



Adsorption and mobility of glyphosate in different soils under no-till and conventional tillage



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ABSTRACT

Glyphosate (N-(phosphonomethyl) glycine) is a post-emergence, non-selective, foliar herbicide. Around 200 million liters of this herbicide are applied every year in Argentina, where the main agricultural practice is no-till (NT), accounting for 78.5% of the cultivated land. In this work, we studied the adsorption of glyphosate in different soils under long-term management (more than 16 years) of NT and conventional tillage (CT). Samples were taken from different regions of Argentina corresponding to: Paraná soil (PAR), a silty clay loam soil (<37% clay), Manfredi (MAN) and Pergamino (PER), both silty loam soils (<26% clay). We found that the adsorption was very high in all the soils, and it was particularly influenced by the soil clay content and CEC and negatively related to pH and phosphorus. In general, the adsorption coefficient (K_f) was higher in the CT samples. We also studied the vertical transport of glyphosate in undisturbed columns (15 cm long) and compared the effect of NT and CT. Less than 0.24% of the applied pesticide leached in all soils. No significant difference was found between the total amount of leached glyphosate between soils or tillage practice. The highest glyphosate concentration (67.53% of the initially applied doses) was found in the top 5 cm of the columns. The strong retention of glyphosate to the soil matrix, as confirmed by the high K_f values obtained in the isotherm studies, was the dominant factor influencing glyphosate mobility through the soil profile.

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1. Introduction

When a pesticide is applied in the field, a great proportion of it reaches the soil where several factors can influence its final destiny. Some factors depend on the intrinsic properties of the pesticide (e.g. adsorption, solubility, and persistence). Other factors depend on the physico-chemical and biological properties of the soil (e.g. organic content, humidity, biomass, pore connectivity, and pH) (Holland, 2004). The soil properties are also influenced by climate factors such as rainfall and temperature, as well as cropping and managing practices.

The tillage system can modify the chemical and biological properties of the soil. It also alters the porous space, modifying the hydraulic properties and the solute and water transport through the soil profile (Larsbo et al., 2009). In soils under conventional tillage (CT), macropores are generally destroyed, and only the intraaggregate space is preserved (Mapa et al., 1986). In no-till (NT) systems the formation of continuous macropores is promoted (Locke and Bryson, 1997), allowing the preferential flow of water and chemical substances to groundwater levels (Harris et al., 1993; Kamau et al., 1996; Ogdén et al., 1999). In some cases, NT can increase the organic matter (OM)

content, which in return promotes the retention of certain pesticides (Levanon et al., 1994; Novak et al., 1996).

Glyphosate (N-(phosphonomethyl) glycine) is a post-emergence, non-selective, foliar herbicide. Around 200 million liters of this herbicide are applied every year in Argentina, where the main agricultural practice is NT, accounting for 78.5% of the cultivated land (Aapresid, 2012). Glyphosate has an amine, carboxylate, and phosphonate group, and it behaves as an amphoteric molecule with four ionization constants: $pK_a = 2, 2.6, 5.8$ and 10.8 (Sprankle et al., 1975). It has a high water solubility (11.6 g L^{-1} at 25 °C) (Montgomery, 1993), that may increase the risk of being transported in the aqueous phase. On the other hand, it has a tendency to highly adsorb to soil particles, which can lower the potential to contaminate surface waters or groundwater (Vereecken, 2005). The ability to adsorb to soil particles contributes to the accumulation of glyphosate in soil. Nevertheless, the degree of adsorption can be affected by several factors. Adsorption has been related to the soil clay content and the cation exchange capacity (CEC) (Hiera da Cruz et al., 2007), suggesting that glyphosate can be complexed by cations released from clays via cation-exchange reaction with solution protons (Glass, 1987). Other important factors that influence adsorption are crystalline and amorphous aluminum and iron oxides (Morillo et al., 2000). Within the soils pH range (between 4 and 8), glyphosate is found in its anionic form and has a high affinity

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for Al^{3+} and Fe^{3+} trivalent cations (Sheals et al., 2002; Gimsing and Borggaard, 2007; Barja and Dos Santos Afonso, 2005). As the soil pH increases, glyphosate's adsorption decreases (Zhao et al., 2009). Additionally, inorganic phosphate competes strongly for the same adsorption sites, thus increasing glyphosate's mobility in soil (Prata et al., 2005).

Soil structure is an important factor influencing glyphosate transport (Aronsson et al., 2011; Gjettermann et al., 2009). Several laboratory and lysimeter studies have indicated that glyphosate may be transported by preferential flow in structured soils (Vereecken, 2005). Kjaer et al. (2011) have demonstrated rapid macropore mediated transport of glyphosate in a field study that was monitored for eight months after pesticide application. The study's results demonstrated that even though glyphosate is a strong sorbing pesticide, leaching can occur via preferential transport pathways. The average concentrations found in the drainage runoff exceeded the EU limit value for groundwater of $0.1 \mu\text{g L}^{-1}$. In another field study, glyphosate percolated to the drainage water in a clayey soil, whereas no leaching was detectable under the same conditions in a sandy soil (Aronsson et al., 2011). Vertical transport has also been studied in laboratory conditions using undisturbed or repacked soil columns (e.g. de Jonge et al., 2000; Dousset et al., 2004; Strange-Hansen et al., 2004; Barrett and McBride, 2006; Gjettermann et al., 2009, 2011). The results from the studies are variable and depend on the selected experimental conditions, such as input flow, herbicide concentration, time duration and the type of soil studied.

