



Glyphosate and atrazine in rainfall and soils in agroproductive areas of the pampas region in Argentina

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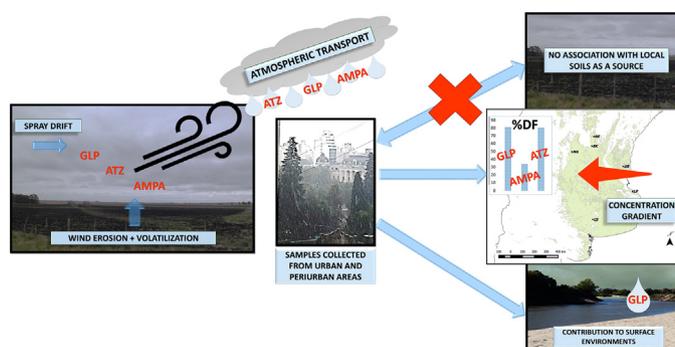
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HIGHLIGHTS

- GLP, AMPA, and ATZ were found in 80% of the rainwater samples in the Argentine pampas.
- Soils as a source of herbicides did not define a local atmospheric fingerprint.
- Median GLP concentrations in rainwater were associated with precipitation dynamics.
- ATZ levels followed no specific pattern for either rainwater or soil samples.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence in the atmosphere of glyphosate (GLP) and atrazine (ATZ) was investigated—those pesticides dominating the market in Argentina—through rain, as the main climatic phenomenon associated with wet deposition, both through analyzing source-receptor relationships with soil along with the climatic influences that may condition that transport and through estimating the annual deposition on the surface of the Argentine pampas. Rainwater samples ($n = 112$) were collected throughout each rainfall in urban areas of the pampas having different degrees of land use and with extensive crop production plus subsurface-soil samples ($n = 58$) from the relevant periurban sites. The herbicides—analyzed by liquid-chromatography–mass-spectrometry—were detected in >80% of the rain samples at median-to-maximum concentrations of $1.24\text{--}67.3 \mu\text{g}\cdot\text{L}^{-1}$ (GLP) and $0.22\text{--}26.9 \mu\text{g}\cdot\text{L}^{-1}$ (ATZ), while aminomethylphosphonic acid (AMPA) was detected at 34% ($0.75\text{--}7.91 \mu\text{g}\cdot\text{L}^{-1}$). In soils, GLP was more frequently registered (41%; $102\text{--}323 \mu\text{g}\cdot\text{kg}^{-1}$) followed by ATZ (32%; $7\text{--}66 \mu\text{g}\cdot\text{kg}^{-1}$) and then AMPA (22%; $223\text{--}732 \mu\text{g}\cdot\text{kg}^{-1}$). The maximum GLP concentrations quantified in rainwater exceeded the previously reported levels for the USA and Canada. No associations were observed between soil and rainwater concentrations in the same monitoring areas—despite the soil's action as a source, as evidenced through the AMPA present in rainwater. Median GLP concentrations were significantly associated with isohyets, in an increasing gradient from the east to the west—as such in an inverse pattern to that of the annual rainfall volumes; whereas ATZ-rainwater levels exhibited no characteristic spatial configuration. The estimated annual deposition of GLP by rainfall indicated that more than one source of a herbicide can lead to its presence in the atmosphere and points out the relevance of rainfall's contribution to the surface levels of a pollutant.

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1. Introduction

A solution to the need for major increases in the crop yields in extensive agriculture has been sought through the implementation of a technological package involving the introduction of genetically modified species that are pesticide-tolerant (Leguizamón, 2014) within a context of pest management principally through the use of synthetic pesticides. Herbicides constitute the most widely used pesticides on the market, with particular emphasis on the employment of glyphosate [*N* (phosphonomethyl)glycine: GLP] and atrazine (2 chloro 4 ethylamino 6 isopropyl amino 1,3,5 triazine: ATZ), both regionally (Leguizamón, 2014) and globally (Benbrook, 2016). During a 2013–2014 agricultural campaign, 18.7 million ha of herbicide-tolerant varieties of soybean and corn were sown in Argentina (MINAGRI, 2017), with 80% of the production corresponding to the pampas region, resulting in a demand for 182.5 million liters (L) or kilograms of formulations of GLP. Although no specific data were available for ATZ, that agent was reported to be the third most heavily used compound among 62 million kg or L of herbicides apart from GLP (CASAFE, 2013). Thus, we would estimate that compound's usage was likely to be some 10–15 million kg or L.

