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Fate of glyphosate and degradates in cover crop residues and underlying soil: A laboratory study

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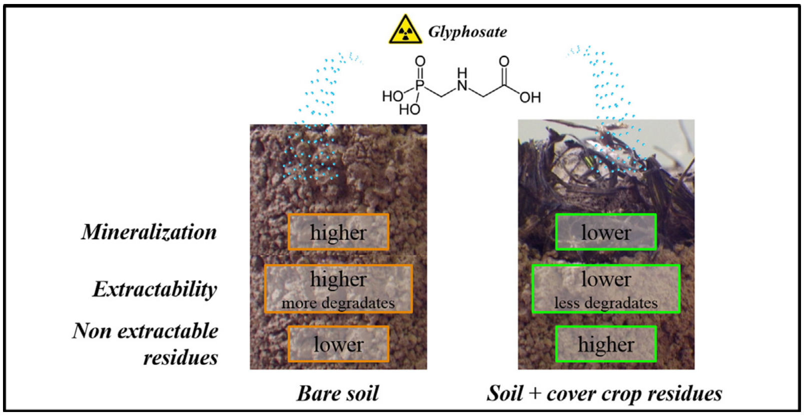
HIGHLIGHTS

- Glyphosate sorption on cover crop residues increases with their decomposition degree.
- Glyphosate degradation and mineralization are lower in mulch than in soil.
- Nonextractable residue formation is one of the main dissipation pathways of glyphosate in cover crop mulch.

GRAPHICAL ABSTRACT



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ABSTRACT

The increasing use of cover crops (CC) may lead to an increase in glyphosate application for their destruction. Sorption and degradation of ^{14}C-glyphosate on and within 4 decaying CC-amended soils were compared to its fate in a bare soil. ^{14}C-Glyphosate and its metabolites distribution between mineralized, water-soluble, NH_4OH-soluble and non-extractable fractions was determined at 5 dates during a 20 °C/84-d period. The presence of CC extends ^{14}C-glyphosate degradation half-life from 7 to 28 days depending on the CC. ^{14}C-Glyphosate dissipation occurred mainly through mineralization in soils and through mineralization and bound residue formation in decaying CC. Differences in sorption and degradation levels were attributed to differences in composition and availability to microorganisms. CC- and soil-specific dissipation patterns were established with the help of explicit relationships between extractability and microbial activity.

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1. Introduction

Conservation agriculture is regarded as a promising combination of agricultural practices to limit soil erosion while increasing soil fertility and decreasing fossil fuel dependency (Gebhardt et al., 1985; Tebrügge and During, 1999). It includes tillage reduction and the associated presence of crop residues at the soil surface. In most cases, it also involves the use of cover crops during the fallow period (Hartwig and Ammon, 2002). Indeed, cover crops are known to provide several ecosystem services, such as preserving water quality by reducing nitrate leaching (Hargrove, 1991; Hartwig and Ammon, 2002; Justes et al., 1999), and, in conservation agriculture systems, cover crops are also expected to mimic tillage by improving soil structure or herbicides by smothering weeds (Teasdale, 1996). Although mechanical techniques are being developed and evaluated (Kornecki et al., 2013, 2009; Teasdale and Rosecrance, 2003), cover crops are still predominantly chemically killed. To this end, non-selective herbicides such as glyphosate are applied (Nascente et al., 2013). With the increase of cultivated area under conservation agriculture, the potential increase in glyphosate use to kill cover crops may lead to increased environmental risks. Indeed, this herbicide and its main metabolite AMPA are already among the most frequently detected pesticides in water bodies (Aparicio et al., 2013; Battaglin et al., 2009; Commissariat général au développement durable, 2011; Daouk et al., 2013).

In soils, glyphosate sorption is highly variable, with sorption coefficient (K_d) values ranging from 15 $L\cdot kg^{-1}$ (Nicholls and Evans, 1991) to 880 $L\cdot kg^{-1}$ (Beltran et al., 1998). Its sorption is mainly due to clay particles and varies according to the nature of the clay (Shoval and Yariv, 1979; Sprankle et al., 1975), soil phosphorus content (Borggaard and Gimsing, 2008; de Jonge and de Jonge, 1999), soil solution and clay cations (Dousset et al., 2007; Morillo et al., 1997; Piccolo et al., 1994; Sprankle et al., 1975), temperature, pH (de Jonge and de Jonge, 1999) and, to a lesser extent, to organic matter content (Ahmad et al., 2001; Day et al., 1997). In plants, although sorption level is lower than in soils, organic matter quantity and quality affects glyphosate sorption. It may vary according to (i) plant species, with, for example, K_d values ranging from 3 $L\cdot kg^{-1}$ on fresh grass clippings (Lashermes et al., 2010) to 28 $L\cdot kg^{-1}$ on fresh phacelia residues (Cassigneul et al., 2015), and (ii) the degree of decomposition of the plants, with an increase in glyphosate sorption with increasing decomposition (Cassigneul et al., 2015).

