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Is organic matter alone sufficient to predict isoproturon sorption in calcareous soils?

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ABSTRACT

Eleven soils collected from Champagne-Ardenne area (France) were used to investigate isoproturon sorption in laboratory conditions. Our results identified the organic matter (OM) and the ratio of calcite content to OM content (Rt) as the main two parameters governing isoproturon retention in soils. While organic matter favored pesticide sorption, calcite had an antagonistic effect since it limited isoproturon retention. The Rt ratio of calcite content to organic matter content in soils appeared to be a parameter that should be considered in predictive models in addition to OM in regions presenting calcareous soils. Adsorption of isoproturon as a function of Rt and OM was successfully described through a simple empirical model.

1. Introduction

The environmental problems associated to the extensive use of pesticides for crop protection have become a worldwide concern. Once they reach soil surface after their application, these agrochemicals may be transported by the infiltrating water leading to groundwater or surface water contamination. Therefore, a thorough understanding of processes controlling pesticide behavior in soils is an absolute necessity for the protection of aquifers and streams. A major focus of environmental scientists is sorption at solid/solution interfaces in soils, since it is known to be one of the key-processes, which determines the availability of contaminant for transfer towards groundwater, unless particle bound transport (colloid, erosion) is occurring (Kjaer et al., 2011). The more the pesticides are adsorbed to soils, the less they are likely to leach due to lower availability for transport in the soil solution (Koskinen et al., 2002; Cooke et al., 2004; Ariaz-Estevez et al., 2008). In soils, pesticides are sorbed on both organic and inorganic constituents. The role of organic matter (OM) in the retention of most pesticides in soils is largely recognized, especially for non-ionic molecules (Chiou et al., 1983; Kile et al., 1995; Coquet, 2002). The contribution of mineral phases is often considered less important and is therefore often overlooked (Worrall et al., 1996; Liu et al., 2008). However, adsorption to organic matter cannot always completely explain the retention (or lack of retention) of a pesticide to the soil (Wauchope et al., 2002). Then, the study of the role of soil parameters other than organic matter deserves further investigations for a more accurate assessment of the risk of groundwater contamination.

Isoproturon (IPU; N,N-dimethyl-N′-[4-(1-methylethyl) phenyl]-urea, Fig. 1) is a neutral urea herbicide with selective and systemic action (Tomlin, 2000). It is a non-ionic pesticide with a water solubility of 70 mg.L^{-1} (at 20 °C) and an octanol–water partition coefficient log K_{ow} of 2.5 (at 22 °C, pH 7) (Agritox, 2012). In the Champagne-Ardenne area (France), this herbicide is massively used for the control of annual grasses in cereal crops. In 2008, the European Parliament identified isoproturon as one of the 33 priority hazardous substances that is subject to phase-out and cessation of discharges in natural settings (Directive 2008/105/EC).

In a previous work (El Arfaoui et al., 2009), we studied the sorption of terbumeton onto the calcareous soils of the Champagne area. Terbumeton is a herbicide presenting properties comparable to those of isoproturon in terms of solubility and hydrophobicity and which behaves as a neutral molecule at the pH range of the studied soils. Our results permitted to suggest the ratio of calcite content to organic matter content (Rt) as a new tool for the prediction of terbumeton retention in calcareous soils. Given the similarity between the two herbicides (terbumeton and isoproturon), the aim of the current study was to identify soil components involved in isoproturon sorption in soils with the intention to confirm the proposed Rt ratio as a useful parameter that could help (if validated) to

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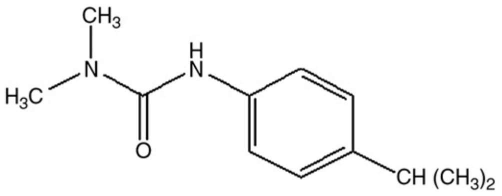

Fig. 1. Structural formula of isoproturon.

assess the mobilization potential of uncharged pesticides and the risk of groundwater contamination.

2. Materials and methods

2.1. Soil characterization

The eleven soils investigated in this work were located in the Champagne area, in the northeast of France. Five sub-samples of each soil were taken from the upper 2–20 cm soil horizon and pooled together. Soils S1 to S9 were from vineyards while soils S10 and S11 were respectively taken from sugar beet and wheat fields. They were dried at 40 °C, sieved to 2 mm and stored in sealed containers at 4 °C. Eight of them were used in a previous study on terbumeton (El Arfaoui et al., 2009). Three new soils were added in this study to enlarge the variability of the soil composition.

The soils were characterized for particle size distribution (without decarbonation), organic matter (OM) and calcite contents, pH and CEC according to French and international norms (AFNOR, 1999, 2003; International Organization for Standardization, 1995, 1998, 2005). The mineralogical composition of soils was determined through the combination of elemental and X-Ray Diffraction (XRD) analyses. More details about these analyses can be found in an earlier paper (El Arfaoui et al., 2009).