When these formulations are applied to the fields, almost 20–30% of the dose sprayed does not reach the target area as a result of primary airborne drift. The magnitude of this effect depends on conditions ranging from the type of formulation and the weather during the operation to difficult-to-quantify variables such as the applicator's expertise (Gil and Sinfort, 2005). Once those herbicides reach the surface layer, the persistence in the soil of GLP, its main degradation product aminomethylphosphonic acid (AMPA), and ATZ is reported to be for months or years (Simonsen et al., 2008; Vonberg et al., 2014). That the concentrations of these herbicides thus persist in the soil (Aparicio et al., 2013; Primost et al., 2017) points to the role of the soil matrix as a source for their eventual reemission into the atmosphere.

Depending on the physicochemical properties of the active compounds, postapplication emissions may occur, reaching losses of almost 90% of the product through volatilization that can last for a few days or for weeks (Bedos et al., 2002) together with the action of wind erosion in dragging and ultimately lifting soil particles loaded with pesticides from that matrix into the air column (Bidleman, 1988). The pesticide dynamics in the environment include continuous transfers between these two matrices. Though this movement normally occurs between only adjacent areas, studies have demonstrated that pesticides can nevertheless travel long distances so as to be detected in extremely remote locations extensively removed from agricultural areas such as polar regions (Baek et al., 2011; Unsworth et al., 1999).

ATZ and its metabolites have been predominantly detected in the vapor phase (Cooter et al., 2002) and at even 200–300 km from the closest cultivated field (Thurman and Cromwell, 2000), whereas GLP and AMPA have been reported in the air near the application areas (Chang et al., 2011; Morshed et al., 2011), thus indicating a short-range transport within the atmosphere principally in association with particulate matter (Bento et al., 2017; Chang et al., 2011). The atmospheric dynamics of these herbicides make them likely to be transported long distances to be later returned to the surface by both wet and dry deposition (Goel et al., 2005; Messing et al., 2013).

Wet deposition is considered the predominant route for herbicide precipitation from the atmosphere, either by dissolution in rainwater for compounds in the vapor phase, or by particle washout (Bidleman, 1988; Goel et al., 2005). In this regard, 97% of GLP can be removed by weekly rains above 30 mm, with maximum concentrations of 2.5 $\mu\text{g}\cdot\text{L}^{-1}$ having been detected in rainwater in the United States (Chang et al., 2011). In an extensive study worldwide, atmospheric ATZ, was detected in rainwater in France (Trautner et al., 1992), Poland (Gryniewicz et al., 2003), the United States (Majewski et al., 2000; Vogel et al., 2008), Germany (Hüskes and Levsen, 1997), and Italy (Trevisan et al., 1993); with maximum values of 40 $\mu\text{g}\cdot\text{L}^{-1}$ having been recorded in the United States (Nations and Hallberg, 1992). In

addition, Goolsby et al. (1997) estimated an annual contribution of 110,000 kg of ATZ to the Mississippi-River basin from the atmosphere, which matrix may therefore be considered as a significant source of this herbicide for surface-water bodies.

Despite the extensiveness of this agricultural practice in Latin America, little information on the dynamics of herbicides within the atmosphere is available in this geographical region. Because GLP was recently categorized as “probably carcinogenic to humans” by the International Agency for Research on Cancer (Portier et al., 2016), and in view of the volumes of these agents applied to fields and detected in the air; an analysis of the extensiveness of the degree of herbicide transport and the possibility of the deposit of those compounds onto land surfaces is both relevant and necessary.

The aim of the present work was therefore to study the presence of herbicides in rainfall (as the main vehicle of wet deposition) and to evaluate the corresponding spatial and temporal variations and those relationships with the soil contents of herbicides and the climatic conditions in the Argentine pampas.

2. Materials and methods

2.1. Study area

The study area comprised four of the five provinces of the Argentine pampas (excluding La Pampa): Buenos Aires, Entre Ríos, Santa Fe, and Córdoba; covering an approximate area of 60 million ha. This region is the source of >90% of the soybean and between 80 and 90% of the wheat, corn, sorghum, barley, and sunflower produced in the country. The predominantly mild and humid climate, with warm summers and no dry seasons, is responsible for those productions. The extent of annual precipitation is between 600 mm in the southwest and 1200 mm in the northeast, while the respective mean annual maximum and minimum temperatures are 18 and 6 °C in the south and 26 and 14 °C in the north. The gradient of annual precipitation varies in direction according to the different areas—namely, in the north the rainfall decreases from east to west, while in the south from north to south. The most frequent distribution of annual precipitation within that entire area involves a maximum in the summer that decreases from the autumn through the winter and spring (Magrin et al., 2007). Seven representative locations within the provinces of the pampas were selected (Fig. 1), consisting of two from Buenos Aires (BA), three from Córdoba (CB), and one each from Santa Fe (SF) and Entre Ríos (ER). Table 1 provides descriptions of each site. The crop cycles were taken into account when defining the high (mostly spring) and low (summer through autumn) seasons of herbicide application that were considered for the analysis of temporal variation.

