Geoderma 323 (2018) 13–21

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Glyphosate dynamics in a soil under conventional and no-till systems during a soybean growing season

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A R T I C L E I N F O

Handling Editor: Morgan Cristine L.S.

Keywords:
Hydraulic conductivity
Solute transport
Pesticide fate
Soil porosity
Glyphosate accumulation

A B S T R A C T

Glyphosate (GLY) is a non-selective herbicide, heavily used world-wide in agriculture, especially under no-tillage (NT) management. The objectives of this work were i - to determine the temporal and vertical variation of GLY and its main metabolite (AMPA) levels during the soybean cycle in a soil under NT and conventional tillage (CT); ii - to determine the relationship of GLY and AMPA levels variation with different soil properties; and iii - to compare initial and final GLY and AMPA levels in the soil during a crop cycle to infer possible accumulation. GLY and AMPA contents were determined in the A horizon (0–40 cm) of a loam soil from Argentinian Pampas Region, in different dates during soybean crop cycle. Soil physical and chemical properties were also determined. GLY and AMPA were detected in all sampling dates in both treatments (GLY and AMPA contents in the soil ranged between 5.7 and 98.5 $\mu g \cdot kg^{-1}$; and 6.6 and 1686.0 $\mu g \cdot kg^{-1}$, respectively). GLY was strongly retained in the top soil in most of the sampling dates for both treatments (> 80% of total GLY was found in the topsoil - 20 cm). CT treatment showed higher GLY temporal variation, favored by higher values of saturated hydraulic conductivity (K_0), total macroporosity (θ_{ma}) and effective macroporosity (ε_{ma}), especially when strong precipitation occurred near the application. GLY vertical transport under NT seemed to be limited by low values of K_0, θ_{ma}, and ε_{ma}. The temporal variation of GLY vertical transport was explained by the temporal variation of the studied soil physical and hydraulic properties. Total extracted GLY accumulated, with an increment between the last and the first sampling date of 54% and 82% during the crop cycle for NT and CT, respectively.

1. Introduction

Glyphosate (*N*-[phosphonomethyl] glycine) (GLY) is a broad-spectrum herbicide, used non-selectively in agriculture to control weeds and herbaceous plants. Since its introduction in 1974, GLY became a widely used herbicide, especially under no tillage (NT) management systems. In Argentina three-quarters of agricultural land is cultivated with transgenic crops (soybean, maize and cotton) (Aparicio et al., 2013). Additionally, around 90% of agricultural lands in Argentina are under NT (AAPRESID, 2015), where chemical control is the most common practice for weed control, during cultivation and fallow periods. Around 200 million L of GLY are applied every year in Argentina, being the most commonly used herbicide in the country (Aparicio et al., 2013).

Several studies reported the presence of GLY and its main metabolite aminomethyl phosphonic acid (AMPA) at different depths along the soil profile (Veiga et al., 2001; Kjær et al., 2005; Candela et al., 2010; Aparicio et al., 2013; Lupi et al., 2015). Also its presence was reported in surface water near to application areas (Vereecken, 2005; Peruzzo et al., 2008; Coupe et al., 2012; Sanchís et al., 2012; Etchegoyen et al., 2017).

Several factors can influence the fate of GLY in the soil. Some of these factors are intrinsic properties of the herbicide (e.g. molecular structure, solubility, and persistence), while other factors correspond to soil properties as clay fraction, organic carbon (OC), pore connectivity, cation exchange capacity (CEC) and pH (Okada et al., 2016). GLY is a small molecule with three polar functional groups (carboxyl, amino and phosphonate groups) which allows a strong adsorption to soil minerals. This may results in a low mobility of GLY in the soil (Vereecken, 2005; Borggaard and Gimsing, 2008). GLY adsorption is positively related to soil CEC and clay content and negatively related with soil pH (Zhao et al., 2009; Paradelo et al., 2015; Okada et al., 2016). On the other

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https://doi.org/10.1016/j.geoderma.2018.02.041
Received 20 September 2017; Received in revised form 23 January 2018; Accepted 25 February 2018
0016-7061/

hand, GLY high water solubility can lead to lixiviation, especially when high precipitation occurs near application (Veiga et al., 2001). Additionally, inorganic phosphate competes strongly for the same adsorption sites, increasing GLY mobility in soil (Prata et al., 2005; Sasal et al., 2015; Okada et al., 2016). Degradation of GLY in soils is mainly due to microbial activity and chemical decomposition. Its degradation can occur rapidly in the soil; with reported half-lives from 1 to 174 days and is generally considered moderately persistent in soil (Mamy, 2004). However, the adsorption process can make the herbicide more persistent (Veiga et al., 2001). Some authors mentioned that greater persistence of pesticides was attributed to their greater retention in soil surface with high OC content (Mazzoncini et al., 1998; Zablotowicz et al., 2000). This results in GLY accumulation, due to a decrease in availability for degrading microorganisms (Aslam et al., 2015). Additionally, some authors mentioned that GLY and AMPA can accumulates in soil or rivers bottom sediments (Aparicio et al., 2013; Imfeld et al., 2013; Napoli et al., 2016). Primost et al. (2017) mentioned that GLY and AMPA can behave as "pseudo-persistent" pollutants due to high GLY applications rates in the field. In contrast, other authors mentioned that the risk of GLY and AMPA accumulation is very low (Yang et al., 2015).

