Using the long-term memory effect of pesticide and metabolite soil residues to estimate field degradation half-life and test leaching predictions

J. Farlin [a],*, T. Gallé [a], M. Bayerle [a], D. Pittois [a], C. Braun [a], H. El Khabbaz [a], C. Lallement [a], U. Leopold [a], J. Vanderborght [b], L. Weihermueller [b]

[a] CRP Henri Tudor, CRTE, Technoport Schlassgoart, 66, Rue de Luxembourg, L-4002 Esch-sur-Alzette, Luxembourg
[b] Helmholtz Zentrum, Institute of Bio-and Geosciences, Jülich, Germany

ABSTRACT

As a consequence of the repeated and widespread use of pesticides in agriculture, pesticide soil residues can be informative tracers of the spatial distribution of soil properties or of the application history. Atrazine, desethylatrazine and terbutylazine soil residues were measured in ninety-six soil samples taken on seventy-one contiguous fields four and a half years after the last atrazine application. The influence of soil texture and the application cycles were still clearly distinguishable in the spatial distribution of the pesticide residues. Half-lives calculated for a first order degradation kinetics from the atrazine and terbutylazine soil residues were within the range of values reported in the literature. The pesticide fate model PEARL calibrated on groundwater measurements underestimated slightly atrazine soil concentrations. The joint simulation of the fate of atrazine and its degradation product desethylatrazine also proved useful to estimate their respective half-lives and sorption parameters, and gave insight into degradation losses occurring during transport through the sandstone aquifer underlying the study site.

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1. Introduction

Beginning with Jury et al. (1982), numerous studies have addressed the problem of predicting solute transport and its spatial variability at the field scale (Ellsworth and Boast, 1996; Gish et al., 1986; Jacques et al., 1999; Kazemi et al., 2008; Lennartz, 1999). For second tier screening of the European pesticide registration procedure, experiments on pesticide fate under field conditions are mandatory to estimate the risk of groundwater contamination (Verschoor et al., 2002). Because the initial decrease in soil pesticide concentration is used to estimate in-situ degradation rates and predict leaching in soils used in pesticide fate assessment models, field studies usually concentrate on the time period directly following application (Sarmah and Close, 2009), possibly discarding the measurements of early time dissipation during which other mechanisms (photodegradation, volatilization) not related to soil dissipation might play a role (EFSA, 2010).

Although the persistent soil residues of compounds such as atrazine (Jablonowski et al., 2009) have also attracted scientific attention, the focus was rather placed on assessing bioavailability of non-desorbable residues (Capriel et al., 1985; Gevao et al., 2001) or the potential damage to susceptible crops on subsequent years (Frank et al., 1983). However, the *historical* and the *spatial* information still contained in the pesticide residues after several half-life cycles have elapsed has to our knowledge seldom been investigated, and in that case, only from the point of view of the effect on environmental dissipation of different management practices such as tillage or irrigation (Isensee and Sadeghi, 1994). Persistent residues, because they are only slowly degraded in the soil, are potential markers that could prove useful for a number of aspects pertaining to pesticide fate modeling.

Regulations in Europe increasingly include pesticide degradation products (metabolites) both in monitoring and risk assessment (European Council, 1998; European Commission, 2003). Since parent compound and metabolites may display different environmental behaviors in terms of mobility and resilience, a coupled analysis of their measured concentrations in the soil and in groundwater could provide precious additional information with which to calibrate a pesticide fate model.

* Corresponding author. Tel.: +352 425991 4648; fax: +352 425991 555.
E-mail addresses: julien.farlin@tudor.lu (J. Farlin), tom.galle@tudor.lu (T. Gallé), michael.bayerle@tudor.lu (M. Bayerle), denis.pittois@tudor.lu (D. Pittois), christian.braun@tudor.lu (C. Braun), hassanya.elkhabbaz@tudor.lu (H. El Khabbaz), ulrich.leopold@tudor.lu (U. Leopold), j.vanderborght@fz-juelich.de (J. Vanderborght), l.weihermueller@fz-juelich.de (L. Weihermueller).

This study's aim was twofold: evaluate what (if any) information can be obtained from the spatial distribution of soil residues concerning initial conditions (application rate and frequency) and the control exerted by soil texture, and explore the possibility of reducing parameter uncertainties in pesticide leaching predictions by taking metabolites and soil residues into account.

Specifically, the following four hypotheses were tested:

1. Pesticide soil residues are correlated to soil texture (Section 3.1)
2. The spatial variability of pesticide application is recorded in pesticide residues (Section 3.1)
3. Long-term bulk dissipation rates estimated from pesticide soil residues can be used as a good approximation for degradation rates (Section 3.2)
4. The joint analysis of parent compound and metabolite can reduce the parameter uncertainties of a leaching model (Sections 3.3 and 3.4).

The first two hypotheses were tested against a dataset consisting of soil pesticide residues measured at 96 locations in an agricultural area in Luxembourg. For the third and fourth hypotheses, soil degradation rates obtained from the residues were compared to literature values and independent estimates calculated from pesticide concentration in groundwater by the physically-based pesticide fate model PEARL. We also present there a method to estimate from the soil residues the ratio of half-lives of a metabolite to its parent compound.

In this article, we assess first how much spatial variability in the pesticide soil residues can be explained by application history and soil texture, then estimate the bulk dissipation half-life of atrazine and terbutylazine from the soil residues, and finally compare this bulk dissipation half-life with the degradation half-life calculated by inverse modeling of pesticide concentration in groundwater.