2.2. Rainwater samples

Each rainfall was monitored individually at every location (Trevisan et al., 1993). The sampling period was according to application campaigns from October 2012 through April 2014 (Table 1; Ghida Daza and Urquiza, 2014). The samples were collected by direct entry of the raindrops into 1-L polypropylene containers (Sakai, 2002) containing 100 ng of [^{13}C , ^{15}N] glyphosate ([^{13}C , ^{15}N] GLP) and 100 ng of [^3H] atrazine ([^3H] ATZ), as quality-control and quality-assurance systems. After each rainfall, the particulate matter in the samples was separated by filtration through nylon membranes of 0.45- μm pore size and the soluble fraction frozen at -20 °C until further analysis.

2.3. Soil samples

The presence of the two herbicides in soils was studied in different regions where no prior data or publications had been available—*i. e.*, at BK, MA, IT, LP, CS, and HE—with each cardinal point being chosen for the presence of periurban surroundings (Fig. 1). The samples were

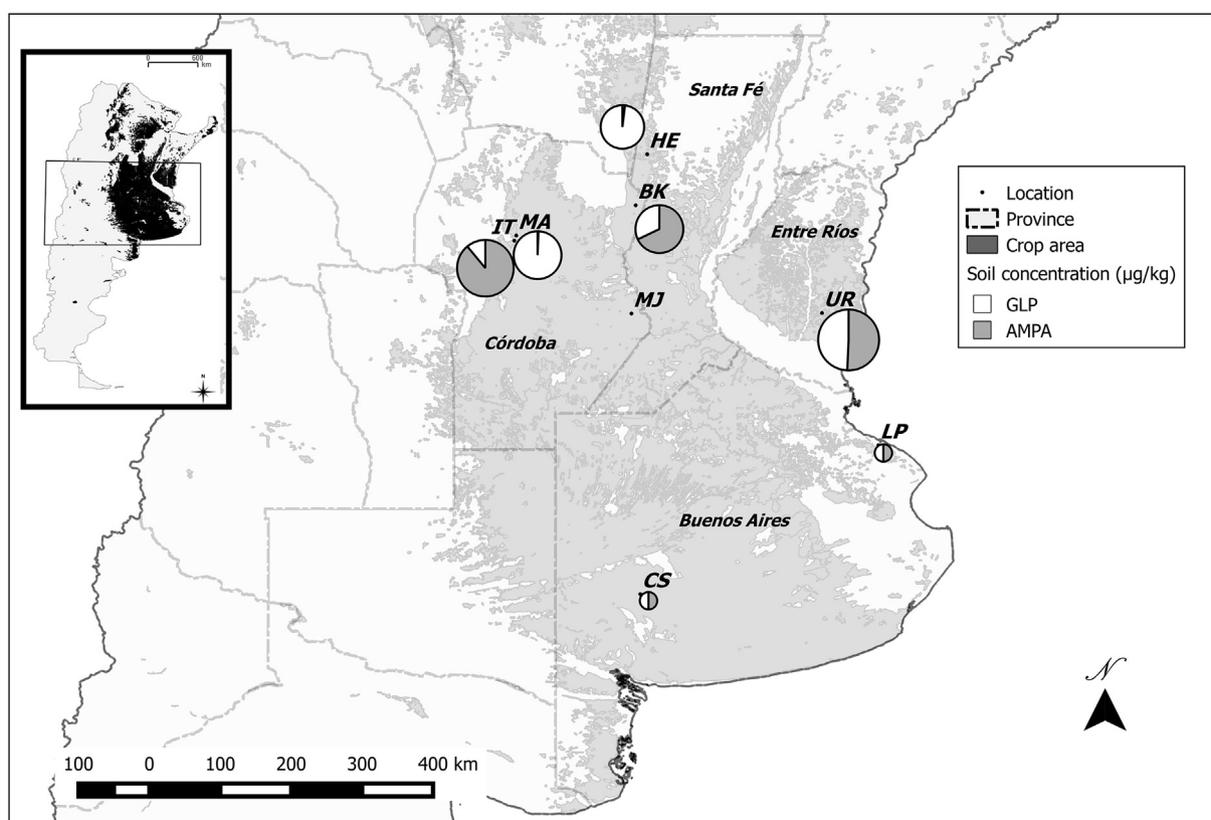


Fig. 1. Study area, monitoring sites, and concentrations of GLP and AMPA in the soils at each site. Of diameters proportional to \log_{10} of the median concentration of GLP + AMPA ($\mu\text{g} \cdot \text{kg}^{-1}$), the pie charts denote the relative areas in hectares of soybeans sown in the different locations indicated in the figure with white representing GLP and gray AMPA. Key to monitoring areas: BK, Brinkman + HE, Hersilia (Santa Fe); I + MA, Malvinas Argentinas + MJ, Marcos Juárez (Córdoba); UR, Urduñarrián (Entre Ríos); LP: La Plata + CS, Coronel Suárez (Buenos Aires). The inset indicates in black the location of the entire monitoring area within Argentina.

collected at the subsurface level, by gathering soil from a defined area of $40 \text{ cm} \times 40 \text{ cm}$ and at a 5-cm depth (Feng and Thompson, 1990). This procedure was repeated 5 times in each field, with a sample being removed from each of the four corners at a distance of 20 m toward the center and a final sample taken from the center (*i. e.*, five points). These subsamples from each field were then mixed and homogenized in-situ and a representative fraction transferred refrigerated to the laboratory. There, the soil samples were homogenized manually, grinded,

