

PESTICIDE TRANSFER IN THE UNSATURATED ZONE: SORPTION AND DEGRADATION PROCESSES IN GEOLOGICAL STRATUM

HÉLÈNE BLANCHOU¹ & ENRIQUE BARRIUSO², VALÉRIE BERGHEAUD², CÉLINE SCHOTT³, JULIEN TOURNEBIZE⁴, LAURINE NICOLA³, GAËLLE TALLEC¹, ANNIET LAVERMAN⁵ & FLORENCE HABETS⁵

¹ EPHE- UMR Sisyphe, 4, place Jussieu, BC105, 75252 Paris cedex 5, ²UMR EGC, Bat. EGER BP1, 78850 Thiverval-Grignon, ³ INRA SAD ASTER, 662, avenue Louis Buffet, 88500 Mirecourt, ⁴ CEMAGREF Unité HBAN, Parc de Tourvoie BP 44, 92163 Antony, ⁵ UPMC CNRS – UMR Sisyphe, 4, place Jussieu, BC105, 75252 Paris cedex 5
Email : helene.blanchoud@upmc.fr, Enrique.Barriuso@grignon.inra.fr

The contamination of groundwater by pesticides is still difficult to understand at the catchment scale. If a lot of experiments described the fate of pesticides in soils, the unsaturated zone is not often studied. However, this compartment needs to be described to understand and model the fate of pesticides towards groundwater. In the Phyt'Oracle project (INSU-CNRS funding), the fate of pesticides in the unsaturated zone in the Orgeval catchment (103 km²) was studied. A core sample was realized from the surface until 40m depth and adsorption and degradation kinetics were measured for atrazine and isoproturon. A sample campaign was also realised for surface soils in different fields of the watershed according to the pedologic map. Furthermore, pesticide uses from the last 20 years and contamination of river and groundwater were also assessed for the model database. In this presentation, only laboratory studies are described.

Samples from horizons were classified according to geological stratum and analyzed for organic carbon, organic matter, total nitrogen and CaCO₃ content. 16 samples were analysed for the adsorption process, using 10ml of a U ring ¹⁴C labeled of isoproturon and atrazine solutions. Solutions were shaken for 24h and analyzed by scintillation for pesticide concentration. 5 samples were softly dried and sifted at 5mm for degradation process. Degradation kinetics were measured after 7, 14, 28 and 70 days of incubation. Mineralisation (¹⁴CO₂), water and methanol extracted and finally bound residues were quantified for each date. Water and methanol extracted residues were also identified by HPLC to determine the pesticide and by-products occurrence.

Organic carbon content is low in the unsaturated zone (from 0,1 to 0,3 %) but is present in each geological stratum. Sorption coefficients (K_d) are homogeneous for atrazine (from 0.2 to 2 L/kg) and isoproturon (from 1 to 3 L/kg) except for the deepest sample (36,6m) for which K_d of atrazine is 13.7 L/Kg. These K_d values are in agreement with those obtained for surface soils in the literature: for atrazine, between 1 and 11 L/kg (Francioso et al., 1992, FOOTPRINT) and between 0.5 and 1 L/kg (Abdelafid et al., 2000) and for isoproturon, between 2 and 6 l/kg (Cooke et al., 2004). Considering the organic carbon content, adsorption process (K_{oc}) in the unsaturated is very different of the surface soil, showing that adsorption in the ZNS is not related to organic carbon content.

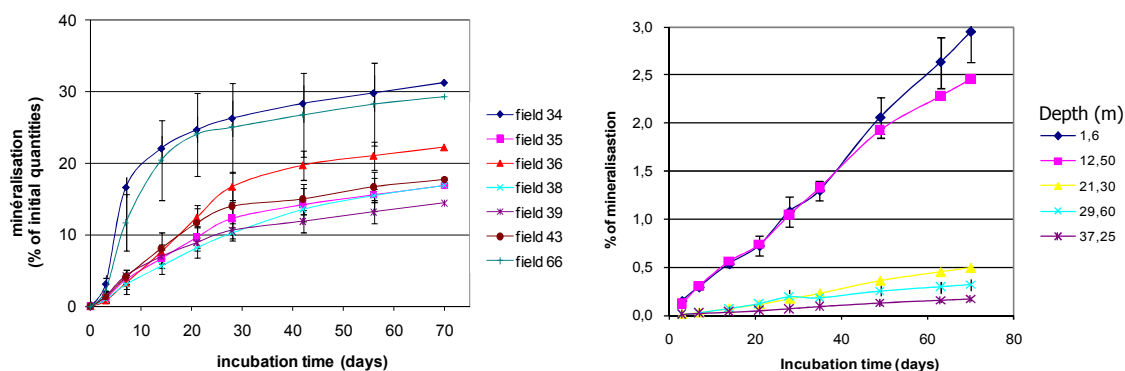


Figure 1. Isoproturon mineralisation in selected soils (left graph) and in different horizons of the non saturated zone (right graph)