2. Material and methods

2.1. Experimental setup

The study area (Fig. 1) is located 10 km north of Luxembourg City on the Steinsel plateau, a sandstone cuesta part of the geological formation known as the Luxembourg Sandstone (Colbach, 2005). The agricultural areas (mainly crop land) occupy the center of the plateau, while the slopes are covered by deciduous woodland. The soil cover is up to 2 m thick, and soil texture ranges from sand to sandy loams. The underlying Luxembourg Sandstone aquifer is a regionally important drinking water resource drained by numerous springs emerging on the western and eastern sides of the plateau. Mean annual precipitation is 800 mm/y, and recharge is estimated to be 180 ± 25 mm/y (mean value not differentiating between land uses). Except during rare intense storms, surface runoff is negligible on the plateau itself. Although the application of atrazine was prohibited countrywide in 2005 concentrations in spring water stayed stable until 2011 and varied between springs from 5 to 40 ng/L (for a total annual atrazine export of up to 2.5 g/y). Desethylatrazine (DEA), a major metabolite of atrazine, was also measured during the same period in concentrations approximately twice as high going from 10 to 110 ng/L. Owing to the fact that the study site is a well constrained geomorphologically and constitutes a relatively simple environmental system (all springs draining the plateau can be sampled easily and two classes dominate both land use and soil type), it is very much akin a natural lysimeter, a fact we took advantage of to combine soil and spring water measurements and perform mass balance calculations.

Soil grab samples of the Ap horizon were collected in the fall of 2009, four and a half years after the last atrazine application in spring 2005. Ninety-six samples were taken in total from 71 contiguous fields using stratified random sampling (de Gruijter et al., 2006), covering the entire agricultural surfaces of the plateau (180 ha). The samples were homogenized and thirty-three pesticides and metabolites were
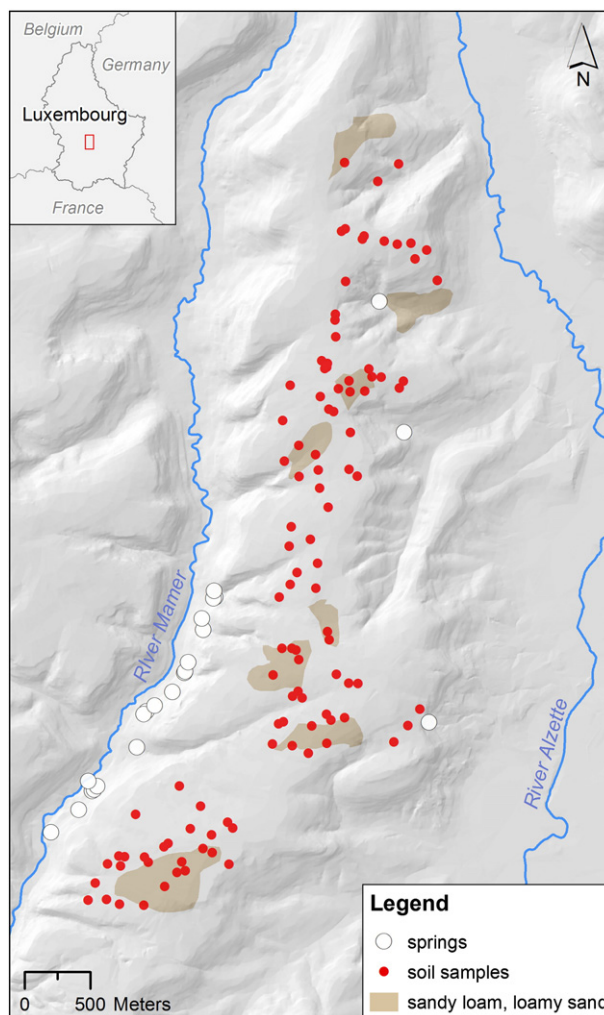

Fig. 1. Study area. Soil type is sand except where shown otherwise. The available 1:100,000 soil map does not differentiate between light loamy sand, loamy sand and sandy loam, which are regrouped in the same class.

measured, as well as soil texture class and organic carbon content (Corg). The frequency with which corn was cultivated on each field was calculated from a dataset detailing crop rotation on a field basis for the years 2006 to 2009. Soil moisture was measured using TDR probes at bihourly intervals in four vertical profiles installed along a 20-meters transect at three different depths (15–20, 30–40 and 50–60 cm) in 2009 and 2010. Pesticide concentrations in the springs were measured either monthly or weekly over two years from 2008 to 2010.

Soil texture classes were determined by the finger test method (Soil mapping manual, 2005) and organic carbon content (Corg) by loss-on-ignition. In this way, more soil classes were determined than previously mapped by the Luxemburgish Soil Survey. The soil samples were dried and sieved prior to pesticide extraction. Five grams per sample was filled into an extraction cell mixed with a hydromatrix (diatomaceous earth). Accelerated solvent extraction (Dionex ASE 200 Accelerated solvent extractor) was carried out at a temperature of 80 °C. Three extraction cycles of 10 min each were run per sample with an acetonitrile/water mixture (90/10) serving as solvent. After the extraction step, the extracts were evaporated to approximately 2 mL with a gentle stream of N_2 in a water bath at 45 °C.

The remaining extracts were transferred into 50 mL flasks and filled up with water (MilliQ; 18 MΩ). Two hundred microliter of a surrogate standard consisting of terbutylazine-D5 and MCPP-D3 (concentration: 50 μg/L) was added as well as 50 μL of formic acid. This step was