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Environmental fate of glyphosate and aminomethylphosphonic acid in surface waters and soil of agricultural basins

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HIGHLIGHTS

- We measured glyphosate and AMPA concentrations in soil, surface water and sediment.
- Glyphosate and AMPA are present in soils under agricultural activity.
- Glyphosate is more frequent in particulate matter and sediment than in water.
- The surface run-off cause the movement of soil particles with glyphosate adsorbed.
- Glyphosate is accumulated in the bottom sediment and is biodegraded to AMPA.

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ABSTRACT

Argentinian agricultural production is fundamentally based on a technological package that combines no-till and glyphosate in the cultivation of transgenic crops. Transgenic crops (soybean, maize and cotton) occupy 23 million hectares. This means that glyphosate is the most employed herbicide in the country, where 180–200 million liters are applied every year.

The aim of this work is to study the environmental fate of glyphosate and its major degradation product, aminomethylphosphonic acid (AMPA), in surface water and soil of agricultural basins. Sixteen agricultural sites and forty-four streams in the agricultural basins were sampled three times during 2012. The samples were analyzed by UPLC-MS/MS ESI(+/−).

In cultivated soils, glyphosate was detected in concentrations between 35 and 1502 $\mu g\ kg^{-1}$, while AMPA concentration ranged from 299 to 2256 $\mu g\ kg^{-1}$. In the surface water studied, the presence of glyphosate and AMPA was detected in about 15% and 12% of the samples analyzed, respectively. In suspended particulate matter, glyphosate was found in 67% while AMPA was present in 20% of the samples. In streams sediment glyphosate and AMPA were also detected in 66% and 88.5% of the samples respectively.

This study is, to our knowledge, the first dealing with glyphosate fate in agricultural soils in Argentina. In the present study, it was demonstrated that glyphosate and AMPA are present in soils under agricultural activity. It was also found that in stream samples the presence of glyphosate and AMPA is relatively more frequent in suspended particulate matter and sediment than in water.

1. Introduction

Argentina is tenth in the world of agricultural nations ranked according to the area under cultivation in a report published by the World Bank, based on figures produced by the Food and Agricultural Organization of the United Nations (FAO). With 31 million hectares given over to agriculture, Argentina ranks behind the United States, India, Russia, China, Brazil and Australia and accounts for 2.2% of the world's total area under cultivation (Stock Exchange of Rosario, Argentina).

Transgenic crops (soybean, maize and cotton) account for three-quarters of the Argentina's total cultivated land. In addition, 78.5% of agricultural lands in Argentina is no-till (NT) (Aapresid, 2012), where the only way of controlling weeds, during cultivation and during fallow periods, is by using chemicals. This means that glyphosate is the most commonly used herbicide in the country, both in its frequency of use as in the intensity. It is applied extensively;

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around 180–200 million liters of this herbicide are used every year (SAyDS, 2008).

Glysophate (N-[phosphonomethyl] glycine) is a broad-spectrum herbicide, used non-selectively in agriculture to control weeds and herbaceous plants. It works by inhibiting the enzyme 3-enol-pyruvylshikimate-5-phosphate synthase (EPSP Synthase), located in the chloroplast, interfering in the biosynthesis of aromatic amino acids used in the synthesis of proteins (Roberts et al., 1998). The EPSP Synthase is an enzyme that forms part of metabolic pathway of the shikimic acid. This is a process that only occurs in plants, bacteria and fungi and does not exist in animals; due to this fact the acute toxicity in animals is low. Nevertheless, some studies have reported adverse effects on aquatic and terrestrial species (Contardo-Jara et al., 2009; Paganelli et al., 2010) and concern has risen on potential environmental impacts due to the widespread use and large amounts annually applied (Schuette, 1998).

The microbial degradation is considered the most important transformation process to determine the persistence of herbicides in the soil (Souza et al., 1999). This process is carried out both in aerobic and anaerobic conditions by the microflora found in the soil. The primary metabolites are glyoxylate and aminomethylphosphonic acid (AMPA) which eventually degrades to water, carbon dioxide, ammonia and phosphate (Dick and Quinn, 1995). The presence of glyphosate could cause changes in the microbial populations and their activities in the soil. In relation to this, there are different results in the literature suggesting effects that can be minimum or transient with regard to the microbial biomass and its activity (Stratton and Stewart, 1992; Busse et al., 2001; Haney et al., 2002; Gómez et al., 2009) or are constant in time according to the history of application (Araújo et al., 2003).

