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Short communication

Contribution of soluble and particulate-matter fractions to the total glyphosate and AMPA load in water bodies associated with horticulture

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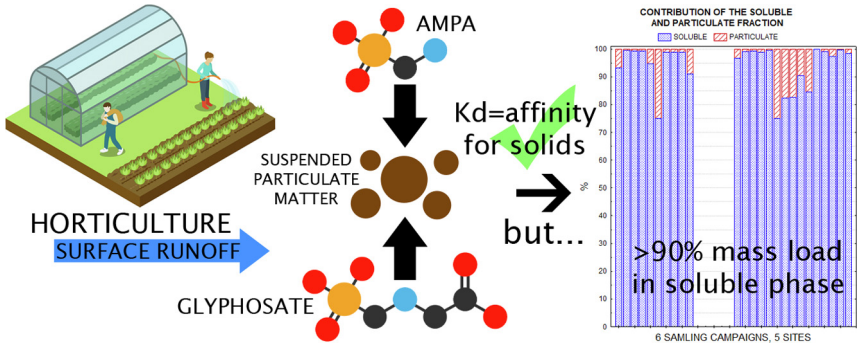
HIGHLIGHTS

- Glyphosate and AMPA were detected as a consequence of their use in horticulture.
- Glyphosate and AMPA were detected in both soluble and particulate fractions.
- The environmental Kd confirmed the compounds' affinity for the particulate fraction.
- The soluble phase contributed more herbicide mass in the water column.

GRAPHICAL ABSTRACT



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ABSTRACT

Glyphosate-based herbicides are used in horticulture to prepare the soil for planting and to remove weeds surrounding greenhouses. Superficial runoff from production units can lead to glyphosate reaching nearby water bodies. Previous publications reported glyphosate's high affinity for suspended solids. The aim of the present work was to investigate the occurrence and concentrations of glyphosate and aminomethylphosphonic acid (AMPA) in soluble and suspended-particulate-matter fractions within the basin of the Carnaval-Stream, a water body traversing a horticultural greenbelt. Glyphosate and AMPA were detected in 67% and 83% of the samples, occurring in both fractions simultaneously at respective maximum concentrations of 17.0 and 4.5 $\mu g.L^{1}$ in the soluble fraction and 35,620 and 19,586 $\mu g.kg^{1}$ in the particulates. Although the calculated partition coefficients Kd confirmed that these compounds had tended to be associated with the particulate matter, the soluble glyphosate and AMPA contributed, on the average, to more than 90% of the total water volume. Although the analysis of suspended particulates is considered a more sensitive strategy for glyphosate and AMPA detection in surface water, these results demonstrate the need to analyze the soluble phase. The continual occurrence throughout a 3-year sampling was sufficient evidence demonstrating the use of glyphosate in horticulture.

1. Introduction

Herbicides are used to kill weeds around greenhouses and for generating chemical fallow before planting in horticulture (Allinson et al., 2014; DP, 2015; Kreuger et al., 2010; Neal, 2015). As a consequence of herbicide use, glyphosate (GLY)—the most widely used herbicide worldwide—and its metabolite upon environmental degradation, aminomethylphosphonic acid (AMPA), have been detected extensively in bottom sediments of watercourses in the region of La Plata (Mac Loughlin et al., 2017). This city is the capital of the Buenos-Aires province (Argentina) and

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contains one of the most relevant horticultural greenbelts in the country; occupying more than 5000 ha, of which area 3000 ha are under cover (*i. e.*, in greenhouses). Within that belt, highly diversified and intensive production systems predominate that are dependent on pesticides (CHP-PBA, 2005; DP, 2015).

Although the presence of GLY and AMPA in water bodies has been studied in other countries (Battaglin et al., 2014; Scribner et al., 2007); despite the wide use of GLY in Argentina, only few studies have been conducted on contamination by that herbicide in water bodies in this country (Aparicio et al., 2013; Bonansea et al., 2017; Primost et al., 2017; Ronco et al., 2016); with those investigations focusing mainly on areas influenced by the extensive agriculture of grains and oilseeds (*i.e.*, maize, wheat, and soybean). In a horticultural system involving a more controlled environment, the number and frequency of application of the active compounds is significatively higher than in extensive field production, mainly because the number of pests that affect monocultures is significantly fewer and since only one or two plantings are done throughout the year, *versus* year-round planting of different vegetables in horticulture (DP, 2015). Those same studies reported that GLY and AMPA were more frequently found associated with the suspended particulate matter (SPM) than in the soluble phase, despite the high solubility of those herbicides (GLY at 10,500 and AMPA at 1,466,561 mg.L^{-1} at 20 °C). As a result of these findings, Ronco et al. (2016) and Primost et al. (2017) recommended analysis of the SPM as a more sensitive strategy for the detection and management of GLY and AMPA in surface waters.

