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Occurrence of glyphosate and AMPA in an agricultural watershed from the southeastern region of Argentina

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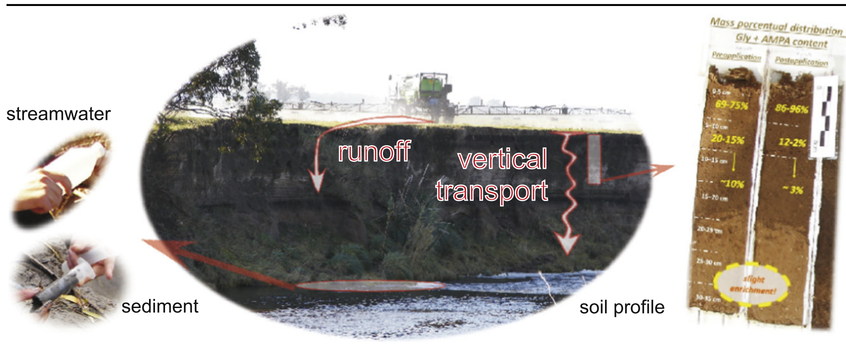
HIGHLIGHTS

- The fate of GLY + AMPA was studied in agricultural soil profiles from soybean fields.
- GLY + AMPA in soil profile were well correlated with organic carbon content and pH.
- GLY was concentrated in the upper soil layer after application.
- GLY and AMPA were detected in streamwater and sediment at lower levels than soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Glyphosate (GLY) and AMPA concentrations were determined in sandy soil profiles, during pre- and post-application events in two agricultural soybean fields (S1 and S2). Streamwater and sediment samples were also analyzed. Post-application sampling was carried out one month later from the event. Concentrations of GLY + AMPA in surface soils (0–5 cm depth) during pre-application period showed values 20-fold higher (0.093–0.163 μg/g d.w.) than control area (0.005 μg/g d.w.). After application event soils showed markedly higher pesticide concentrations. A predominance of AMPA (80%) was observed in S1 (early application), while 34% in S2 for surface soils. GLY + AMPA concentrations decreased with depth and correlated strongly with organic carbon (r between 0.74 and 0.88, $p < 0.05$) and pH (r between −0.81 and −0.76, $p < 0.001$). The slight enrichment of pesticides observed from 25 cm depth to deeper layer, in addition to the alkaline pH along the profile, is of high concern about groundwater contamination. Sediments from pre-application period showed relatively lower pesticide levels (0.0053–0.0263 μg/g d.w.) than surface soil with a predominance of glyphosate, indicating a limited degradation. Levels of contaminants (mainly AMPA) in streamwater (ND-0.5 ng/mL) denote the low persistence of these compounds. However, a direct relationship in AMPA concentration was observed between sediment and streamwater. Despite the known relatively short half-life of glyphosate in soils, GLY + AMPA occurrence is registered in almost all matrices at different sampling times (pre- and post-application events). The physicochemical characteristics (organic carbon, texture, pH) and structure of soils and sediment in addition to

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the time elapsed from application determined the behavior of these contaminants in the environment. As a whole, the results warn us about vertical transport trough soil profile with the possibility of reaching groundwater.

1. Introduction

Glyphosate (N-[phosphonomethyl] glycine) is a broad spectrum systemic herbicide. It was introduced in the market in 1974 as an active ingredient by Monsanto Co, in the Roundup product. Glyphosate base salts are very soluble in water, although it is strongly retained in soil matrix. Particularly, the glyphosate-phosphonic moiety would be responsible of its adsorption on oxides and specially on the poor crystalized fractions (Sheals et al., 2002). In this way, Ulén et al. (2012) reported a correlation between glyphosate and phosphorus (both bounded to particles) in drainage water from clay soils in a leaching experiment. Otherwise, organic matter is also an important soil property that influences the degree of glyphosate adsorption (Albers et al., 2009). Besides, soil pH plays an important role in adsorption, considering that it governs the electrostatic interaction between adsorbents and glyphosate (Pessagno et al., 2008). Once in the topsoil, glyphosate horizontal mobility is related to runoff process and sediment transport. Moreover, if rainfall occurs shortly after the herbicide application on bare soil, there is a strong risk for pesticide offsite movement (Yang et al., 2015). In addition, even soils with high glyphosate adsorbing capacity might be subjected to severe loss of herbicide with unfavorable soil structure (Todorovic et al., 2014).

