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Dissipation and adsorption of isoproturon, tebuconazole, chlorpyrifos and their main transformation products under laboratory and field conditions

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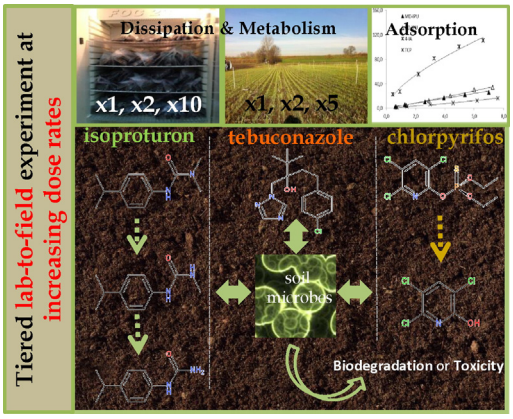
HIGHLIGHTS

- The environmental fate of 3 pesticides was evaluated via a lab-to-field approach.
- Lab and field persistence increased in the order IPU < CHL < TCZ.
- IPU was demethylated and CHL was hydrolyzed.
- Adsorption of parent compounds increased as IPU < TCZ < CHL.
- Transformation products showed low adsorption affinity except 4-IA.

GRAPHICAL ABSTRACT



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ABSTRACT

Assessment of dissipation constitutes an integral part of pesticides risk assessment since it provides an estimate of the level and the duration of exposure of the terrestrial ecosystem to pesticides. Within the frame of an overall assessment of the soil microbial toxicity of pesticides, we investigated the dissipation of a range of dose rates of three model pesticides, isoproturon (IPU), tebuconazole (TCZ), and chlorpyrifos (CHL), and the formation and dissipation of their main transformation products following a tiered lab-to-field approach. The adsorption of pesticides and their transformation products was also determined. IPU was the least persistent pesticide showing a dose-dependent increase in its persistence in both laboratory and field studies. CHL dissipation showed a dose-dependent increase under laboratory conditions and an exact opposite trend in the field. TCZ was the most persistent pesticide under lab conditions showing a dose-dependent decrease in its dissipation, whereas in the field

Abbreviations: IPU, isoproturon; TCZ, tebuconazole; CHL, chlorpyrifos; MD-IPU, monodesmethyl-isoproturon; DD-IPU, didesmethyl-isoproturon; 4-IA, 4-isopropylaniline; TCP, 3,5,6-trichloro-2-pyridinol.

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Tebuconazole
Chlorpyrifos
Dissipation
Adsorption
Lab-to-field assessment

TCZ exhibited a biphasic dissipation pattern with extrapolated DT_{90s} ranging from 198 to 603.4 days in the ×1 and ×2 dose rates, respectively. IPU was demethylated to mono- (MD-IPU) and di-desmethyl-isoproturon (DD-IPU) which dissipated following a similar pattern with the parent compound. CHL was hydrolyzed to 3,5,6-trichloro-2-pyridinol (TCP) which dissipated showing a reverse dose-dependent pattern compared to CHL. Pesticides adsorption affinity increased in the order IPU < TCZ < CHL. IPU transformation products showed low affinity for soil adsorption, whereas TCP was weakly adsorbed compared to its parent compound. The temporal dissipation patterns of the pesticides and their transformation products will be used as exposure inputs for assessment of their soil microbial toxicity.

1. Introduction

Pesticides still constitute an integral part of modern agriculture despite the environmental and health risks associated with their use (Muñoz-Leoz et al., 2011). Upon their application, either intentionally or unintentionally, they reach the soil environment which acts as a sink for their further distribution to other environmental compartments depending on their soil dissipation rates (Arias-Estévez et al., 2008). Thus, good knowledge of the dissipation and metabolism of pesticides in soil is an essential part of risk assessment since it determines the scenario of exposure of the soil ecosystem. The level and the duration of exposure has to be known in order to assess the toxicity of pesticides to non-target soil organisms including microorganisms, which have been identified by the European Food Safety Agency as one of the specific protection goals (EFSA, 2010). Recently, Martin-Laurent et al. (2013), proposed a revision in the regulatory framework regarding the assessment of the soil microbial toxicity of pesticides. This involves the implementation of a tiered lab-to-field experimental approach where the dissipation and transformation of the studied pesticides (measure of exposure) coupled with standardized advanced biochemical and molecular methods (measure of toxicity) could provide a more robust estimation of the soil microbial toxicity of pesticides (Karpouzas et al., 2014). Within this framework, we studied the dissipation and the transformation of a range of dose rates of three model pesticides; isoproturon (IPU), tebuconazole (TCZ), and chlorpyrifos (CHL) which were chosen based on their widespread use in Europe.