In view of the widespread use of GLY in horticulture, and the detection of that compound along with its environmental metabolite in other watercourses in Argentina, we decided to study the occurrence and concentrations of the two agents in a watercourse that flowed through a purely horticultural region, which water is thus affected exclusively by that productive activity in the form of both field cultivation and greenhouses. In addition, since GLY and AMPA were reported to be mostly found in the particulate fraction of water bodies, we studied the partitioning in both the soluble fraction and the particulates.

2. Materials and methods

Acetonitrile and methanol (HPLC-grade) were obtained from J. T. Baker (USA) and pesticide-residual-grade dichloromethane from U.V.E. (Buenos Aires, Argentina). A Sartorius Arium® purification system (Göttingen, The Netherlands) produced nanopure water for use in the laboratory. Analytical grade sodium tetraborate, potassium phosphate dibasic, and ammonium acetate were purchased from Merck Millipore (Darmstadt, Germany) and standards of GLY (99%) and AMPA (98.5%), isotopically labelled glyphosate-2-^{13}C, ^{15}N (GLY-2-^{13}C, ^{15}N), and 9-fluorenylmethyloxycarbonyl chloride (FMOC-Cl) from Sigma Aldrich (St. Louis, MO, USA).

Samples were obtained during 6 biannual campaigns comprising the seasons winter 2015 (**C1**), summer 2016 (**C2**), winter 2016 (**C3**), summer 2017 (**C4**), winter 2017 (**C5**), summer 2018 (**C6**) and involving the 5 sites along the upper and middle Carnaval-Stream basin—**S1** through **S5**—with that stream being a representative watercourse impacted by horticulture on the outskirts of La Plata, Buenos Aires, Argentina (Fig. 1). The average annual temperature is 16 °C, with January as the warmest month (29 °C) and July as the coldest (5 °C). Precipitation is greater during the summer, reaching the maximum in March (124.5 mm), and lower during the winter, with June presenting the lowest rainfall (52.4 mm).

The sampling was conducted in the different seasons indicated above upon consideration of the various vegetables being produced year-round and the consequent pesticide applications

