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Mapping field spatial distribution patterns of isoproturon-mineralizing activity over a three-year winter wheat/rape seed/barley rotation

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HIGHLIGHTS

- ▶ Spatio-temporal variability in isoproturon mineralization activity was monitored.
- ▶ Isoproturon treatment led to high isoproturon mineralization activity.
- ► Isoproturon treatment diminished variability in mineralization activity.
- ▶ Isoproturon mineralization activity was correlated with soil pH and CEC.
- ▶ Simple model using pH and CEC can predict Isoproturon mineralization activity.

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ABSTRACT

The temporal and spatial variability of the activity of soil microorganisms able to mineralize the herbicide isoproturon (IPU) pesticide was investigated over a three-year long crop rotation between 2008 and 2010. Isoproturon mineralization was higher in 2008, when winter wheat was treated with this herbicide, than in 2009 and 2010, when rape seed and barley were treated with different herbicides. Under laboratory conditions, we showed that isoproturon mineralization was not promoted by sulfonylurea herbicide applied on barley crop in 2010. IPU mineralization was shown to be highly variable at the field scale in years 2009 and 2010. Principal component analyses and analyses of similarities revealed that soil pH and equivalent humidity, and to a lesser extent soil organic matter content and cation exchange capacity (CEC) were the main drivers of isoproturon-mineralizing activity variance. Using a rather simple model that yields the rate of isoproturon mineralization as a function of soil pH and equivalent humidity, we explained up to 85% of the variance observed. Mapping field-scale distribution of isoproturon mineralization over the three-year survey indicated higher variability in 2009 and in 2010 as compared to 2008, suggesting that isoproturon treatment applied to winter wheat promoted isoproturon mineralization activity and reduced its spatial variability. Field-scale distribution of isoproturon mineralization showed important similarity to the distribution of soil pH, equivalent humidity and to a lesser extent to soil organic matter and cation exchange capacity (CEC) thereby confirming our model.

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1. Introduction

The use of pesticides in conventional agriculture has attracted much attention due to their potential harmful effects not only on plants, animals and microorganisms but also on humans. The harmful effects of pesticides are linked to their environmental fate, which in turn plays a central role in determining their behavior in natural media, including soils. In recent years, much attention has been paid for predicting the fate of pesticides, and microbial

degradation has emerged as a main process leading to the dissipation of pesticides after they get into soils. Degradation, which predominantly involves soil microorganism activity, is considered as a key process affecting the dynamics of pesticides in soil environments. It is governed by a number of soil and environmental factors that can induce significant spatial variations in the process. One important lingering environmental question regarding microbial pesticide biodegradation is the extent to which degradation takes place at the field scale. This is an important issue for predicting the fate of pesticides in soils.

Isoproturon (IPU), a substituted phenylurea herbicide, is used for controlling pre- and post-emergence annual grasses and broadleaved weeds in wheat, barley and winter rye crops (Ertli et al., 2004; El-Sebai et al., 2007). Being of one of the most extensively

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used pesticides in Europe, its use has recently been restricted and banned in several European countries, but it still remains extensively used worldwide. (Stangroom et al., 1998; El-Sebai et al., 2007). IPU is relatively recalcitrant in the soil and has a DT50 ranging from 6 to 90 d (El-Sebai et al., 2007). As a result of its widespread repeated use and persistent properties, IPU is frequently detected in water resources at concentrations higher than 0.1 μ g L⁻¹, the European Union drinking water limit (Spliid and Koppen, 1998; Muller et al., 2002). Ecotoxicological data suggest that IPU and some of its metabolites are harmful not only for microbial communities (Widenfalk et al., 2008), aquatic invertebrates (Mansour et al., 1999), macrophytes (Yin et al., 2008; Knauert et al., 2010; Kumar et al., 2010) and fresh-water algae (Dewez et al., 2008; Vallotton et al., 2009; Dosnon-Olette et al., 2010) but also for humans and animals (Behera and Bhunya, 1990; Hoshiya et al., 1993; Hazarika and Sarkar, 2001; Orton et al., 2009). Lowering IPU contamination in soil and water resources is therefore of particular interest.

Microbial biodegradation has been reported as a primary mechanism for the dissipation of isoproturon and of many other phenylurea herbicides from aquatic and telluric environments (Fournier et al., 1975; Gaillardon and Sabar, 1994; Cox et al., 1996; Pieuchot et al., 1996; Bending et al., 2003; El-Sebai et al., 2007; Hussain et al., 2011). Studies have reported that in response to repeated exposure to pesticides, soil microorganisms adapt to the rapid biodegradation of several herbicides including IPU (Cox et al., 1996; Karpouzas et al., 1999; Sorensen and Aamand, 2001; Bending et al., 2003, 2006; El-Sebai et al., 2005; El-Sebai et al., 2007; Hussain et al., 2011). Mineralization of isoproturon has already been reported in agricultural fields repeatedly treated with it in the United Kingdom (Cullington and Walker, 1999), Denmark (Sorensen and Aamand, 2003) and more recently in France (El-Sebai et al., 2005, 2007; Hussain et al., 2011).

