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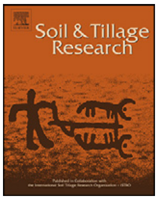

Sorption and mineralisation of S-metolachlor in soils from fields cultivated with different conservation tillage systems

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ABSTRACT

Conservation tillage is promoted to improve the sustainability of agricultural systems and reduce the environmental impact of agricultural activities. These techniques strongly influence soil properties that can modify the fate of pesticides. S-metolachlor (SMOC) is a selective chloroacetamide pre- and post-emergence herbicide used on a variety of crops including maize, soybean, sunflower and sorghum and frequently detected in natural waters. The purpose of this study was to evaluate the effects of conservation tillage management, crop rotation, fallow period management and soil type on sorption and mineralisation of SMOC. During spring 2010, soil samples were collected from 51 agricultural fields located in the central basin of the Midi-Pyrenees (south-west France) at two depths in the topsoil layers (0–5 cm and 5–10 cm). Soils were mainly Calcisols, Luvisols and Cambisols. The SMOC adsorption coefficient (K_d) was measured for each sample using a batch equilibration technique. Mineralisation was monitored during laboratory incubations made at field capacity and 25 °C for 113 days. K_d values ranged from 0.8 to 8.7 L kg^{-1} with a mean of 3.0 L kg^{-1} and a CV of 44%. Sorption was positively correlated with organic carbon (OC) content ($\rho = 0.74$) and negatively with pH ($\rho = -0.42$). The presence of cover crop during the fallow period was found to enhance SMOC sorption. The mineralisation of SMOC after 113 days was found to be highly variable between samples and ranged from 0.8% to 28.3% of applied ^{14}C-SMOC with a higher mineralisation in the 5–10 cm-depth samples. It was positively correlated with soil pH ($\rho = 0.58$) and with total microbial biomass ($\rho = 0.32$). Mineralisation was also negatively correlated with OC content ($\rho = -0.34$) and adsorption coefficient K_d ($\rho = -0.49$). A better correlation ($\rho = 0.66$) was obtained between mineralisation and the ratio 'total microbial biomass/adsorption coefficient (K_d)' of each sample. This correlation could be interpreted as an illustration of the competition between retention and degradation, directly depending on the modification of soil organic matter and microbial activity by the different conservation tillage systems.

1. Introduction

Conservation tillage is promoted to enhance the sustainability of agricultural systems and reduce the environmental impact of agricultural activities. Reduced intensity of tillage leads to significant and complex changes (usually interrelated) in soil physical, chemical and biological properties. Often these changes strongly modify the fate of the applied pesticides (Alletto et al., 2010). Although many studies have been made, mainly on the north American continent, the environmental fate of pesticides under conservation tillage presents many contradictions and remains poorly understood (Alletto et al., 2010; Aubertot et al., 2005). A better understanding of pesticide retention and degradation processes that control their movements in soils is needed to assess their persistence and their risks of transfer in the environment under conservation techniques.

One of the main changes resulting from the implementation of conservation tillage compared with conventional methods is the accumulation of organic residues on the soil surface (mulch) and the increase in soil organic matter in the top few centimetres of the soil profile (Balesdent et al., 1990; Tebrügge and During, 1999). Generally, organic carbon content is high in surface soil due to the presence and decomposition of the mulch, and gradually decreases with depth (Lal et al., 1994; Pinheiro et al., 2004; Six et al., 1999). These changes in organic matter location have a strong influence on soil properties, which greatly modify pesticide fate (Alletto et al., 2010). For most pesticides, organic carbon content and pesticide adsorption are positively correlated, resulting in a higher adsorption in the surface soil under conservation tillage than under conventional tillage (Locke, 1992; Reddy and Locke, 1998; Zablotowicz et al., 2000).

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Soil pH may also be modified by tillage techniques but in different ways according to the study. Conservation tillage can lead to an increase in pH (Reddy and Locke, 1998), no change (Comia et al., 1994; Rasmussen, 1991) or most often, to a decrease in pH, especially in surface soil due to the accumulation of organic matter and fertilisers (Arshad et al., 1999; Doran, 1980; Levanon et al., 1994). Soil pH can also play a role in pesticide sorption; thus in general sorption increases when soil pH decreases because the charges for the polar or ionic pesticides are modified and/or the variable charges of the soil constituents decrease, favouring the adsorption of non-polar pesticides (Barriuso and Calvet, 1992; Barriuso et al., 1992; Grey et al., 1997).

Mineralisation is regarded as the final stage in pesticide degradation, leading to its complete removal from the soil. Soil microbial activity can be correlated with mineralisation of the molecules (Lavorenti et al., 2003), but not always (Reddy and Locke, 1998). The increase in soil microbial activity under conservation techniques does not always imply that specific microbial populations involved in the degradation of a compound are more abundant (Gaston and Locke, 2000). In some cases, crop residues on the soil surface under conservation tillage seemed to disrupt degradation (Locke and Harper, 1991; Sorenson et al., 1991), and compared with conventional tillage, lag phases may occur in the activation of mineralisation (Seifert et al., 2001). Competition between retention and degradation is also frequently mentioned to explain lower pesticide mineralisation under conservation tillage (Zablotowicz et al., 2000). In addition, a greater availability of carbon under conservation tillage compared with conventional tillage favours the development of non-specialised microorganisms in competition with microorganisms specialised in pesticide degradation. This could defer the use of pesticides as a source of carbon and thus their degradation in soil (Locke and Harper, 1991).

