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Changes in sorption of indaziflam and three transformation products in soil with aging

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ABSTRACT

To evaluate environmental risks of pesticides in soil, it is necessary to determine aging effects on sorption processes. Few studies have been carried out on their metabolites. The effect of incubation time on sorption of indaziflam and indaziflam-triazinediamine (FDAT), indaziflam-triazine indanone (ITI) and indaziflam-carboxylic acid (ICA) metabolites was determined on a mollisol and two depths of an oxisol. Soils were treated with [^{14}C]-indaziflam and [^{14}C]-metabolites, incubated for 112 days, then sequentially extracted with 0.01 N $CaCl_2$, acetonitrile:water (4:1), and acetonitrile. Apparent sorption coefficients ($K_{d,app}$) were calculated based on compound concentrations in solution and sorbed to soil. Decreases in total remaining chemicals were due to mineralization and formation of bound residues. $K_{d,app}$ values increased in the first two weeks of incubation, then tended to equilibrate. On average, sorption followed ITI > indaziflam ≫ ICA > FDAT. A significant increase in the sorption potentials of compounds and formation of bound residues was observed with the increase of incubation time (especially within the first 14 days), which would decrease the mobility potential of these molecules in the soil and therefore the possible contamination of underground water sources.

1. Introduction

To assess and predict the environmental risk of pesticides, information on the processes affecting the chemicals in soil is required. Pesticide fate and behavior in soil involve several distinct and often simultaneous phenomena including chemical, biological and photochemical degradation, transport and accumulation, volatilization and leaching (Senesi, 1992). Sorption and desorption are arguably the most important processes as they directly or indirectly control the other processes and determine the amount of pesticide/metabolites that reaches the target organism (Oliveira et al., 2000). Several factors are directly linked to the potential sorption/desorption of a pesticide including the chemical nature of the substance, soil physicochemical characteristics, climate characteristics (temperature, humidity, wind, and light), and aging time in the soil.

Sorption of pesticides to soil is most often characterized by the batch sorption method, which produces sorption coefficients that can be used in transport and risk assessment models. However potential problems exist with this method that may lead to inaccurate computations of environmental contamination risk. Batch equilibration is a slurry method and therefore fails to represent realistic soil/solution ratios. Additionally, many models do not account for pesticide desorption, which can differ from predictions based on the sorption isotherm of that pesticide. If a compound is hysteretic, it can lead to an overestimation of its true leaching potential (Delle Site, 2001; Oliveira et al., 2011; Yang et al., 2009). Also, the single sorption coefficient determined by batch equilibration may not represent sorption of a pesticide that has been in the field for any length of time.

The study of the effect of time on the behavior of molecules in contact with soil can be characterized by the calculation of apparent sorption coefficients ($K_{d,app}$), which are determined after a given incubation period of the pesticide in soil (Barriuso et al., 2004). $K_{d,app}$ is determined by sequential solvent extractions of aged pesticide residues where the chemical in solution extracted by aqueous $CaCl_2$ is the solution concentration (C_e') and the concentration of the sorbed chemical compound (C_s') is given by the extraction with an organic solvent. The aqueous extraction removes the entire compound in solution as well as the readily desorbable fraction, which is weakly bound to soil, while extraction with organic solvents promotes the removal of a fraction more tightly bound to the soil matrix. It is expected that the higher the contents extracted with water, the lower the sorption, $K_{d,app}$, of these compounds.

There has been research to determine the effect of aging on pesticide sorption (Boivin et al., 2005; Koskinen et al., 2002; Laabs and Amelung, 2005). In many cases, sorption has been shown to increase with aging

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(Cox et al., 1998; Mamy and Barriuso, 2007; Regitano and Koskinen, 2008; Scribner et al., 1992; Sharer et al., 2003), which could change the potential transport or risk classification (Oliveira et al., 2013). While most studies have been done with parent compound in surface soil, very few have been done with metabolites or in subsurface soil.