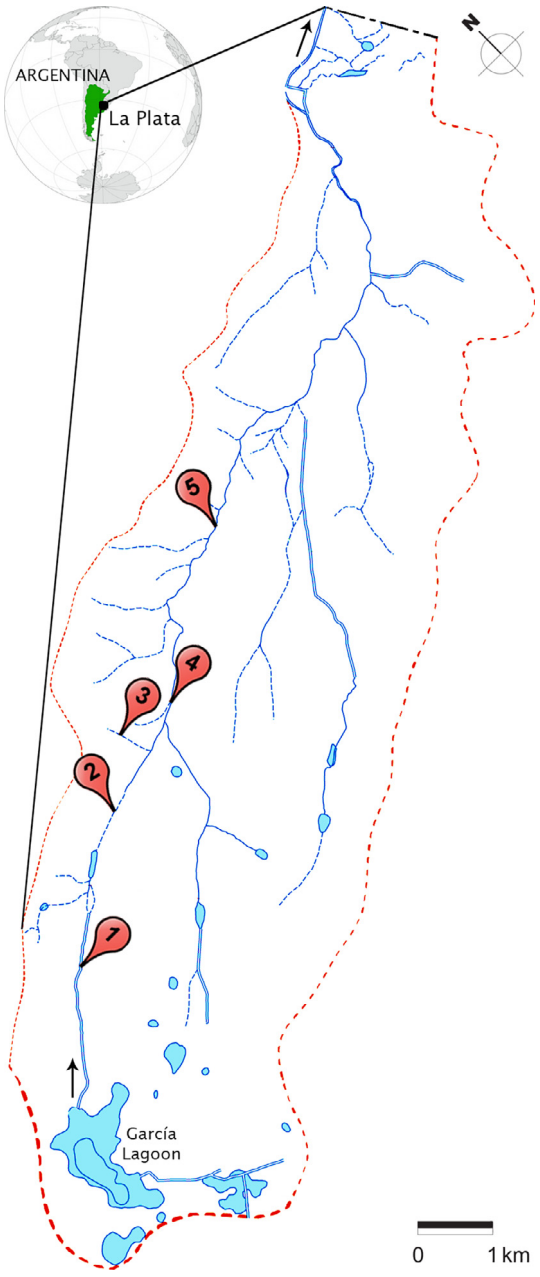

Fig. 1. The numbered pins indicate the locations of the sampling stations along the main course and tributaries of the Carnaval Stream within the outskirts of La Plata (Argentina). The coordinates of the sampling sites are as follows: (S1) 34°57′7.79″S, 58° 7′56.18″W; (S2) 34°55′51.58″S, 58° 6′47.13″W; (S3) 34°55′44.93″S, 58° 6′44.94″W; (S4) 34°55′1.63″S, 58° 6′30.33″W; (S5) 34°54′4.79″S, 58° 5′49.86″W. The inset to the upper left denotes the location of the study area within Argentina.

throughout the study period, both in terms of the different active ingredients used and the fumigation frequency (CHP-PBA, 2005; DP, 2015). The basin has its origin in the peripheral horticultural belt of the city. The main channel is 14.5 km in length. In the upper and middle sections (approximately 8 km), the main land-use activities are horticulture and, to a lesser extent, floriculture. In the lower basin some industries and residential areas are present, before the watercourse reaches the Río-de-La-Plata estuary.

The dissolved-oxygen concentration (DO), temperature (T °C), conductivity (ʊ), and pH in the stream water were measured *in situ* with a multiparameter instrument (Lutron WA-2017SD). To separate the soluble and particulate fractions, 100 mL of surface water were filtered *in situ* through a preweighed 0.45-μm pore size

nylon filter (diameter, 47 mm) placed in a Sartorius 250-ml polycarbonate holder attached to a Silfab N8VP portable vacuum pump. Of the filtered water, 10 mL were transferred to a propylene plastic tube and spiked with 10 ng of GLY-2-^{13}C, ^{15}N. Samples were taken in triplicate at each sampling site. In the laboratory, the nylon filters were placed in a desiccator for 24 h for drying, weighed to determine the SPM weight (±0.0001 g) then stored at − 20 °C until analysis.

For GLY and AMPA analysis, 2 mL of filtered water were adjusted to pH 9 with sodium borate and derivatized with FMOC-Cl (1 mg.mL^{-1} in acetonitrile) before column chromatography (Ronco et al., 2016). For SPM analysis, the nylon filter was first spiked with 30 ng de GLY-2-^{13}C, ^{15}N and extracted by sonication into 3 mL of 100 mM phosphate dibasic buffer followed by FMOC-Cl derivatization (Ronco et al., 2016). The isotopically labelled GLY was used as an internal standard throughout the analysis procedure to evaluate the extract-holding time and recovery. Reagent blanks, duplicates samples, and matrix-matched calibration curves were included in each analytical batch for quality control and assurance.

A Waters Acquity ultrapressure liquid chromatograph coupled to a Quattro Premier XE Tandem Quadrupole mass spectrometer was used for instrumental analysis. The chromatographic conditions and operational parameters were those described in Aparicio et al. (2013) and Primost et al. (2017). The quantification was carried out by means of an external calibration curve (Aparicio et al., 2013; Primost et al., 2017). The analytical criteria recommended by SANTE (2015) were applied for the identification and confirmation of the analytes.

In summary, surface-water samples (both the soluble and the particulate phases) were obtained biannually from 5 sites along the Carnaval basin during a 3-year period: a total of 30 water and 30 SPM samples were analyzed for the presence of GLY and AMPA, each in triplicate. The recovery for both matrices was above 90%. In the water, the limit of detection (LOD) and quantification (LOQ) were 0.03 and 0.10 μg.L^{-1} for GLY and 0.04 and 0.14 μg.L^{-1} for AMPA, respectively. The LOD and LOQ obtained for the SPM were 0.06 and 0.20 μg.kg^{-1} for GLY, and 0.08 and 0.30 μg.kg^{-1} for AMPA. Since the concentration data did not follow a normal distribution, nonparametric tests were used for its analysis.