In addition, several studies have also shown that IPU mineralization activity was not evenly distributed across agricultural fields (Beck et al., 1996; Bending et al., 2001; Walker et al., 2001, 2002; El-Sebai et al., 2007). Beck et al. (1996) determined variability in the degradation time-course of isoproturon on 25 different sampling points within a same field and found that the time required for 50% of the initial IPU concentration to dissipate ranged between 31 and 483 d. More recently, within-field spatial heterogeneity of isoproturon degradation activity was reported in different regions of the world including Denmark, the United Kingdom and France (Bending et al., 2001, 2003, 2006; Walker et al., 2001; Rodriguez-Cruz et al., 2006; El-Sebai et al., 2007).

Variations in soil physico-chemical properties such as pH, texture, temperature, moisture or organic matter have been reported to affect the degradation of pesticides (Sorensen et al., 2003; Bending et al., 2003; El-Sebai et al., 2005, 2007, 2011; Vieublé-Gonod et al., 2009). Soil properties affect not only the availability and biodegradability of pesticides (Walker et al., 1992; Welp and Brummer, 1999) but also the diversity, the size and the activity of microbial populations (Smith et al., 1997; Hundt et al., 1998). The spatial variability of IPU degradation within a British agricultural field was correlated (i) with soil pH and microbial biomass (Walker et al., 2001) and (ii) with soil pH and the extent of the proliferation of IPU-degrading organisms (Bending et al., 2003). The same two factors were also found to account for the variability of isoproturon mineralization activity determined for 50 soil samples within an agricultural field in France (El-Sebai et al., 2005, 2007). A significant correlation between pH and IPU degradation has been demonstrated not only in agricultural soils (Walker et al., 2002; El-Sebai et al., 2005, 2007) but also in pure broth cultures (Bending et al., 2003; Hussain et al., 2009, 2011; Sun et al., 2009; Hussain et al., 2011). Similarly, the spatial heterogeneity of IPU-mineralizing activity within an agricultural field was also found to be enhanced by the presence of compost (Vieublé-Gonod et al., 2009).

Such stimulation of the mineralization activity was hypothesised to derive from the microbial characteristics of the compost, the physical properties of the soils and the physico-chemical conditions in the area with high mineralization activity. Since the rate of IPU degradation has been reported to be influenced by a number of soil physico-chemical and microbial properties and also by the repeated use of pesticides, a detailed knowledge of these parameters in relation to spatial variability in the IPU degradation rate is important to better understand IPU dissipation from agricultural soils.

In order to tackle this question spatial and temporal variability of IPU-mineralization activity was monitored within an agricultural field by following the mineralization of IPU under a winter wheat/rape seed/barley crop rotation, in connection with the variability of soil physico-chemical and microbiological properties. A special effort was made to search for key parameters driving of IPU-mineralization activity and to develop a simple model predicting IPU-mineralization activity. Mapping field spatial distribution patterns of isoproturon-mineralizing activity was carried out over the three year survey.

2. Materials and methods

2.1. Chemicals

Analytical grade IPU (99.0% purity) and ¹⁴C-ring-labelled IPU (specific activity 18 mCi mmol⁻¹; 99% radiochemical purity) were purchased from Riedel-de-Haen (Germany) and International Isotopes (Munich, Germany), respectively. The commercial product Archipel® was purchased from Syngenta.

2.2. Soil sampling and soil properties

The study was carried out on soil collected from an agricultural field located at the experimental farm of the National Institute of Agronomical Research (INRA) of Epoisses (Breteniere, France). Thirty-six separate soil surface samples (0-20 cm) were collected in April 2008, 2009 and 2010 from the plot, following a grid made of 4 columns (with 17, 26 and 24 m in-between each of them) and nine rows (with 20 m in-between each of them). The field had been cultivated under a winter wheat/rape seed/barley rotation and periodically treated with IPU for more than 10 years. Over the three-year time-span (2008-2010), the field was treated with (i) IPU herbicide, applied on Oct. 12th, 2007, several months before the 2008 sampling, at 1.2 kg ha⁻¹, (ii) the two herbicides Roundup Typhon, which contains 360 g L⁻¹ of glyphosate (Makheshim Agan France) and Treflan®, which contains trifluraline (Dow AgroSciences), applied on Aug. 27th, 2008 at 1.5 L ha⁻¹ and 2.5 L ha⁻¹, respectively; (iii) Colzor Trio® (Syngenta) made of a mixture of clomazone (30 g L^{-1}), dimethachlor (187.5 g L^{-1}) and napropamide (187.5 g L^{-1}) applied on Aug. 29th, 2009 at 3.5 L ha⁻¹, (iv) the herbicide Archipel® (Syngenta) made of a mixture of mesosulfuronmethyl (0.75 g L^{-1}), iodosulfuron-methyl sodium (0.75 g L^{-1}) and Mefenpyr-dimethyl, applied on March 24th, 2010 at 0.25 kg ha⁻¹, just before the 2010 sampling. The moisture content of each soil sample was estimated before the experiment started. The soil samples were sifted through 5-mm mesh sieves and the samples were sub-divided into two major groups and a minor one. The first major group was air-dried for physico-chemical analysis, whereas the second was kept at 4 °C for biological analysis. The third, smaller group was stored at -20 °C for soil DNA extraction.

The physico-chemical properties of the soil samples, i.e. granulometric properties, equivalent humidity, organic matter content, carbon, nitrogen, C/N ratio, pH and cation exchange capacity (Table 1) were determined by the Laboratory of Soil Analysis (INRA, Arras, France) using ISO procedures.

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