and filtered through a sieve of 2-mm pore size for subsequent storage at $-20 \text{ }^\circ\text{C}$ until the time of analysis.

2.4. Chemicals and reagents

The solvents used in the chemical and chromatographic analyses were of high-performance-liquid-chromatography (HPLC) grade, while all the salts were of analytical grade (JT Baker-Mallinckrodt

Table 1
Summary of agricultural activities and the demographic and climatic values most relevant to the study region.

Province	Córdoba				Santa Fe	Entre Ríos	Buenos Aires	
Location	B° Ituzaingó Anexo (IT)	Malvinas Argentinas (MA)	Marcos Juárez (MJ)	Brinkmann (BR)	Hersilia (HE)	Urduñarrián (UR)	Coronel Suarez (CS)	La Plata (LP)
Georeferencing coordinates	31° 27' 54.81" S 64° 5' 6.18" W	31° 22' 42.88" S 64° 3' 8.27" W	32° 41' 49.64" S 62° 6' 21.76" W	30° 52' 1.40" S 62° 2' 4.14" W	30° 0' 14.38" S 61° 50' 21.43" W	32° 41' 17.57" S 58° 53' 10.19" W	37° 26' 29.22" S 61° 57' 25.20" W	34° 55' 26.64" S 57° 55' 57.53" W
Populated geographic área (Km ²) ^(a)	0.5	3.6	7.2	3.75	5.2	21.5	27.3	921
Population (# inhabitants) ^(a)	3848	1287	27,004	9890	3165	8986	23,621	649,613
Sample Period	October 2012 – April 2014							
Prevalent crop type ^(b)	Soybean-Corn						Soybean-Wheat	Horticultural
Months of soybean cultivation ^(c)	September through July							
Months of corn cultivation ^(c)	September through May							
Months of increased use of GLP ^(c)	September through January							
GLP-application dosage l/ha ^(d)	4–10							

^a Instituto Nacional de Estadísticas y Censos-INDEC de la República Argentina, 2010.

^b Ministerio de Agricultura, ganadería y pesca de nación.

^c Instituto Nacional de Tecnología Agropecuaria.

^d Ghida Daza and Urquiza, 2014.

Baker Inc., USA). Nanopure water was obtained in the laboratory by means of a Sartorius Arium water-purification system (Sartorius AG, Göttingen, Netherlands). Standards of GLP (99%), AMPA (98.5%), [^{13}C , ^{15}N]GLP, [^5D]ATZ and 9 fluorenylmethyloxycarbonyl chloride (FMOC-Cl; HPLC grade at >99%) were acquired from Sigma Aldrich (St. Louis, MO, USA).