3. Results and discussion

Table 1 lists the *in-situ* physicochemical parameters. Throughout the 6 campaigns, **S1** contained the maximum amount of SPM. The conductivity was always significantly higher during the summer campaigns because of a higher use of underground water for crop irrigation. The minimum and maximum pHs were between 6.24 and 8.16, which range is normal in the surface water of the pampas region (Ronco et al., 2016). The DO was lower in summer and higher during the winter, as the temperature inversely affected the oxygen solubility, following a characteristic seasonal behavior.

To the best of our knowledge, no other reports have appeared on the occurrence of GLY and AMPA in surface water as a result of horticultural practices. In Australia, Allinson et al. (2014) investigated the presence of 10 herbicides in a horticultural-production catchment, but did not determine GLY, although the use of that compound in the region was acknowledged in the article. In Sweden, Kreuger et al. (2010) excluded GLY from their investigation, as that specific herbicide was not used specifically in horticulture in that region and the quantification required a customized analytical method, even though GLY was the most widely sold compound. In Argentina (Aparicio et al., 2013; Lupi et al., 2015; Primost et al., 2017; Ronco et al., 2016) and the United States (Battaglin et al., 2014; Scribner et al., 2007), the areas studied were mainly subjected to extensive agriculture with GLY-resistant crops. Therefore, the comparisons made in the present work were between different production systems: horticulture *versus* extensive agriculture.

3.1. Detection frequency

GLY was detected in 67% of the water and SPM samples (in all samples except for those in **C1** and **C3**); and AMPA in 83% of the water and SPM samples (in all samples except for those in **C3**). The sampling for **C3** was deliberately conducted after heavy rains (132 mm during the previous week) with the objective of determining if, after such heavy precipitation, a mobilization or dilution of the compounds occurred. As neither GLY nor AMPA were detected, the likelihood was that dilution was the main effect under such weather conditions (Aparicio et al., 2013).

Differences in the detection frequencies of herbicides between water and particulate fractions have been reported in various watercourses. In the United States, Battaglin et al. (2014) detected GLY in 52.5% and AMPA in 71.6% of the water samples, while Scribner et al. (2007) found GLY in 38.7% and AMPA in 57.7% of the streams investigated. In Argentina, Primost et al. (2017), studying streams through soybean plantations, detected GLY and AMPA in 100% of the SPM samples, but GLY in 27% and AMPA in 55% of the water samples at those same sites. In diverse agroproductive systems, Aparicio et al. (2013) found GLY and AMPA in about 15% and 12% of the water samples and in 67% and 20% of the SPM samples, respectively. In the main tributaries of the Paraná Basin, Ronco et al. (2016) detected GLY in 15% and 20% of the respective water and SPM samples, but AMPA was not present in the water samples and was detected in only 4% of the SPM samples. In all of those examples, the presence of GLY and AMPA was more frequently associated with the particulate matter. In the present work, in all the instances where one of those compounds was detected, that herbicide was present in both matrices examined.

In the United States, GLY was found in the absence of AMPA in only 2.3% of the samples analyzed, while the AMPA without detectable GLY was found in 17.9% of the samples (Battaglin et al., 2014). In contrast, when the two compounds were detected simultaneously, both GLY and AMPA occurred in 100% of the samples. As AMPA is an environmental degradation product, that metabolite

Table 1
Physicochemical parameters measured at the study sites*.

