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Predicting isoproturon long-term mineralization from short-term experiment: Can this be a suitable approach?

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HIGHLIGHTS

- Prediction of isoproturon mineralization in acid soils was reliable.
- Prediction of isoproturon mineralization in neutral soils was overestimated.
- Isoproturon dissipation in a neutral soil could be correctly predicted.
- Formation of NER and ^{14}C-microbial biomass in a neutral soil were overestimated.
- Bound residues and ^{14}C-microbial biomass contributed mainly to mineralization at later stage.

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ABSTRACT

A worldwide used pesticide – isoproturon (IPU) – was selected to test whether short-term experiments can be used to predict long-term mineralization of IPU in soil. IPU-mineralization was measured for 39 and 265 days in four different agricultural soils with a low mineralization dynamic. Additionally, in one soil IPU dissipation, formation and dissipation of metabolites, formation of non-extractable residues (NER) and ^{14}C-microbial biomass from ^{14}C-IPU were monitored for 39 and 265 days. The data from short-term and long-term experiments were used for model fitting. The long-term dynamics of IPU mineralization were considerably overestimated by the short-term experiments in two soils with neutral pH, while in two other soils with low pH and lower mineralization, the long-term mineralization of IPU could be sufficiently predicted. Additional investigations in one of the soils with neutral pH showed that dissipation of IPU and metabolites could be correctly predicted by the short-term experiment. However, the formation of NER and ^{14}C-microbial biomass were remarkably overestimated by the short-term experiment. Further, it could be shown that the released NER and ^{14}C-microbial biomass were the main contributors of $^{14}CO_2$ formation at later incubation stages. Taken together, our results indicate that in soils with neutral pH short-term experiments were inadequate to predict the long-term mineralization of IPU.

1. Introduction

Pesticides are extensively used to enhance crop production worldwide. Isoproturon (IPU), a typical phenylurea herbicide used to control annual grasses and broad-leaved weeds, is among the most extensively used pesticides in European cereal production (Sørensen et al., 2003). Once introduced into soil environment, IPU undergoes dissipation processes including sorption, degradation, mineralization, formation of non-extractable residues (NER), and transport into plants and groundwater. Microbial degradation is the most important process in IPU dissipation. Microbial degradation can be either metabolic degradation or co-metabolic degradation (Piutti et al., 2002).

Metabolic degradation will happen in soils that inhabit an adapted microbial community which will use IPU as energy and C-source and the kinetic of IPU mineralization in those soils is characterized by high mineralization rates that reach their maximum in a short time after application. In soils with adapted IPU-degraders it was shown that ^{14}C-IPU is mineralized up to approximately 50% (Grundmann et al., 2007); the rest of the radioactiv-

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ity is most probably incorporated in microbial biomolecules. Co-metabolic degradation occurs in soils that do not contain adapted IPU degraders; and the mineralization kinetic is characterized by nearly constant and low mineralization rates.

Due to widespread and extensive application, IPU has been detected in groundwater exceeding the critical approved European threshold for drinking water (Johnson et al., 2001). Pesticides can be allowed for use only after it has been demonstrated that there is no negative impact on the environment (Fenlon et al., 2011). However, once the pesticide is released into the environment, it may act different to the predicted behavior and may even exceed environmental quality standards, like it is the case with IPU (Fenlon et al., 2011). Therefore, the experiments and models used to predict long-term behavior of pesticides in soil should be carefully selected to avoid incorrect predictions.

Mineralization of pesticides in soil can normally best be described with three-half-order kinetic models (Jacobsen and Pedersen, 1992; Gimsing et al., 2009; Bælum et al., 2012); these models exist in three forms and assume zero growth, linear growth or exponential growth of the microbial degraders. Jacobsen and Pedersen (1992) used the single first-order kinetic model to describe mineralization data in cases where the microbial population was not expected to grow. Scow et al. (1986) developed a two compartment first-order kinetic model to describe mineralization of pesticides in soil. There also exist a large number of different kinetic models to describe dissipation of pesticides in soil (Sanchez et al., 2003; FOCUS, 2006; Diez and Barrado, 2010; Swarcewicz and Gregorczyk, 2013). They range from monophasic to biphasic, multi compartment first-order, and first-order sequential models.

Beside the scientific interest, increasing costs for analysis as well as man-power might affect the time range for conducting laboratory experiments; parallel mathematical tools might help e.g. to extrapolate the results from a short-term experiment to the long-term behavior of a certain chemical in soils. Therefore, the objectives of the study were (i) to determine short and long-term mineralization of IPU in four different agricultural soils – with a low mineralization dynamic (Folberth et al., 2009) – in laboratory experiments, (ii) to conduct additional short and long-time experiments in one soil concerning IPU dissipation, metabolites dissipation, formation of NER and formation of ^{14}C microbial biomass, (iii) to model the data from the short-term experiments and compare the modeled data with the measured data from the long-term experiments, and to evaluate whether the long-term behavior of IPU in soil can be sufficiently predicted with mathematical models based on data of short-term experiments, (iv) to identify the contributors to long-term mineralization.

