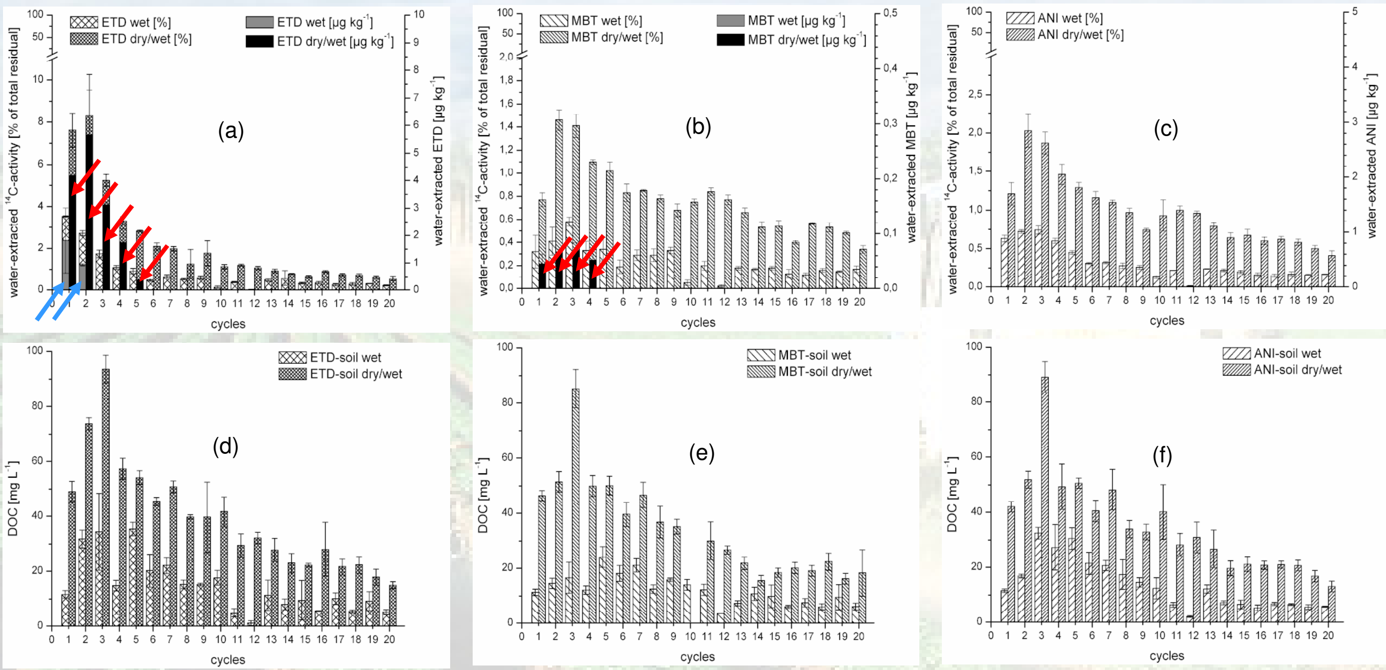

Figure: Water-extracted ^{14}C-activity (left y-axis, in % of total residual ^{14}C-activity in the sample) and LCMS/MS detected compound (right y-axis, in mg kg^{-1} soil) in the water extracts of (a) ETD-soil, (b) MBT-soil, and (c) ANI-soil. Standard deviation of n = 9. Dissolved organic carbon (DOC), in mg L^{-1} water extract of (d) ETD-soil, (e) MBT-soil, and (f) ANI-soil. Standard deviation of n = 9.

RESULTS & DISCUSSION

•The total water-extracted ^{14}C-activity was significantly higher after soil drying, accounting for 44% (ETD), 15% (MBT), and 20% (ANI) after 20 dry-wet cycles vs 16% (ETD), 5% (MBT), and 6% (ANI) after 20 cycles in the constantly moistened soil.

•LC-MS/MS analyses of the raw water extracts of the previously dried soils revealed the parent compound ETD and MBT in detectable amounts (15.0 µg kg^{-1} ETD and 0.23 µg kg^{-1} soil MBT in total, in 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 was found.

•Since the higher amount of water-extracted ETD must be attributed to the generally lower sorption affinity of ETD in soil [9], the low desorbed fraction of MBT could be due to microbial degradation [10] and the generally longer aging time under outdoor conditions (12 vs 9 years). Since anilazine is known to form soil bound residues rapidly after application [11], it was not expected to detect any parent or metabolite compounds in the aqueous extracts.

•DOC content in the water extracts 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% DOC 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 (r=0.80-0.91).

•The findings demonstrate the long-term persistence of various pesticides and a readily water-extractable pesticide residues fraction which can easily be removed from the soil (triggered by drying and wetting), representing a potential risk for leaching.

MATERIAL & METHODS

•Soils: Orthic Luvisol (C_{org}: 1.2%, sand: 6.4%, silt: 78.2%, clay: 15.4%, pH: 7.2) from outdoor lysimeter (1 m^2 x 1.1 m) studies.

•Pesticides: thiadiazolylurea herbicide ethidimuron (ETD; 1-(5-ethylsulfonyl-,3,4-thiadiazol-2-yl)-1,3-dimethylurea), applied as [thiadiazol-2-$^{13/14}$C]ethidimuron; dimethylurea herbicide methabenzthiazuron (MBT; 1-(1,3-benzothiazol-2-yl)-1,3-dimethylurea), applied as [phenyl-U-^{14}C]methabenzthiazuron; triazine fungicide anilazine (ANI; 4,6-Dichloro-N-(2-chlorophenyl)-1,3,5-triazin-2-amine) applied as [benzene-ring-U-^{14}C]anilazine. All pesticides in the lysimeter soils were subject to environmental aging until sampling in April 2006. Details for pesticide application are given in the Table.

•Triplicates (10 g) of ETD-, MBT-, and ANI-soil were either A) directly mixed with distilled water, or B) firstly dried at 45°C prior water addition (1+2; w:w). All samples were simultaneously shaken (1 h at 150 rpm), and subsequently centrifuged. The resulting supernatants were filtered (0.45 µm) prior analyses (^{14}C-activity; dissolved organic carbon (DOC); pesticides/metabolites using LC-MS/MS). For setup A, all moistened soil samples were stored in the dark at 3°C after removal of the supernatant, until all samples of setup B were completely dried, and the cycle could be repeated. Both setups A and B were subject to 20 successive water shaking extractions, with 20 intermittent drying cycles for setup B.

Table: Application time and total quantities of applied ^{14}C-labeled and non-labeled ETD, MBT and ANI on lysimeter soils. a.i. active ingredient; *in total after three applications, 1988, 1992, and 1994; **in total after 5 consecutive annual applications, 1985-1989. Sampling of all lysimeter soils was performed in April 2006.

Soil	Date of application [dd/mm/yy]	Applied a.i. [mg m^{-2}]	Total applied a.i. [kg ha^{-1}]	Applied ^{14}C-activity [MBq m^{-2}]	Specific ^{14}C-activity [kBq mg^{-1}]
ETD-soil	13.11.1997	123	1.23	107.3	870.0
MBT-soil	29.11.1994 (last application)	879*	8.79*	261.6*	297.7
ANI-soil	13.06.1989 (last application)	1978**	19.78**	372.5**	188.4

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