	C1	C2	C3	C4	C5	C6
Parameter**	WINTER 2015	SUMMER 2016	WINTER 2016	SUMMER 2017	WINTER 2017	SUMMER 2018
DO (mg.L^{-1})	7.4 ± 1.6	6.5 ± 1.4	7.3 ± 1.8	4.0 ± 2.3	5.2 ± 0.5	2.2 ± 1.5
T (°C)	14.3 ± 2.5	27.5 ± 2.0	11.8 ± 1.2	23.3 ± 2.4	19.3 ± 1.1	24.3 ± 1.3
υ (μS.cm^{-1})	343 ± 32	375 ± 274	138 ± 21	783 ± 86	412 ± 181	892 ± 70
pH	7.47 ± 0.36	6.56 ± 0.29	7.04 ± 0.25	7.74 ± 0.28	7.52 ± 0.31	7.41 ± 0.20
SPM (mg.L^{-1})	92.4 ± 87.3	87.8 ± 104.8	43.8 ± 8.8	51.1 ± 77.3	87.3 ± 76.9	88.0 ± 115.3

* The values are the mean ± the standard deviation for each sampling campaign.
** DO, dissolved-oxygen concentration; υ, conductivity, SPN, soluble particulate material.

usually cooccurs with its parent compound (Aparicio et al., 2013). The present findings on the occurrence of both GLY and AMPA provide new evidence on the use of this particular herbicide within the greenbelt production zones around cities (Bonansea et al., 2017) since GLY is now not being used exclusively on GLY-resistant crops, but rather the use of that active ingredient has expanded to areas where nonresistant vegetables are grown. This nonselective presence of that herbicide in both agroproduction systems makes GLY a potential marker compound for indication of contamination in water bodies as a result of any type of concurrent cultivational activity.

3.2. Concentrations

The median (minimum–maximum) concentrations of GLY and AMPA, respectively, were 3.1 (0.2–17.0) and 1.4 (0.2–4.5) $\mu g.L^{-1}$ in the soluble fractions of the water samples and at a total particulate weight of 3735 (245–35,620) and 662 (43–19,586) $\mu g.kg^{-1}$ or 0.2 (0.0001–5) and 0.02 (0.0006–1) $\mu g.L^{-1}$ in the SPM samples within the water column (Fig. 2, panels A and 2B, respectively).

In USA streams, Battaglin et al. (2014) found a median GLY concentration of 0.03 $\mu g.L^{-1}$, which value is 100 times lower than that of the present work (3.1 $\mu g.L^{-1}$). The median concentration of AMPA (0.20 $\mu g.L^{-1}$), there, moreover, was the same as the minimum in this work. The maximum levels of the metabolite, however, were higher in the USA, though in the same order of magnitude. As to the data for GLY in the water, the minimum of the present study was in the same order of magnitude as the average values in previous publications from Argentina (Primost et al., 2017; Ronco et al., 2016). The maximum concentration (17 $\mu g.L^{-1}$) was higher than all those previously reported, with the sole exception of a single sample near intensive crops where 125.0 $\mu g.L^{-1}$ were found (Bonansea et al., 2017). The AMPA concentrations reported in the other publications were within the minimum–maximum range of the present study. According to our findings, the use of GLY in horticulture caused higher concentrations in the Carnaval Stream than in water bodies impacted by extensive crops.

In the SPM fraction, the median GLY concentrations at the different sampling sites doubled the value reported by Ronco et al. (2016) for the Paraná River tributaries and doubled the maximum for the Suquía River in the Córdoba province (Bonansea et al., 2017). In fact, that figure quadrupled the concentrations for first- and second-order waterways draining soybean fields in Urdinarrain, Entre-Ríos province, Argentina (Primost et al., 2017) and was an order of magnitude higher than the maximum value reported in the southeast of the Province of Buenos Aires (Aparicio et al., 2013). The maximum concentration found in the Suquía River (685 $\mu g.kg^{-1}$) was similar to the median of our study (662 $\mu g.kg^{-1}$), and the maximum in Buenos Aires (210 $\mu g.kg^{-1}$) was 3 times lower than the median.

The relationship between the total GLY and AMPA concentrations (*i. e.*, soluble + SPM) in each sample was investigated by a simple linear regression (Fig. 3). A statistically significant correlation was found between the herbicide and its metabolite ($r^2 = 0.6058$, $p = 0.00005$) demonstrating the relationship between the parental compound and its environmentally degraded metabolite (Primost et al., 2017).