2. Materials and methods

2.1. Chemicals

[U-^{14}C]IPU, 3-(4-isopropylphenyl)-1,1-dimethylurea, with a specific radioactivity of 3.96 MBq mg^{-1} and a purity of >98% was obtained from International Isotope (Munich, Germany). Non-labeled IPU (purity 99.9%) and the metabolites 3-(4-isopropylphenyl)-1-methylurea and 3-(4-isopropylphenyl)-urea (purity 99.5%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany).

3-[4-(2-hydroxyisopropylphenyl)]-1-methylurea (purity 91.4%), arelon, and arelon formulation components were provided by Agrevo (Frankfurt-Hoechst, Germany). ^{14}C-IPU was mixed with the commercial product arelon and the arelon formulation components to a final IPU concentration of 500 mg mL^{-1}, and a specific radioactivity of 686 Bq μg^{-1} (Schroll and Kühn, 2004). The solvents were HPLC grade and purchased from Sigma–Aldrich (St. Louis, MO, USA). The scintillation cocktails were obtained from Perkin Elmer (Waltham, MA, USA). All other chemicals were of analytical grade and were purchased from Merck (Darmstadt, Germany).

2.2. Soil

Four typical agricultural soils from different sites in Germany (Scheyern, Kelheim, Neumarkt and Marsdorf) with various soil properties, different pH and a low IPU mineralization capacity (Folberth et al., 2009) were used (SD, Table S1). All the soils were collected from 0 to 10 cm, sieved (<2 mm) and stored at 4 °C. Prior to starting the experiments, soil samples were equilibrated for one week at 20 ± 1 °C at a soil moisture close to the optimal water content at −15 kPa (Schroll et al., 2006).

2.3. IPU mineralization in soil

The mineralization of ^{14}C-IPU in four different soils was conducted in a discontinuously aerated laboratory system (Schroll et al., 2006). Microcosms contained 50 g (dry weight) soil spiked with 5.0 $\mu g\ g^{-1}$ ^{14}C-IPU (150 Bq g^{-1}), corresponding to the pesticide concentration in the field (Schroll and Kühn, 2004). The experiment was performed at a soil density of 1.3 g cm^{-3} and a soil water potential of −15 kPa (Schroll et al., 2006). The microcosms were incubated in the dark at 20 ± 1 °C. During incubation, the microcosms were aerated three times per week for 1 h at an air exchange rate of 1 L h^{-1} to trap $^{14}CO_2$ resulting from the total degradation of the ^{14}C-pesticide, followed by a measurement of radioactivity in the trapping solution via scintillation counting (Schroll et al., 2006; Folberth et al., 2009). Short-term experiments were conducted for 39 days and long-term experiments were run for 265 days. All the experiments were conducted in 4 replicates except for soil Scheyern which started with 18 replicates and on days 0, 25, 39, 60, 88, and 265 three replicates were sacrificed for soil sample analysis.

2.4. Sample analysis

For soil Scheyern the soil samples were subjected to quantification and characterization of extractable ^{14}C-residues, quantification of non-extractable ^{14}C-residues (NER), and soil ^{14}C-microbial biomass analysis at different time points (see Section 2.3). Extractable ^{14}C residues (IPU and its metabolites) were quantified by accelerated solvent extraction and characterized by HPLC analysis after SPE sample clean up (SD, S1). The NER were measured by combusting the soil after ASE extraction (SD, S2), therefore the term NER used throughout the text means the total (apparent and real) bound residues. Soil ^{14}C-microbial biomass was assessed by measuring microbial biomass carbon with the chloroform fumigation extraction method (SD, S3).

2.5. Curve fitting

Data from the short and long-term experiments considering mineralization, soil ^{14}C-microbial biomass and NER were analyzed using single first-order model (SFO) (Jacobsen and Pedersen, 1992), two compartment first-order model (Scow et al., 1986), and three-half-order kinetic model, zero form (ZF), linear form (LF) and exponential form (NF) (Brunner and Focht, 1984) (SD, S4). The data of IPU and IPU-metabolites in soil from the short and long-term experiments were fitted using SFO model (FOCUS, 2006), two compartment first-order model (Diez and Barrado, 2010) and multi-compartment first-order model (Gustafson and Holden, 1990) (SD, S5). Data were fitted to these models using Sigma Plot (Systat-Software, Inc. Chicago). The best fit was chosen based on an F-test ($P < 0.05$), R^2-value, standard deviation of the parameters, and residuals of the fitted model as well as how realistic the parameter estimates were.