



Evidence of the biodegradation of 2,4-D bound residues in soil with ^{13}C labelling techniques

Lerch T.Z. (1,2), Dignac M.-F (1), Barriuso E. (2), Mariotti A. (1)

(1) Laboratoire de Biogéochimie et Ecologie des Milieux Continentaux (UMR 7618), Batiment EGER, Campus INRA-INAPG, 78850 Thiverval-Grignon, France (2) Unité Environnement et Grandes Cultures, (UMR1091), Batiment EGER, Campus INRA-INAPG, 78850 Thiverval-Grignon, France (thomas.lerch@grignon.inra.fr)

When assessing the leaching risk of pesticides, it is important to account for their degradation by soil microorganisms and their binding to soil organic or mineral particles (Barriuso et al., 1994). Questions still remain about the long-term consequences of the accumulation of non-extractable residues in soil and their possible remobilization (e.g. Khan & Bheki, 1990, Barriuso & al., 2004). In this work, we used ^{13}C labelling techniques to follow the formation, the nature and the fate of bound residues in a cultivated soil. First, soil samples were incubated during 6 months with [^{13}C]2,4-D in sealed flasks. We measured the distribution of labelling in the CO_2 evolved, microbial biomass measured by fumigation-extraction, the water, methanol and dichloromethane soluble fractions, and the residual bulk soil. The residual bulk soil sampled after 15 days or 3 months was analysed using Pyrolyse-GC-c-IRMS and ^{13}C -NMR then re-incubated with or without fresh soil. The enriched ^{13}C - CO_2 evolved was measured during 3 months to evaluate its biodegradability.

In the first incubation, the fate of the pesticide was similar to that found in previous studies using [^{14}C]2,4-D. After 8 days a maximum of 7% of the initial amount of pesticide is incorporated in the biomass. After one month about 55% was mineralised and 45% remained in the soil as bound-residues. After 6 months, the CO_2 and the biomass were still enriched in ^{13}C . These results suggest that a part of the bound-residues was still bioavailable. Although Pyrolysis-GC-c-IRMS analyses showed a great heterogeneity in the samples the molecular form of the bound residues appeared to differ from the original 2,4-D. Bound residues mainly involved 2,4-DCP and other unidentified metabolites. ^{13}C -NMR did not provide any information because the ^{13}C

enrichment was to low. Whatever their chemical structure is, the re-incubation of these bound residues clearly showed their biodegradability. After 3 months, the mineralization reached 7.1% and 4.7% of the initial amount of non-extractable residues aged 15 days and 3 months respectively. The addition of fresh soil caused an increase of about 40% in the mineralization of the youngest residues but had no significant effect on old residues. The investigation of the chemical structure and bioavailability of non extractable residues by ^{13}C labelling techniques is appropriate for long term studies. This approach is necessary to include the remobilisation of bound residues of organic pollutants into existing models.

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