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

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Introduction

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

The aim of this work is to study the environmental fate of glysophate and its major degradation product, aminomethylphosphonic acid (AMPA), in surface water and soil of agricultural basins.

Materials and Methods

Sixteen farms were selected for soil sampling in the southeast of the Province of Buenos Aires (Figure 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 to 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 (Figure 2).

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 water samples were collected in 1 L polypropylene bottles on three dates following the soil samplings (April, August and September 2012) and stored at -20ºC until analysis.

The samples and standards were injected into the Waters Acquity UPLC MS/MS system (Waters) equipment calibrated for positive detection, using a column Acquity UPLC BEH C18 column (1.7 μm, 50 x 2.1 mm) (Waters).

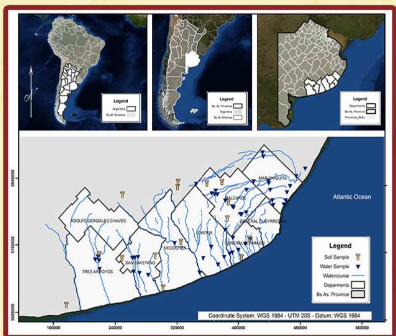

Fig 1. Geographic location of the study area. It is indicates the location of soil sampling after sowing in each farm and sample water, particulate matter and sediments at three moments after soil sampling.

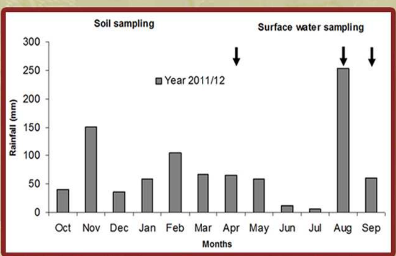

Fig 2. Monthly rainfall expressed in mm. The soil sampling was conducted between November and January, according to availability of soybean farms. The black arrows indicate months of the water, particulate matter and sediment sampling.

Results and Discussion

In cultivated soils, glyphosate was detected in concentrations between 35 to 1502 μg Kg-1, while AMPA concentration ranged from 299 to 2256 μg Kg^{-1} (Table 2) 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.

Table 1. Agricultural management practices information of the farms plots.

Farms	TFA (yr)	Crop rotation	Last spraying dosage
		(*)	g ha^{-1} of formula
1	8	P/Su/W/S	2.2
2	10	C/Su/S	2.2
3	10	R(S)/S/W(S)/R(S)	1.4
4	15	C/Su/M	0.5
5	15	Su/W/Su/R(S)	0.5
6	13	W/So/Su	1.4
7	6	S/W/S	3.7
8	19	S/W(So)/S	3.3
9	6	W/S/R-O/S	1.0
10	6	S/R(S)	0.7
11	10	S	1.4
12	5	S	1.4
13	10	S/W(S)/S	1.9
14	10	Su/W/S	2.1
15	4	W(S)/C/S	3.3
16	10	W/S/W/S/W(S)	2.4

A **TFA**: Time from the first glyphosate application.
(*) **C**: Corn;
P: Potato;
Su: Sunflower;
W: Wheat;
S: Soybean;
R: Rye;
O: Oats;
So: Sorghum

Table 2. Glyphosate and AMPA concentrations in soil studied (μg kg-1) and time from the last application.

Farms	Treatment	TLA (d)	Concentration (μg kg^{-1})	
			Glyphosate	AMPA
			ug kg^{-1} soil	
1	Glyphosate	188	190.5	732.8
	Control		<LD	<LD
2	Glyphosate	94	140.9	1052.1
	Control		<LD	<LQ
3	Glyphosate	11	489.6	796.2
	Control		<LQ	20
4	Glyphosate	1	1502.3	299.3
	Control		41.4	22.3
5	Glyphosate	48	429.8	539.8
	Control		<LQ	43.2
6	Glyphosate	73	186.8	895.2
	Control		<LD	18.1
7	Glyphosate	10	257.1	921.3
	Control		<LD	<LD
8	Glyphosate	40	886.5	958.6
	Control		<LD	<LQ
9	Glyphosate	40	34.7	491.2
	Control		<LD	<LQ
10	Glyphosate	4	386.7	789.7
	Control		<LD	<LD
11	Glyphosate	10	79	581.7
	Control		<LD	36.9
12	Glyphosate	8	316.3	458
	Control		<LD	<LQ
13	Glyphosate	8	206.7	518.9
	Control		<LQ	33.5
14	Glyphosate	14	37	727.5
	Control		<LD	<LD

TLA: Time from the last application.
LD: Limit of Detection

Conclusion

Glyphosate and its principal metabolite AMPA are present in the soil of the agricultural basin studied in a concentrations range from 35 to 1502 and 299 to 2256 μg kg^{-1}, respectively

The surface run-off can cause the movement of soil particles which carry glyphosate adsorbed and end up in surface water courses where the glyphosate can also be desorbed, biodegraded and accumulate in the bottom sediment. This information is non-existent so far and is an important contribution to the knowledge of the environmental distribution of these molecules.