Release of aged $^{14}$C-atrazine residues from soil facilitated by dry-wet cycles

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Intermittent dry-wet cycles may have an important effect on soil structure and aged pesticide residues release (1). A laboratory study was conducted to assess the maximum potential of water extractable aged atrazine residues influenced by soil drying and wetting. The used soil was obtained from an outdoor lysimeter (gleyic cambisol; $C_{org}: 1.45\%$), containing environmentally aged (22 years) $^{14}$C-atrazine residues. For the experiment, soil from 0-10 cm depth was used since most residual $^{14}$C activity was previously found in this layer (2, 3). Triplicate soil samples with a residual water content of approx. 8% were either dried (45˚C) prior water addition or directly mixed with distilled water (soil+water: 1+2, w:w). The samples were shaken (150 rmp, 60 min, at 21˚C), centrifuged (approx. 2000 g), and the supernatants were filtered. Water-extracted residual $^{14}$C activity was detected via liquid scintillation counter. The total water-extracted $^{14}$C activity (the amount of residual $^{14}$C activity in a sample equals 100%) was significantly higher ($p<0.01$) in the dry-wet water extracts, accounting for 8.2% vs 1.9% in the water extracts from the constantly moistened soil, after a total of 10 alternating dry-wet cycles. LC-MS/MS analyses of the dry-wet and constantly moistened soil water extracts revealed 2-hydroxy-atrazine as the main atrazine metabolite in detectable amounts, accounting for 2.5 $\mu$g kg$^{-1}$ and 0.9 $\mu$g kg$^{-1}$, respectively, in total after 10 successive water extraction cycles.

For both setups the water-extracted dissolved organic carbon (DOC) was significantly higher in the previously dried soils, compared to the constantly moistened soils, accounting for 17% vs 10% released as DOC of total organic carbon in the soil. In both cases, the DOC content correlated positively with the measured $^{14}$C-activity in the aqueous liquids (dry-wet: $r=0.91$; constantly moistened: $r=0.93$). This result gives evidence that atrazine residues are associated with organic carbon, which can also be released into solution.

The finding of this study demonstrates a significant effect of dry-wet cycles on the remobilization of long-term aged atrazine residues in soil. In terms of changing climatic conditions this might be considered as an increased risk for pesticide residues remobilization in soils.