Mineralisation in the fields (surface soils) of the catchment is between 15 and 30% of the initial quantities. This mineralisation is very low in the unsaturated zone: from 1 and 3% (1 to 12m depth) to less than 0.5% for isoproturon (figure 1) and also for atrazine after 70 days.

Atrazine residues extracted with water decrease with depth in the unsaturated zone but are not correlated to the time of contact. It is not observed for isoproturon, where the extractability of residues has the same profile in each horizon (figure 2, right graph). This percentage of residues extractable with water decreases slowly with time of incubation. Only a few percentages of not extractable residues are found after 70 days. In the surface soils (fig. 2, left graph), not extractable residues of isoproturon increase with time of incubation until 70% of total quantities. The extracted part with water is maximal at the beginning of incubation (until 45%) and then decrease to be negligible after 28 days.

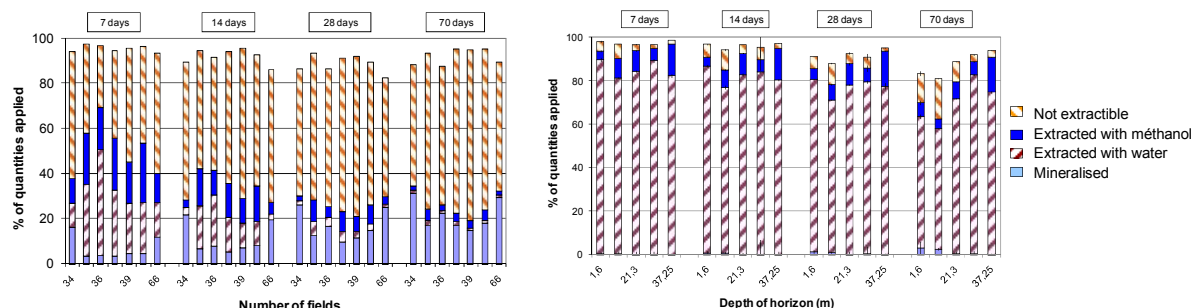


Figure 2. Extractability of isoproturon residues in selected soils (left graph) and in the unsaturated zone at different depths (right graph) after 7 to 70 days of incubation

To conclude, fate of atrazine and isoproturon in the unsaturated zone cannot be compared to what is observed in soils in the Orgeval catchment. Once the pesticides reached the unsaturated zone, mineralisation processes can be neglected. Some by-products are found, especially for isoproturon, but atrazine remains the main residue found even after 70 days, corresponding to a half time of 100 to 200 days (100 to 420 days for isoproturon). Adsorption of pesticides is reversible and bound residues don't occur. These processes will be included in the transfer of pesticide model, STICS-Phyto-MODCOU developed at the catchment scale.

KEY WORDS: Isoproturon, atrazine, unsaturated zone, Orgeval, Phyt'Oracle.

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REFERENCES

- Abdelhafid R. Houot S. & Barriuso E. (2000) Dependence of atrazine degradation on C and N availability in adapted and non-adapted soils. *Soil Biology & Biochemistry*, 32, 389-401.
- Cooke C. M., Shaw G. & Collins C. D. (2004) - Determination of solid-liquid partition coefficients (K_d) for the herbicides isoproturon and trifluralin in five UK agricultural soils. *Environmental Pollution*, 132, pp. 541-552.
- FOOTPRINT (2009) - The FOOTPRINT Pesticide Properties DataBase. Database collated by the University of Hertfordshire as part of the EU-funded FOOTPRINT project (FP6-SSP-022704): <http://www.eufootprint.org/ppdb.html>
- Francioso O., Bak E. & Sequi P. (1992) - Sorption of atrazine and trifluralin in relation to the physico-chemical characteristics of selected soils. *The Science of the Total Environment*, 123/124, pp. 503-512.