S-metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(methoxy-1-methylethyl) acetamide] (SMOC) is a selective chloroacetamide herbicide widely used for pre- and post-emergence weed control in a variety of crops including maize, soybean, sunflower and sorghum (Ahrens, 1994). SMOC is more persistent in soils than other acetanilide herbicides (Funari et al., 1998), moderately sorbed on soil components (adsorption coefficient $K_d \approx 2.8$ L kg^{-1}) (Bowman, 1989; Weber et al., 2004) and relatively highly soluble in water ($S_w = 530$ mg L^{-1} at 20 °C). Due to these properties, SMOC has the potential to migrate into ground and surface waters and is frequently detected by environmental monitoring (Institut Français de l’Environnement, 2007; Laabs et al., 2000; Ritter et al., 2000; Vecchia et al., 2009).

Our purpose was to investigate the variability of S-metolachlor sorption and mineralisation under several soils and agricultural systems using conservation techniques. More precisely, the hypotheses tested in this study were that (a) the effect of soil organic matter on SMOC sorption is due to tillage management (= location and quantity of residues) and crop rotation and fallow period management (= nature of residue); (b) SMOC mineralisation could be increased on fields with previous SMOC application and (c) a high sorption of SMOC could limit its biological degradation. A relatively large number of situations (soil types, crop and tillage practices) were chosen in order to get statistically significant trends.

2. Materials and methods

2.1. Tillage systems and soil sample characteristics

Soil samples were collected from 51 agricultural fields located in the central basin of the Midi-Pyrenees, south-west France, from April to June 2010. According to the World Reference Base for Soil Resources (ISSS-ISRIC-FAO, 1998), soils were mainly classified as Luvisols, Cambisols and Calcisols. All these fields had been cultivated with conservation techniques for 2–23 years, but with differences in tillage operations according to the crop. Winter crops were always sown with no tillage, while for spring crops three types of conservation techniques were used: deep tillage (DT) with a working depth >10 cm; reduced tillage (RT) with a working depth ≤10 cm; or no tillage (NT). This difference in tillage management of spring crops is used in this article to classify the tillage system.

On each field, after sowing, the amount of crop residues left on the soil surface was estimated by the use of the line-transect method (Lopez et al., 2003). This involved to stretch 5 m measuring tapes diagonally at about a 45° angle across the crop rows and to count the number of 10 cm marks along the tape that intercepted a piece of crop residue. The percentage of residue cover for the sampling area was then obtained by a multiplication of this count by 2.

For each field, soil samples were collected at two depths: 0–5 cm and 5–10 cm. Soil samples were air-dried for 48 h and the ratio crop residue/soil (g/g) was estimated. Soil samples were then sieved (5 mm) and, for some samples, crop residues, that were removed during the sieving, were cut into pieces <1 cm across and added to the soil in order to maintain the initial ratio of crop residue/soil of the sample. The physicochemical properties of each sample were determined, including crop residues for the quantification of the organic carbon content. Soil textures were classified as silty loam, silty clay loam and silty clay according to the USDA soil texture diagram, with approximately 1/3 of calcareous soils (Fig. 1). Samples were then stored in the dark at 4 °C until being used in laboratory experiments. Duplicate amounts (15 g) were dried in an oven at 105 °C for 24 h to determine soil water content. Soil microbial biomass of each sample was determined by the fumigation–extraction method (AFNOR, 2011).

2.2. Chemicals

Pure analytical standards of S-metolachlor and ^{14}C-S-metolachlor U-phenyl-labelled, 99.9% radiochemically pure) were supplied by Syngenta Agro SAS (Basel, Switzerland). Solvents came from Carlo Erba (Val de Reuil, France).

2.3. Sorption

SMOC adsorption coefficients (K_d) were measured with a batch equilibration technique. A solution of ^{14}C-SMOC at 1 mg L^{-1} (50 Bq mL^{-1}) was prepared by isotopic dilution in calcium chloride solution (0.01 M $CaCl_2$). Samples of air-dried soil (3 g) were weighed into Corex centrifuge tubes (25 mL) and a 9 mL aliquot of herbicide solution was added to each. Each tube was sealed with a Teflon-lined cap. These Corex centrifuge tubes were chosen for their low sorption of SMOC after blank tests. For each soil sample, five replicates were made. The tubes containing treated soil were left for 24 h in an end-over-end agitator to reach equilibrium at room temperature (20 ± 1 °C), and then centrifuged at 1500 × g for 10 min. ^{14}C content of the supernatant was measured by scintillation counting after removing a 1 mL aliquot of the supernatant and mixing with 4 mL of scintillating liquid (Ultima Gold XR, Packard).

Herbicide sorption was calculated as the difference between the amount initially added and the supernatant concentration after equilibrium. Sorption distribution coefficients (K_d) were calculated using the equation:

$$K_d = \frac{Q_{eq}}{C_{eq}}$$

where Q_{eq} is the quantity of ^{14}C-SMOC at equilibrium (mg kg^{-1} soil) and C_{eq} is the concentration of ^{14}C-SMOC at equilibrium (mg L^{-1}).