Once glyphosate reaches the soil, it can be mineralized by microbial activity (Rampoldi et al., 2014; Gimsing et al., 2009; Dick and Quinn, 1995). The main pathway described for glyphosate mineralization in the environment is via the glyphosate oxidoreductase enzyme, which yields aminomethylphosphonic acid (AMPA) and glyoxylate. The AMPA molecule accumulates in the soil since its generation is faster than its degradation (Simonsen et al., 2008). Glyphosate can also be hydrolyzed to sarcosine, by the activity of the C–P lyase enzyme. Contrary to AMPA, sarcosine is easily degradable does not accumulate in soil (Borggaard and Gimsing, 2008) and is not an exclusive metabolite of glyphosate's degradation.

Very few studies have addressed the effect of tillage practices on glyphosate adsorption and mobility using samples from long-term field trials. Therefore, the focus of this work was to compare the effect of NT and CT management practices in different soils from Argentina on the adsorption and leaching of glyphosate. For this purpose, first we performed batch isotherm studies to compare the adsorption between soils and tillage systems. To study the vertical movement, we used undisturbed soil cores from long-term field trials under NT and CT. The transport of an inert molecule (bromide) in these columns was previously described in Okada et al., 2014. In the latter work, the authors described bromide transport using the convection–dispersion equation and compared the effect of tillage and soil on the velocity and the hydrodynamic dispersion coefficient. Thus, the second objective of the present work was to study the effect of different soils under NT and CT on glyphosate transport. The formulated hypotheses are: (i) glyphosate's adsorption is influenced by the physico-chemical properties of the soils; (ii) the vertical transport of glyphosate is higher in soils under NT than in CT.

2. Material and methods

2.1. Soils and sampling

Soil samples were obtained from long-term field trials from three different Experimental Stations of the National Institute of Agronomical Technology (INTA). The Manfredi (MAN) experimental site is located in Córdoba Province and was established 30 years ago. The soil corresponds to a coarse-silty, mixed, thermic Entic Haplustoll of the Oncativo series (INTA, 1987). Samples were taken from treatments under NT and CT with a maize-soybean rotation. Parana (PAR)

experimental site is located in Entre Ríos Province. The soil belongs to the Tezanos Pinto series, which is characterized as a fine, mixed, thermic Acuic Argiudoll (INTA, 1998). It is a deep soil and moderately well drained. Soil samples were taken from a long-term field trial (16 years) under NT and CT, with a wheat/soybean–maize rotation. Pergamino (PER) site is located in Buenos Aires Province. The soil is classified as fine, thermic, illitic, Typic Argiduoll (Pergamino series) (INTA, 1972). They are well-drained soils with medium permeability. The field trial was established 34 years ago under NT and CT, and it has a maize–wheat/soybean rotation.

Undisturbed soil columns were sampled in a completely randomized blocks design, resulting in 4 columns from each tillage practice of the studied soils (total number of columns = 24). Core samples were obtained introducing stainless steel cylinders of 8 cm wide inner diameter and 15 cm length into the top soil. Samples were then sealed with plastic lids and stored at 4°C until the transport studies were conducted.

Disturbed soil samples from 0 to 15 cm depth of top soil were also collected from each block of the sampled columns for the adsorption isotherm experiments ($n = 24$). Subsamples from each replicate were also used for physical and chemical analysis.

Particle size distribution was obtained by the pipette method (Soil Conservation Service, 1972), and organic carbon content (OC) was measured through oxidation using the chromic acid method (Walkley and Black, 1934). CEC was determined by displacement with 1 M ammonium acetate at pH 7 (Chapman, 1965), and pH was measured by an electrode in a soil:water ratio of 1:2.5. Available phosphorous (P-Bray) was determined according to Bray and Kurtz (1945). Specific surface area (SSA) was measured by the ethylene glycol monoethyl ether method (Heilman et al., 1965; Carter et al., 1986). Al and Fe amorphous oxides were extracted with 0.2 M acidified ammonium oxalate (pH 3) (Blackmore et al., 1987). Al was determined using the Aluminon method (Barnhisel and Bertsch, 1982) and Fe using a specific atomic adsorption lamp.

2.2. Chemicals

Stock solutions for the standard curves of all the glyphosate measurements and the isotherm studies were prepared using pure analytical glyphosate (PESTANAL^R, 99.9%) purchased from Sigma-Aldrich, and AMPA (PESTANAL^R, 99%). HPLC-grade methanol and HPLC-grade acetonitrile (ACN) for analytical procedures were purchased from Seasinglab. Nanopure water was obtained by purifying demineralized water in ELGA Purelab ultra (Illinois, USA). For the column experiment, the stock solution of glyphosate was prepared using commercial glyphosate (ATANOR II®, 35.6% acid equivalent).

2.3. Glyphosate and AMPA analysis

To quantify glyphosate and AMPA from water samples of the column experiments and isotherm studies, an aliquot of 3 ml of each sample was transferred to a 15 mL polyethylene flask. Then, 0.5 ml of borate buffer (0.04 mM $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{H}_2\text{O}$, pH = 9) and 0.5 ml of ACN were added. After shaking, the samples were derivatized with 0.5 ml of 9-fluorenylmethylchloroformate (FMOC-CL) dissolved in ACN (6g L^{-1}), and incubated overnight at room temperature. As a clean-up step, to remove any organic impurities and minimize matrix effects, 4.5 ml of CH_2Cl_2 were added to the samples and shaken vigorously. Samples were centrifuged for 10 min to separate the aqueous fraction from the organic solvent. The supernatant was collected and filtered through a $0.22 \mu\text{m}$ nylon filter, and then analyzed by liquid chromatography (LC) coupled to a tandem mass spectrometer (MS/MS).

To extract and quantify glyphosate and AMPA from the soil samples of the column experiments, 5 g of soil from each depth were subsampled and placed into 50 mL tubes for analysis in the lab. Previous to the extraction method, samples were spiked with 50 μl of an

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