Indaziflam is a relatively new herbicide that is applied directly to soil and has preemergent action for controlling mono- and some dicotyledonous weeds. According to the United States Environmental Protection Agency (USEPA, 2010), the indaziflam molecule is degraded through oxidation of the indanyl radical to indaziflam-triazine indanone (ITI) and indaziflam-carboxylic acid (ICA). These metabolites along with the parent compound are further degraded to form fluoroethyldiaminotriazine (indaziflam-triazinediamine, or FDAT). Residues are eventually converted into bound residues and CO_2.

Little has been published on sorption–desorption processes of indaziflam in soil and even less on its metabolites. In the first published data about sorption and desorption of indaziflam, this compound showed low to moderate mobility in soil samples from glacial regions (USA) and tropical regions (Brazil) (Alonso et al., 2011). While sorption is generally high for indaziflam, it ranges from high to very low for its metabolites (Alonso, 2012); FDAT had the lowest sorption, and therefore the highest leaching potential in the soil. This study determined sorption of aged indaziflam and its metabolites in a glacial surface mollisol soil as well as in surface and subsurface depths of a tropical oxisol soil.

2. Material and methods

2.1. Soils and chemicals

A mollisol previously untreated with indaziflam was collected in Rosemount, MN (44° 45′ N, 93° 04′ W) from a 0–10 cm depth. Samples of an untreated oxisol were collected at depths of 0–10 and 20–30 cm in Rio Verde — GO, Brazil (17° 47′ S; 50° 58′ W). Samples were air-dried, passed through a 2-mm sieve and stored at 4 °C. Select soil properties are listed in Table 1. Sand, clay, and silt contents were determined by the hydrometer method. Soil pH was measured in a 1:2 soil/deionized water mixture. The organic carbon content was determined by oxidation with potassium dichromate (Nelson and Sommers, 1982).

Pure analytical standards used were indaziflam (*N*-[(1*R*,2*S*)-2,3-dihydro-2,6-dimethyl-1*H*-inden-1-yl]-6-[(1*R*)-1-fluoroethyl]-1,3,5-triazine-2,4-diamine) (99.6% purity), FDAT (6-[(1*R*)-1-fluoroethyl]-1,3,5-triazine-2,4-diamine) (96.1% purity), ITI (*N*-[(1*R*,2*S*)-2,3-dihydro-2,6-dimethyl-3-oxo-1*H*-inden-i-yl]-1,3,5-triazine-2,4-diamine), and ICA (2*S*,3*R*)-3-[[4-amino-6-[(1*R*)-1-fluoroethyl]-1,3,5-triazin-2-yl]-amino]-2,3-dihydro-2-methyl-1*H*-indene-5-carboxylic acid. These pure standards and their respective radioactive analytical standards, ^{14}C-labeled (triazine-2,4,-^{14}C) indaziflam (radiochemical purity = 97.9%, specific activity = 3.96 MBq mg^{-1}), ^{14}C-labeled (triazine-2,4-^{14}C) FDAT (radiochemical purity = 90.0%, specific activity = 3.79 MBq mg^{-1}), ^{14}C-labeled (indane-1-^{14}C) ITI (radiochemical purity = 92.0%, specific activity = 4.49 MBq mg^{-1}), and ^{14}C-labeled (carboxyl-^{14}C) ICA (radiochemical purity = 92.5%, specific activity = 4.31 MBq mg^{-1}), were graciously provided by Bayer Crop Science (Wuppertal, Germany). Structures are shown in Fig. 1. Radiolabeled and non-radiolabeled standards were carefully mixed in methanol to prepare a final solution concentration of 40.0 μg mL^{-1} containing ~8.3 MBq L^{-1} for indaziflam and ITI, and ~3.7 MBq L^{-1} for FDAT and ICA. Solutions were stored in foil-covered flasks at 4 °C in the dark.

Table 1
Select physicochemical properties of the mollisol surface and oxisol surface and subsurface soils.