3.2.1. Comparison between campaigns

In comparing the sampling campaigns (Fig. 4), we considered the different sampling sites as replicates within the system and on that basis found a statistically significant difference among the different seasonal campaigns (Kruskal-Wallis test, $p = 0.0007$). As mentioned above, when, after heavy rains, the **C3**

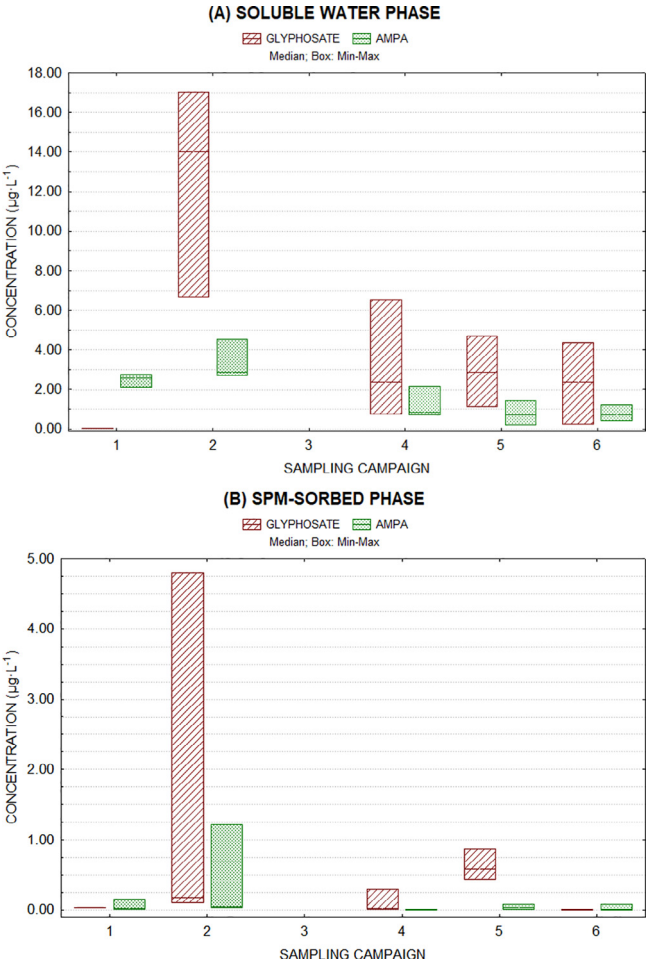

Fig. 2. The concentrations of glyphosate and AMPA (in $\mu g.L^{-1}$) are plotted on the y axis for each of the sampling campaigns indicted on the × axis. In the box plots, the horizontal line indicates the median and the upper and lower borders the maxima and minima. (Panel A) Concentrations in the filtered water. (Panel B) Concentrations in the SPM of the water column.

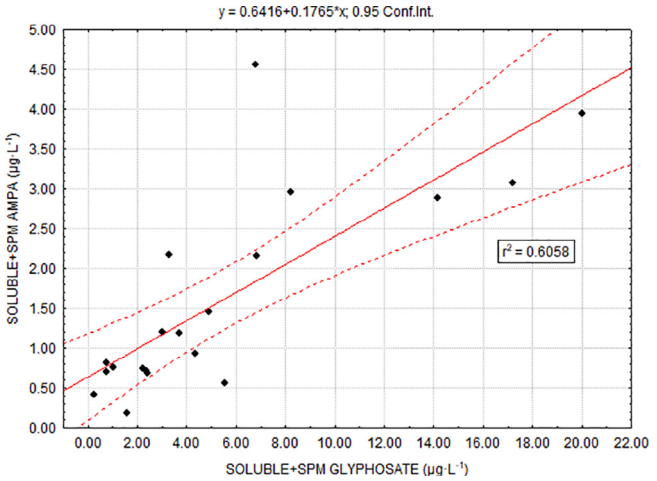

Fig. 3. Relationship between the total (soluble + SPM) concentration of glyphosate (x-axis) and the total AMPA concentration (y-axis) in each individual sample. The solid red line indicates the linear-regression function and the dotted red lines the associated confidence intervals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