However, the prediction of GLY and AMPA mobility considering only adsorption capacity is not quite correct, because the soil is a highly complex medium involving many interacting processes (Bergström et al., 2011). In this sense, some authors emphasized that in order to study solute transport in soil it is necessary to take into account the top soil physical and hydraulic properties, such as pore size distribution (PoSD) and hydraulic conductivity (K) (Gjettermann et al., 2000; Kjær et al., 2011; Larsbo et al., 2014). Candela et al. (2007), from miscible displacement experiments, found that sorption is a process dependent on the pore-water velocity and residence time of soil solution. Several laboratory and lysimeter studies indicated that GLY is transported by preferential flow in structured soils (Vereecken, 2005). De Jonge et al. (2000) concluded that GLY leaching was due to preferential transport through macropores. Kjær et al. (2005) reported no leaching of GLY and AMPA in sandy soils with low macroporosity, and the opposite for structured clayey soils with high macroporosity. Borggaard and Gimsing (2008), mentioned that soil with high macroporosity may increase the leaching risk, but only when a large precipitation occurs close to the application. In addition, several authors mentioned that in soils without continuous macropores, GLY lixiviation is not possible (De Jonge et al., 2000; Fomsgaard et al., 2003; Stone and Wilson, 2006). Iversen et al. (2011) mentioned that K is a good proxy variable for the risk of preferential solute leaching. Larsbo et al. (2014) mentioned that K could be used to estimate preferential transport under field conditions. These authors found that soils with small macroporosity and low K exhibited a greater degree of preferential transport. However, there is few information in the literature about K influence on GLY and AMPA vertical transport.

Pore size distribution and pore connectivity are affected by tillage practices, and therefore they may also affect flow and solute transport (Lipiec et al., 2006). The replacement of conventional tillage (CT) by NT at local scale, generally resulted in lower infiltration rates, reported by several authors in a wide range of soil textures in Argentinean Pampas region (Ferreras et al., 2000; Sasal et al., 2006; Álvarez et al., 2009; Soracco et al., 2010; Lozano et al., 2013), especially in silty soils with platy structure development. This kind of structure can exhibit a pattern of soil porosity with a preferential horizontal orientation, affecting water entry into the soil profile (Lozano et al., 2013), and therefore solutes fate.

Some studies from different regions analyzed the relationship between solute transport and tillage system. Jarvis et al. (2007) reported that NT system promotes the formation of continuous macropores favoring preferential flow of water and solutes, while CT usually results in uniform flow and transport in the uppermost disturbed layer, generating a barrier for macropore preferential flow. Larsbo et al. (2009) studied different herbicides' migration in undisturbed soil columns in clayey and silty-clay soils under NT and CT. These authors observed higher levels of lixiviation under NT, due to a higher macropore connectivity. In the other hand, Gjettermann et al. (2000) studied GLY lixiviation in a sandy loam soil, finding significantly higher leached levels in the recently tilled soil. Okada et al. (2014) compared the effects of long-term tillage in different soils on solute transport. These authors found that in clayey soils the solute dispersion was higher under NT. In the other hand, several authors did not found significant differences in GLY and AMPA content at different depths between NT and CT (Fomsgaard et al., 2003; Rampazzo et al., 2013).

In Argentina few studies have been reported at local and regional scales about GLY and AMPA behavior in agricultural soils (Lupi et al., 2015). Peruzzo et al. (2008) found an increase of GLY and AMPA levels in silty loam Argiudolls under NT after its application, especially when large precipitation occurred. Okada et al. (2016) analyzed the soil management influence on GLY dynamics using undisturbed soil columns in laboratory from silty loam and silty clay loams soils. These authors did not found a significant difference between NT and CT systems. In both managements 80% of GLY remained in the first 5 cm top soil. Lupi et al. (2015) studied in the Argentina South Pampa Region GLY and AMPA levels at different depths before and after application in two agricultural soybean fields. They mentioned that most of the herbicide was retained in the upper 10 cm of soil profile. However, although GLY and AMPA concentrations diminished drastically along the soil profile, both compounds were found even at 35 cm of depth.

There are few studies, especially in Argentina, following the evolution of GLY and AMPA levels in the soil during the crop cycle under different tillage systems, and the dependence with physical, chemical and hydraulic properties. The joint study of GLY and AMPA temporal and vertical dynamics, and temporal variation of soil physical, chemical and hydraulic properties, would allow us to better understand the influence of tillage systems on GLY transport, and the contamination hazard.

We hypothesized that: i - the level of GLY and AMPA in the soil profile presents higher temporal and vertical variation during the crop cycle under CT as compared with NT; ii - temporal and vertical dynamics of GLY and AMPA are related with soil hydraulic properties; and iii - the processes involved in GLY and AMPA levels balances lead to accumulation during the crop cycle.

The objectives of this work were: i - to determine the temporal and vertical variation of GLY and AMPA levels during the soybean cycle in a soil under NT and CT; ii - to determine the relationship of GLY and AMPA levels variation with different soil properties; and iii - to compare initial and final GLY and AMPA levels in the soil during a crop cycle to infer possible accumulation.

2. Materials and methods

2.1. Site, treatments and sampling dates

The experiment was carried out near the city of Chascomús, Argentina (located at 35°44′37.61″ south and 58°03′10.22″ west). The soil was classified as a fine, illitic, thermic abruptic Argiudoll (Soil Survey Staff, 2006), Luvic Phaeozem (IUSS Working Group WRB, 2007). The climate in the region is temperate without freezing and thaw process. The mean annual precipitation is 946 mm. Precipitation was recorded during the experiment period (June 2015–August 2016).

Before the treatments were applied, the plots were under CT and with the same crop rotation for > 20 years. In the year 2000 an experimental design with complete randomized blocks with two treatments (plots of 30 m wide and 50 m long for each treatment) was applied: a) no tillage (NT), in which only a narrow (0.05 m) strip of the soil was drilled to deposit crop seeds, b) conventional tillage (CT) in which the soil was ploughed (disc plough + tooth harrow) at 0.20 m depth, and later smoothed using the tooth harrow each year in October,