Soil	Depth (cm)	% OC	% sand	% clay	% silt	pH
Mollisol	0–10	2.52	33	15	52	6.0
Oxisol	0–10	2.17	39	59	2	6.2
Oxisol	20–30	1.79	31	67	2	6.0

2.2. Soil treatment

Experiments were carried out in triplicate in glass centrifuge tubes with Teflon lined caps. Eight grams of a surface and subsurface oxisol soil was treated with 200 μL of [^{14}C]-indaziflam solution (40.0 μg mL^{-1}), while 20 g of the same soils was treated with 500 μL of [^{14}C]-FDAT solution (40.0 μg mL^{-1}). Eight grams of mollisol samples was treated with 200 μL of [^{14}C]-indaziflam and [^{14}C]-ITI solutions (40.0 μg mL^{-1}) whereas 20 g samples were treated with 500 μL of [^{14}C]-FDAT and [^{14}C]-ICA solutions (40.0 μg mL^{-1}). Solutions were added dropwise using a microliter syringe. The final amount of chemical added to soil samples equaled 1 mg kg^{-1} soil, a value close to the normal soil application rate of indaziflam assuming an equivalent rate of 0.1 kg ha^{-1} and uniform distribution in the surface soil (1 cm). The moisture of soil samples was standardized to 20% of soil mass.

2.3. Soil incubation

Soil samples were incubated at 28 ± 1 °C in the dark for up to 112 days (16 weeks). Biometer flasks with treated soil and a vial containing 4 mL of 1 N NaOH were used to monitor mineralization (evolution of $^{14}CO_2$). Vials with NaOH were replaced weekly and flasks were aerated and moisture content was adjusted twice a week. To determine the amount of evolved $^{14}CO_2$, a 1-mL aliquot of NaOH solution was added to 5 mL of scintillation cocktail (EcoLyte, cocktail, ICN Biomedicals, Costa Mesa, CA) and samples were left in the dark for 24 h. The concentration of ^{14}C in solution was determined by liquid scintillation counting (LSC) for 5 min in a liquid scintillation analyzer (Packard 1500 — Packard Instruments, Downer Grove, IL.).

2.4. Soil extraction and analysis

Samples were collected and processed after 0, 7, 14, 28, 56, 84, and 112 days of incubation. After each incubation period, removed soil samples received 20 mL of 0.01 N $CaCl_2$ (first extraction), were shaken for 1 h on a tabletop shaker, and then left to sit overnight (24 h) at 20 ± 2 °C in the dark. Samples were then shaken for 10 min, and centrifuged (820 g) for 30 min, and the supernatant (10 mL) was transferred to glass flasks. A 1-mL aliquot of this extract was removed, and mixed with 5 mL of the scintillation cocktail and the radioactivity was determined by LSC. The remaining supernatant was later used to determine the amount of parent chemical in the extracted ^{14}C by HPLC (see below).

Ten milliliters of 4:1 (v/v) acetonitrile:deionized water was added to the remaining soil and $CaCl_2$ solution in the tubes. The tubes were then shaken for 20 min, and centrifuged (820 g) for 30 min, and a 10-mL aliquot of the supernatant was removed and stored. This procedure was repeated with the addition of 10-mL acetonitrile. The remaining soil and solution were filtered and washed with 10 mL of deionized water. The two aqueous organic extracts and the washing solution were combined. The acetonitrile was removed by evaporation at 40 °C using a Zymark Turbovap. The samples were evaporated to a final volume of ~6 mL, and then brought up to a volume of 10 mL with acetonitrile. Aliquots (1 mL) of the final aqueous organic solution were removed and analyzed by LSC as previously described. Again, the remaining solution was used to determine the amount of parent chemical in the extracted ^{14}C by HPLC (see below).

Samples were analyzed by HPLC using a Waters chromatograph system with a 2996 photodiode array detector, 1525 pump, and a 717 (Waters Corporation, Milford, MA, USA) and a Zorbax SB-C18 column (4.6 × 150 mm, 5 μm film thickness) (Agilent, Santa Clara, CA, USA). The mobile phase was a gradient of 0.05% formic acid in water and acetonitrile starting at 10% acetonitrile and changing to 50% by 35 min. The flow rate was 0.75 mL min^{-1}, and the injection volume was 100 μL.