Glyphosate degradation half-life determined in a wide range of soils was found to vary from a few days up to several months and even years, with similar variation in half-life values in laboratory and field studies (Gimsing et al., 2004; Nomura and Hilton, 1977; Smith and Aubin, 1993; Sprankle et al., 1975; Vereecken, 2005). Glyphosate degradation is predominantly due to microorganisms (Gimsing et al., 2004; Sprankle et al., 1975), and involves enzymatic reactions cutting either the C–N or the C–P bond, leading to the formation of amino-ethyl phosphonic acid (AMPA) or sarcosine (Ternan et al., 1998). It is supposed to be co-metabolic and it is assumed that glyphosate degradation is coupled with mulch decomposition (Aslam et al., 2014), microorganisms using glyphosate as a carbon source (Mijangos et al., 2009). In field conditions, when glyphosate is applied to kill a cover crop, the treatment is generally performed at an early vegetative stage of the plant. This leads to the formation of a mulch at the soil surface, subject to a rapid decay according to the climatic conditions. Very little is known about the effects of the type of mulch (in relation to plant species) on glyphosate degradation, while several studies have shown that the diversity and activity of microorganism communities in soils are strongly influenced by the nature of the cover crop (Carrera et al., 2007; Nair and Ngouajio, 2012; Schutter and Dick, 2002; Zablotowicz et al., 2007). Improving this knowledge would lead to a greater understanding of environmental consequences of agricultural practices, especially in conservation agriculture systems.

The general objective of this study was to assess the environmental behavior of glyphosate in cover crop mulches. More precisely, the specific objectives were (i) to identify and quantify glyphosate behavior in a mulch of cover crop residues and the underlying soil and (ii) to assess the variability of glyphosate fate across a set of mulches of different cover crops. In order to quantify precisely each process involved in glyphosate dissipation, laboratory experiments were conducted using radiolabeled glyphosate on soil microcosms with or without mulches. Four cover crop species, among the most used by northern countries farmers, were chosen to investigate the effect of mulch on the fate of glyphosate at the soil surface.

2. Materials and methods

2.1. Soil and mulch sampling

Common vetch (*Vicia sativa*), white mustard (*Sinapis alba*), hybrid ryegrass (*Lolium hybridum*) and a mixture of common vetch + oat (*Avena sativa*) were grown as cover crops (CC) on the Lamothe INP-EI Purpan experimental station (near Toulouse, SW France) on a clay loam soil (Stagnic Luvisol according to IUSS Working Group WRB (2007)) from June to September 2012. Prior to this cover crop, the whole field had grown a durum wheat–sunflower rotation without glyphosate application for more than 10 years. Aerial parts of the 4 cover crops were collected, dried at 40 °C and cut into 1 cm square pieces. The underlying 0–5 cm topsoil was collected, sieved (5 mm mesh) and stored at 4 °C. CC-associated soils were sampled on each CC plot to record any possible plant-specific soil-borne microbial populations (Kowalchuk et al., 2002; Mijangos et al., 2009). However, these populations were not characterized.

2.2. Herbicides

Both experiments were conducted with a mixture of technical-grade and [phosphonomethyl-^{14}C] glyphosate (Sigma-Aldrich), prepared in 0.01 M $CaCl_2$. Specific radioactivity and radiochemical purities of GLY were 81.4 $MBq\cdot mmol^{-1}$and 98.8%, respectively.

2.3. Experiment 1: glyphosate adsorption on decaying cover crop residues

2.3.1. Incubations and CC characterization/description

CC were subjected to accelerated decomposition in the dark for 6, 28 or 56 days at 28 °C and in non-limiting moisture conditions. Each CC was moistened and placed on top of its associated soil in a plastic tray (24 ∗ 37 ∗ 7 cm). Soils had been previously brought to field capacity (pF 2.5). At days 0, 6, 28 and 56 of the incubation, CC were dried (40 °C), ground (1 mm or 50 μm) and analyzed (i) in duplicate for their carbon and nitrogen content (NH 1500 CN, Fisons Instruments) and (ii) on a single aliquot for their biochemical composition as assessed by Van Soest fractionation (Van Soest and Robertson, 1979). CC and soils characteristics are described in Table 1.

2.3.2. Sorption characterization

Sorption of glyphosate onto CC residues and soil was determined using a batch equilibration technique (OECD, 2000), as detailed in Cassigneul et al. (2015). The sorbent:glyphosate solution ratio was 1:9 ($g\cdot mL^{-1}$) for soil and 1:5.8 for CC residues. Amounts of sorbed glyphosate were described using the partition coefficient K_d ($L.kg^{-1}$) and the normalized organic carbon content K_d i.e. K_{oc} ($L\cdot kg^{-1}$ OC).

2.4. Experiment 2: glyphosate degradation in microcosms of soil and cover crop residues

2.4.1. Microcosm setup/construction/description

Microcosms, i.e. cylinders containing soil (118 g dw) covered by CC mulch (2.5 g dw), were set up as detailed in Aslam et al. (2014). The