IPU [*3-(4-isopro-pylphenyl)-1,1-dimethylurea*] is a phenylurea herbicide used for the control of annual grasses and broad-leaved weeds in spring and winter cereals (Collings et al., 2003). It shows variable persistence in soil with DT_{50} values varying from 3 to 200 days (Alletto et al., 2006). Its extensive use has resulted in its common detection in surface and groundwater resources (Skark and Zullei-Seibert, 1995; Skark et al., 2004). Mono-desmethyl-isoproturon [*3-(4-isopropylphenyl)-1-methylurea* (MD-IPU), di-desmethyl-isoproturon [3-(4-phenyl)-urea] (DD-IPU), 4-isopropyl-aniline (4-IA) and several hydroxylated compounds (Lehr et al., 1996; EFSA, 2015) have been identified as the most common transformation products of IPU in soil. Some of these have been found to exert higher toxicity than the parent compound (Hussain et al., 2015; Alletto et al., 2006; Tixier et al., 2002). However, little is known regarding their dissipation kinetics and adsorption in soil.

TCZ [*(RS)-1-p-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazol-1-yl methyl)pentan-3-ol*] is a systemic triazole fungicide which is used for the control of a range of plant fungal pathogens in different crops including winter cereals (D'Angelo et al., 2014; Keinath, 2015). It is rather persistent in the soil environment with DT_{50s} ranging from 49 to 610 days (Strickland et al., 2004; EFSA, 2014). Monitoring studies in agricultural areas where TCZ is used have verified its frequent presence in surface and groundwater systems (Herrero-Hernández et al., 2013; Sancez-Gonzalez et al., 2013). Although its dissipation and transformation in soil has been studied previously (Álvarez-Martín et al., 2016; Herrero-Hernández et al., 2013; Potter et al., 2005; Strickland et al., 2004), little is known regarding the fate of its transformation products in the environment (Storck et al., 2016).

CHL [*O,O-diethyl O-3,5,6-trichloro-2-pyridinyl phosphorothioate*] is one of the most extensively used organophosphate insecticides with a broad spectrum of activity (Joseph and Zarate, 2015). Its degradation in soil proceeds mainly via hydrolysis, abiotic and biotic, with DT_{50} values ranging from 10 to 120 days (Racke, 1993). Hydrolysis of CHL leads to the formation of 3,5,6-trichloro-2-pyridinol (TCP) which is known to have adverse effects on soil microbial activity and on the degradation of the parent compound (Racke et al., 1990). However, to date limited knowledge is available regarding the dissipation and adsorption of TCP in agricultural soils where CHL has been applied.

The main objectives of the present study were a) to determine the dissipation of the three model-pesticides applied to soil at different dose rates under laboratory (×1, ×2 and ×10 the recommended dose rate) and field conditions (×1, ×2 and ×5 the recommended dose rate), b) to follow the dynamics of formation and dissipation of the main transformation products of the model pesticides and c) to determine the soil adsorption affinity of the model pesticides and their main transformation products. This will provide a thorough view of the soil persistence of the studied pesticides and their transformation products which defines the scenario of exposure of non-target soil organisms to be taken into account to estimate potential toxicity risks in follow up studies.

2. Materials and methods

2.1. Pesticides

Analytical standards of IPU (99.9%), MD-IPU (99.5%), DD-IPU (99.0%), TCZ (98.8%), CHL (97%), and TCP (99.0%) were purchased by Dr. Ehrenstorfer, (Germany). The analytical standard of 4-IA (99.0%) was purchased by Sigma-Aldrich (Germany). Commercial formulations of IPU (QUINTIL® 500SC), TCZ (FOLICUR 25SE) and CHL (CARPOSAN 48EC), were provided by Phytorus (http://www.phytorus.eu/en/), Bayer CropScience (Germany) and ISAGRO (Italy), respectively.

2.2. Microcosm experiment

The soil used was collected in July 2013 from a field site situated in North Italy (area of Mortizza, 45°05′20.8″N 9°45′59.4″E (Google Maps) which was also used for the execution of the field experiment described below. The physicochemical characteristics of the soil are shown in Supplementary Data Table 1. The field site did not have a recent history of treatment with IPU, TCZ, and CHL. Topsoil samples (0–10 cm depth) were collected from the field site following the W non-systematic pattern of sampling, according to ISO 10381-1 and -2 guidelines (2002), and mixed thoroughly to provide a single bulk soil sample. The soil was then partially air-dried, sieved to pass through a 2 mm mesh sieve and divided into 10 subsamples (6 kg each). For each pesticide, three subsamples were treated with appropriate amounts of aqueous solutions of IPU, TCZ and CHL (prepared from their commercial formulations) aiming to the application of ×1, ×2 and ×10 the recommended dose rates (Supplementary Data Table 2). The final soil subsample received the same amount of water without pesticide to serve as non-treated control. After pesticide application the soils were left to equilibrate for 1 h and water was added to adjust moisture to 40% of the water holding capacity. Soil samples were separated into 150-g subsamples which were placed in aerated plastic bags and incubated in the