On the other hand, glyphosate vertical mobility is related mainly to preferential flow and particle-facilitated transport in well-structured soil (Kjær et al., 2011). Although glyphosate is directly applied on surface soil, leaching column experiments indicated that up to 50% of the particles in the leachate came from the top 0.5 cm of the soil, and particles would be generated both inside the column and as a result of the splash process during intensive rain (Styczen et al., 2011). Furthermore, studies in a wide geographic region scale in the United States, concluded that both, the glyphosate and its main metabolite (aminomethyl)phosphonic acid (AMPA) are mobile and occurred widely in the environment, being detected in rivers, rain water and groundwater (Battaglin et al., 2014). The glyphosate-based herbicide consumption increased widely in Argentine with introduction of genetic modified organism in 1995, and 197 million kg of glyphosate-based products was applied in 2012. Argentina is the top exporter of soybean oil and soybean meals in the world's export market, and the third-largest exporter of soybeans. Despite the growing importance of soybean production in Argentine and the widely use of glyphosate, few studies have been reported at local and regional levels about glyphosate and AMPA behavior in agricultural watersheds. Particularly, Aparicio et al. (2013), found pesticide levels in surface soil from Buenos Aires province, one of the most important soybean production areas, which ranged between 0.035–1.502 μg/g and 0.299–2.256 μg/g for glyphosate and AMPA, respectively. The relationship of a glyphosate-based commercial product and phosphorus fertilizer application in a runoff experiment was recently evaluated in Aquic Argiudoll soil (Sasal et al., 2015). However, there is no evidence of field studies about glyphosate behavior through soil profile and its potential transport to groundwater. In the agricultural production, based on no-till system, genetic modified organism and intensive use of agrochemicals have been object of demonstration and struggle in rural villages in Argentine (Arancibia, 2013). Moreover, information about risk for human health considering glyphosate as a carcinogenic compound was reported (De Roos et al., 2005; Paganelli et al., 2010). The recent classification of glyphosate toxicology as *probably carcinogenic to human* (Group 2A) by the International Agency for Research on Cancer (IARC, 2015) evidence the need of performing studies about glyphosate behavior mainly focused on the protection of human health. The knowledge about the chance of glyphosate to reach groundwater is essential and urgent in order to generate prevention policies. The levels of glyphosate and AMPA found in the region encourage us to study the occurrence and fate of these contaminants in aquatic and terrestrial environments. Several studies have revealed that glyphosate-based formulations affect the aquatic communities modifying the structure and quality of freshwater ecosystems (Sandrini et al., 2013; Vera et al., 2010). Therefore, the knowledge about persistence, degradation and transport of glyphosate and AMPA in soil profiles is necessary to evaluate the behavior of these compounds in order to find possible strategies of prevention or mitigation of watershed contamination. The aim of this work was to determine glyphosate and AMPA levels in different matrices (streamwater, sediment and soil) with spatial and temporal samplings considering pre- and post-application periods. Also, raining events were considered in order to evaluate the behavior of these contaminants in a typical soybean agricultural watershed.

2. Materials and methods

2.1. Study area

Pampean region of Argentina, is responsible of 80% of soybean production with intensive use of agrochemicals, being glyphosate the most applied herbicide. The Quequén Grande River (QGR) basin has a total area of 9.990 km^2, which is drained by several streams with a north–south orientation and is located in the south of de Pampa region of Buenos Aires Province. The QGR drains in the Atlantic Ocean and is the most important stream of the basin with an approximately mean flow rate of 12 m^3/s rising to 758 m^3/s during flooding episodes, as was observed in 1985. The mean annual temperature is 14 °C with a minimum of 7.3 °C and a maximum of 21 °C. The climate is subhumid with mean rainfall of 891 mm for the 1960–2009 period and with heavy rains during summer months. The occurrence of natural vegetation between farms and stream is scarce, permitting the contaminants to reach the aquatic environment.

2.2. Sampling area

The matrices were sampled at two different moments considering the pesticide (glyphosate-based herbicide) application events (November–December). Therefore the pre- and post-application periods were June (2012) and January (2013), respectively. The samples were collected at three distinct areas. The first one was a buffer zone (natural area) adjacent to a river gully which was separated from the fields by a truck and a row of trees (soil control area — CA_S: 38°14′35.0″S, 59°06′44.5″W, sediment and water control area — CA_W: 38°11′53.93″S, 59°7′0.12″W). Also, soil samples from CA were located on a gentle hill and have never been directly sprayed. The agricultural sampling stations were settled at Site 1 (S1: 38°14′38.5″S, 59°06′52.5″W) 150 m far from the river shore and Site 2 (S2: 38°14′51″S, 59°05′52.2″W) adjacent to the river (Fig. 1). Both plots located 250 m (S1) and 2500 m (S2) far from CAS, were used for extensive agriculture (system barley–soybean) since the year 2010. The applied rate of glyphosate was considered according to INTA (National Institute of Agriculture Technology) recommendation and on the basis of information provided by the plots owner. The formulated product applied on bared soil was Roundup Full II (at 1.1 kg/ha active ingredient) using a bloom sprayer. Moreover agricultural areas were in fallow period and during the first sampling date scarce litter in surface soil (0–5 cm) was found. Topographic differences laid between both