Besides, carbon distribution in soil organic matter was investigated in whole soil samples using Cross Polarization/Magic Angle Spinning ^{13}C Nuclear Magnetic Resonance spectroscopy (CP/MAS NMR). Solid-state ^{13}C NMR spectra were acquired on a Bruker Avance 500 MHz spectrometer using the CP/MAS technique with ^{1}H decoupling and a contact time of 2 ms. MAS frequency was set to 10 kHz. For each sample, between 63 000 and 980 000 scans were accumulated depending on organic carbon content. Before spectra were recorded, soil samples were ground and sieved to 100 μm. The spectra were divided into 4 chemical shift regions, each assigned to a prevailing functional group as follows: 0–50 ppm: alkyl-C; 50–120 ppm: O-alkyl-C; 120–160 ppm: aromatic C; 160–220 ppm: carboxylic C (Preston, 1996; Baldock et al., 1997). The area of each chemical shift region was integrated using the MestRec program (Cobas and Sardina, 2003) and expressed as a percentage of the spectrum total area to obtain the relative carbon distribution.

2.2. Pesticide

Isoproturon (IPU) was a technical grade material (99.5% purity) supplied by Dr. Ehrenstorfer (Augsburg, Germany). A stock solution of isoproturon at 2.10^{-4} mol.L^{-1} (41.20 mg.L^{-1}) was prepared in ultra-pure water (ALPHA Q, 18 MΩ.cm^{-1}).

2.3. Sorption studies

Isoproturon sorption isotherms were obtained using the batch equilibrium technique at room temperature (20 °C). Duplicate 1-g soil samples were pre-hydrated during 24 h in 20 mL of ultra-pure water, before different volumes of IPU stock solution were added to obtain a range of initial concentrations varying from 10^{-6} to 10^{-5} mol.L^{-1} (0.20 to 2.06 mg.L^{-1}). Then, the final volume of soil suspensions was adjusted to 25 mL by addition of ultra-pure water, thus giving a solid load of 40 g.L^{-1}. The soil suspensions were shaken for 24 h, a time duration proven sufficient to ensure that sorption equilibrium was reached for the different soil samples. This equilibration time was previously determined through kinetic experiments conducted at a pesticide concentration of 10^{-5} mol.L^{-1} by varying the contact time between soil and IPU from 10 min to 72 h (El Arfaoui et al., 2010).

After shaking, the soil suspensions were filtered through a 0.22 μm nylon membrane and the supernatants were analyzed by High Performance Liquid Chromatography (HPLC) to determine their isoproturon concentrations. Controls without soil were prepared in the same way and showed no significant retention of isoproturon on filters. The device used was a Varian ProStar Chromatograph (Les Ulis, France) equipped with a photodiode array detector operating at 242 nm. The column was a C_{18} reverse phase Kromasil (5 μm × 200 × 3.0 mm) and the samples were isocratically eluted at a flow rate of 0.7 mL.min^{-1}. The mobile phase was an acetonitrile/water mixture (50/50%v/v). The amount of adsorbed isoproturon at equilibrium (C_s) was calculated as the difference between the initial and the equilibrium (C_e) IPU concentrations in solution. Sorption isotherms were obtained by plotting C_s against C_e. These data were used to determine the K_d distribution coefficient between the solid and the liquid phases (Eq. (1)):

$$K_d = C_s/C_e. \tag{1}$$

2.4. Statistical analysis

In order to determine K_d values, isoproturon adsorption isotherms were fitted by Ordinary Least Square (OLS) Regression. The K_d coefficient corresponds to the slope of the linear fit through zero.

In order to identify soil components and physico-chemical properties involved in isoproturon adsorption on the studied soils, a statistical analysis of correlations as well as model selection procedure (through cross-validation) was performed using the R program (Version 2.14-2) (R. Development Core Team, 2012). In order to study the correlation between K_d and the other variables, both Spearman (ρ) and Kendall (τ) correlation coefficients were considered. The obtained values of ρ and τ coefficients allow to determine if two random variables are correlated or not. Spearman and Kendall coefficients are comprised between −1 and 1. Positive ρ or τ values indicate that the correlation is positive while negative ρ or τ values mean that the tested variables are negatively correlated. Tests at level 5% of the null hypothesis $\rho = 0$, and the null hypothesis $\tau = 0$, were performed using the Spearman and Kendall correlation tests, respectively. Recall that the Kendall correlation test is preferred to the Spearman one for small sample sizes, which is the case of the present statistical study. The R program gives the values of the statistic test and the corresponding p-values. Note that a $p\text{-value} < 0.05$ leads to reject the null hypothesis, which means that there is a significant correlation between variables.

To establish the “best” model of prediction of K_d using the more significant variables, a leave-one-out cross-validation procedure was used by means of root mean squared error of prediction (RMSEP). Consider a model $K_d = f(\text{soil components, physico-chemical properties}) + e$, where e is the residual standard error. For any soil S_i, denote by y_i the value of the observed K_d, and by $\hat{y}_i$ the K_d value of the soil S_i predicted by the model under evaluation (which is constructed using all the soils except the soil S_i). The squared error of prediction of y_i by $\hat{y}_i$ is $(y_i - \hat{y}_i)^2$. The mean squared error of prediction is defined by $\text{MSEP} = 1/n \sum_{i=1}^{n} (y_i - \hat{y}_i)^2$, and the root mean squared error of prediction is $\text{RMSEP} = \sqrt{1/n \sum_{i=1}^{n} (y_i - \hat{y}_i)^2}$ in which n stands for the number of objects. All models were compared using the