It is known that glyphosate is adsorbed by mineral clays and by organic matter and is released from these sites by the competence with inorganic phosphates (Schuette, 1998; Prata et al., 2003). With regard to this last aspect, due to the fact that soybean requires high levels of this nutrient, the expansion and intensification of agriculture has highlighted the impoverishment of phosphorous within the Pampa region (Echeverría and García, 1998). On the other hand, published information about the mechanisms of the movement and environmental fate of glyphosate and AMPA in the environment is scarce, with much of it coming from controlled laboratory studies (Mamy et al., 2005; Borggaard and Gimsing, 2008; Tsui and Chu, 2008). Recently, studies about the transport of glyphosate and AMPA in streams located in United States show that glyphosate and AMPA have been frequently detected in surface waters of agricultural basins where it is used and their concentrations are influenced by source, hydrology and water movement pathways (Coupe et al., 2012).

Retention, degradation, and presence of glyphosate in water have scarcely been reported in the literature. The environmental fate of glyphosate and its metabolite degradation has not been studied taking into account the different environmental matrices (sediment, water and particulate matter dissolved in water) of agricultural basins. The environmental fraction of glyphosate transported is very important to develop agronomic management strategies to minimize their impact. Moreover, the analysis of contamination levels and the identification of the compartments where this herbicide accumulates can help to guide ecotoxicological studies.

In view of current production methods, the intensification of farming should not lead us to the accumulation of molecules such as glyphosate and AMPA in the environment. The aim of this study was to examine the environmental fate of glyphosate and AMPA and quantify their concentration in each one of the environmental compartments: soil and surface water (differentiating between water, suspended particulate matter and sediment) of agricultural basins.

2. Materials and methods

2.1. Selection of test sites

Sixteen farms were selected for soil sampling in the southeast of the Province of Buenos Aires (Fig. 1). At each site or farmer, an agricultural plot in which had been used glyphosate was selected. Another plot with the same soil type where there was no history of use of glyphosate in the past 10 years was also selected as control. Plots had a surface area of 60–150 hectares and were located at the same position of the relief. In each case, information about crop rotation over the past two years was recorded as well as the history of glyphosate use over the same period (i.e., time from the first glyphosate application, crop rotation, last spraying dosage) (Table 1).

In order to study glyphosate and AMPA residues in surface water (differentiating water and suspended particulate material) and in sediment, forty-four streams in the southeast of the Province of Buenos Aires were chosen that corresponded to the same catchment area where the soil samples were taken (Fig. 2).

2.2. Testing and conditioning of samples

Soil testing was carried out using two different soil sampling probes, one in the areas that had not been treated with glyphosate and another in the area that had been treated. The soil sample consisted of 50 subsamples to have representation of the plot. The sampling was performed 0–5 cm deep. The probe was cleaned by discarding several extractions in order to avoid any contamination between samples. The samples were conditioned using a hot-air heater set at 30 °C, and then dry milled. Two mills were used, one for treated samples and another for untreated samples. The mills were cleaned between samples. The samples were then passed through a 2 mm sieve.

The water samples were collected in 1 L polypropylene bottles on three dates following the soil samplings (April, August and September 2012) and stored at −20 °C until analysis. Prior to analysis, they were thawed overnight to 4 °C. The samples were filtered through a 0.45 μm nylon membrane to separate the water from the suspended particulate matter, which was filtered out. The sediment samples were collected in a PVC tube using a sediment sampler at the same place that the water samples were collected. Approximately 10 cm of sediment were extracted, which the first 5 cm were separated with a clean knife, air-dried at 30 °C, dry milled and then sieved through 2 mm.

In the EEA INTA laboratory at Balcarce, soil texture of all the samples was determined (Gee and Bauder, 1986), as well as cation-exchange capacity (Chapman, 1965), pH and total organic carbon (Nelson and Sommers, 1982) (Table 2).

2.3. Extraction and qualification of glyphosate and AMPA

A representative sub-sample of water (2 ml), particulates material (0.4 g), sediment (2 g) and soil (5 g) were overload with 10, 15 and 25 μl of isotope-labeled glyphosate (1,2-^{13}C, ^{15}N) stock solution (10 mg L^{-1}) respectively, taking care that its distribution on the particulates, sediment and soil was uniform, followed by a rest of 30 min, in order to stabilize the system. After that, particulates material, sediment and soil were extracting with 1, 3, 5 and 25 ml of extract solution of potassium dihydrogen phosphate in accordance with the method proposed by Peruzzo et al. (2008). Briefly, samples were sonicated (exposed to sonic waves) and then centrifuged to separate the suspended material. Supernatants were adjusted to pH = 9 with 40 mM borate buffer and then derivatized with 9-fluorenylmethylchloroformate (FMOC-CL) in acetonitrile. It was left to rest overnight in darkness at room temperature. At the

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