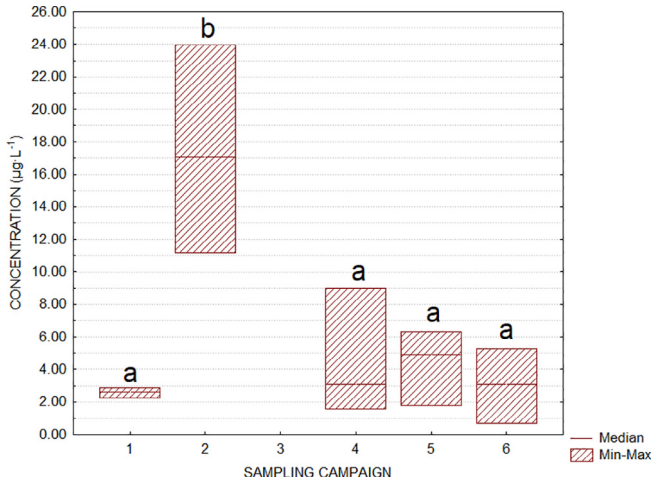

Fig. 4. The concentrations of the soluble + the SPM values for glyphosate + AMPA (in $\mu g.L^{-1}$) are plotted on the y axis for each sampling campaign indicated on the × axis. In the box plots, the horizontal line denotes the median and the upper and lower values the maxima and minima. The letter "b" at C2 indicates a significant difference from the values for the other sampling campaigns ($p = 0.0007$).

Site was monitored, no pesticides were detected (*i. e.*, with all the values falling below the LOD). In contrast, no differences were found among the campaigns **C1**, **C4**, **C5**, and **C6**—all those carried out in the summer and winter of different years. Campaign **C2** (January 2016), however, differed markedly from the rest, which exception might have resulted from a recent input of herbicides (Aparicio et al., 2013). We therefore concluded that the entry of GLY and AMPA into the environment was independent of the time of the year for horticultural production since that activity, in fact, occurred all year round.

3.3. Contribution to total load and partition coefficient Kd

Since we had determined the concentration of GLY and AMPA in both the soluble and the SPM fractions, as well as the corresponding weights per unit volume, we could calculate the extent to which each fraction contributed to the total herbicide load in the water column. Fig. 5 illustrates the results for each sample. The contribution of the soluble fraction was, for GLY and AMPA, far greater than the sorbed fraction: on the average, the soluble fraction represented 92.7% of the GLY contribution and 95.7% of the AMPA, at maxima of 99.9% and 99.9%, respectively.

With the same data, the partition coefficient (Kd)—the ratio of solid-phase–to–solute concentrations—was calculated for the two compounds in each individual sample. The Kd median (minimum–maximum) values (expressed in $L.kg^{-1}$) were 833 (81–7564) and 325 (25–3584) for GLY and AMPA, respectively. No statistically significant differences were observed between the Kd values for the two compounds (Wilcoxon's test, $p > 0,05$). Possible relationships between concentrations, Kd values, and the physicochemical parameters measured (DO, T, ʊ, pH, and SPM; *cf.* Table 1) were investigated by means of the Spearman correlation matrix, but no significant quotients were found.

In the south of the pampas region of the Buenos-Aires province, Lupi et al. (2015) reported a sediment-runoff–partition-coefficient value of 26 $L.kg^{-1}$. The difference between previously reported values and those reported here could be attributed to variations in the particle sizes of the two solid matrices. Amiot et al. (2014) found a Kd value from an experimentally produced water-erodible soil fraction (<250 µm) that was two times higher than 2-mm sieved

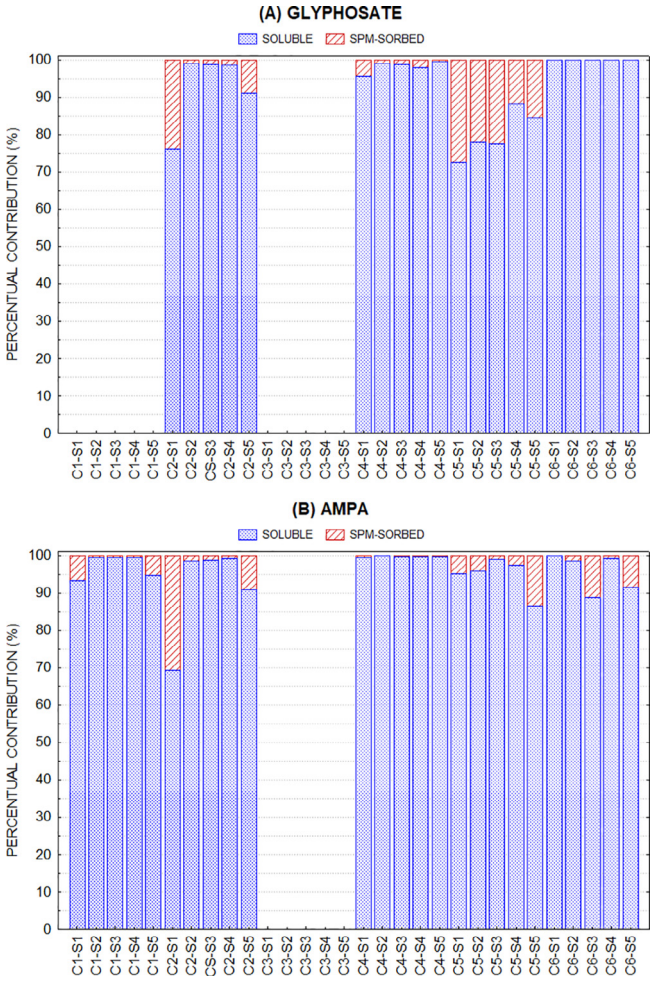

Fig. 5. Percent contribution (y-axis) of the soluble (blue bar color) and particulate (red bar color) fractions to the (Panel A) glyphosate and (Panel B) AMPA load in each individual sample among the different replicates (x-axis). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

soil. If the natural size heterogeneity and composition of particulate matter is considered, the high variability observed is to be expected.

Although the partition coefficient Kd indicated that GLY and AMPA had a tendency to be sorbed to the particulate material, the amount of particulate matter per unit of volume in the water column is at most 205 $mg.L^{-1}$ (**C6**, *cf.* Table 1). Therefore, the contribution of those two compounds calculated at, on the average, less than 10% of the total concentration. Regardless of the contribution to the water column, through sedimentation, the suspended particulate material becomes part of the benthos matrix, in which fraction accordingly the GLY and AMPA were frequently found in the Carnaval basin and at high concentrations (Mac Loughlin et al., 2017).

While the analysis of the SPM still remains the more sensitive method for quantitating the presence of GLY and AMPA since the filtration produces a concentration of that phase, the analysis in soluble fraction is routinely carried out on that matrix without any form of concentration. Even though Ronco et al. (2016) and Primost et al. (2017) recommended the analysis of SPM as being the more sensitive method of detection, the present results clearly indicate that the soluble fraction should not be omitted from the overall analysis, since that fraction contributes more than 90% of the total GLY and/or AMPA found in the water column.

4. Conclusions

In a water body passing through a horticultural region in the Carnaval basin, GLY and AMPA were frequently detected at concentrations in both the soluble and the particulate phases that were notably higher than in other similar areas of Argentina where extensive agriculture was practiced. Maximum concentrations in soluble and particulate phase were 17.0 $\mu g.L^{-1}$ and 35,620 $\mu g.kg^{-1}$ for GLY, and 4.5 $\mu g.L^{-1}$ and 19,586 $\mu g.kg^{-1}$ for AMPA, describing a non-distinguishable behavior between seasons. We report here the experimental Kd values from a natural environment: 81–7564 $L.kg^{-1}$ for GLY and 25–30,584 $L.kg^{-1}$ for AMPA, asserting that these compounds have indeed an affinity for the particulate phase. Despite that partitioning, in the studied water body, the soluble fraction provided the main contribution to the total weight load, representing on the average more than 90% of that value. Other studies did not detect GLY and/or AMPA in the soluble fraction, but did detect them in the particulate fraction. According to our findings, each particular situation should be considered as a unique scenario, regardless of the type of agronomic practice. Therefore, we maintain that the analysis of those compounds in the soluble phase should always be taken into consideration when studying surface water bodies. A fundamental corollary indicated by the present results is furthermore that the particulate fraction is not the only means by which GLY and AMPA mobilize in an aquatic environment. Moreover, since GLY and AMPA were found at such significant concentrations in the soluble fraction of the water column, a reassessment of water quality guidelines for the protection of aquatic life for GLY and AMPA are hereby indicated.

Declaration of Competing Interest

The author declare no conflict of interest.

Acknowledgments

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