2.5. Chemical analysis

2.5.1. Sample preparation for chemical analysis

2.5.1.1. GLP and AMPA. Of each sample, 5 g of soil was weighed in a 50-mL Falcon™ propylene tube and spiked with 500 ng of [^{13}C , ^{15}N]GLP. GLP and AMPA levels were determined according to Aparicio et al. (2013). The analytes were extracted with 25 mL of a 0.1 M K_2HPO_4 solution and the resulting extracts sonicated 3 times for 10 min with agitation between cycles followed by centrifugation for 10 min at 3500g. A 2-mL aliquot of both the rain water samples and soil extracts was first adjusted to pH = 9 with sodium tetraborate (40 mM), and then 2 mL of FMOC-Cl solution in acetonitrile were added (Sancho et al., 1996). The preparation of the standard solutions for the calibration curves and the reagent blanks was done under equivalent operational conditions to those used in the assays. All derivatized samples were finally extracted with 5 mL of dichloromethane, centrifuged and the aqueous supernatant filtered through a membrane of 0.45- μm pore size for HPLC-mass-spectrometry determination.

2.5.1.2. ATZ. Of each sample, 5 g of soil was spiked with 150 ng of [^5D]ATZ (at a nominal concentration in the instrumental analysis of 10 ng·mL $^{-1}$) and extracted by the so-called QuEChERS method—signifying “Quick, Easy, Cheap, Effective, Rugged, and Safe”—described in Bruzzoniti et al. (2014). For extraction, 15 mL of 1% (v/v) of acetic acid in acetonitrile was added and the mixture shaken manually for 1 min, sonicated for 10 min; then 7.00 g of anhydrous MgSO_4 and 2.00 g of sodium acetate were added, followed by a manual stir for 1 min. Next the sample was centrifuged for 10 min at 3500g and 1 mL of the organic upper phase mixed with 1 mL of water. The resulting solution was finally filtered through a membrane of 0.45- μm pore size for subsequent instrumental analysis.

2.5.2. Instrumental analysis

Analysis was carried out with a binary-pump Agilent 1100 HPLC system (Agilent Technologies Inc., Miami, FL, USA) coupled with a mass quadrupole VL mass spectrometer with an electrospray-ionization source (Agilent Technologies Inc., Miami, FL, USA). For GLP a reverse C_{18} chromatographic column was used (X-SELECT™ 75 mm \times 4.6 mm of 3-mm pore size from Waters Corp., Milford, MA, USA) kept at 25 ± 1 °C. A methanol:water gradient was used (with the mobile phases previously conditioned with 5 mM ammonium acetate) at 0.5 mL·min $^{-1}$. As described in Meyer et al. (2009), selected-ion monitoring in the negative-ionization mode was applied for detection of GLP-FMOC, [^{13}C , ^{15}N]GLP-FMOC, and AMPA-FMOC. The quantification of both ATZ and [^5D]ATZ was conducted in the isocratic mode with 0.1% (v/v) formic acid in acetonitrile/water (70/30) as the mobile phase and same column as used for the GLP analysis. For detection, the electrospray-ionization source was applied in positive mode. In all runs, nitrogen was used as an auxiliary gas at 8 L/min at a source temperature of 330 °C with ion settings corresponding to deprotonated and protonated compounds and two daughter ions for quantification and identification, respectively. The data acquisition and analysis was conducted by means of an Agilent Chemstation Rev. 10A.02 software. (Ronco et al., 2016).

2.6. Quality controls and quality assurance

Quality controls during the sampling and analysis of the major components involved the use of reagent blanks, duplicate samples, and isotopically labelled GLP ([^{13}C , ^{15}N]GLP) and ATZ ([^5D]ATZ) to evaluate the holding time and recovery for the complete procedure in each sample. For quality control and assurance in the laboratory analysis of GLP, AMPA, and ATZ the linearity, reproducibility, detection, and quantification limits; the matrix effect; and the recovery were tested according to SANCO (2009).

2.7. Data analysis

A descriptive statistical analysis was performed for both matrices throughout the entire region. The Kruskal-Wallis nonparametric test (Conover, 1999) and pairwise comparisons were used with the GLP, AMPA, and ATZ concentrations (in $\mu\text{g}\cdot\text{L}^{-1}$) at the different sites, after checking that a normal distribution did not apply. Only single measurements above the limit of detection (LOD) were considered, and concentrations between the LOD and the limit of quantification (LOQ) were replaced with a value of one-half the LOQ (Delistraty and Yokel, 2007). To study the association between the temporal pattern (*i. e.*, the high- and low-application campaigns) and the frequency of detection (>LOD versus <LOD), contingency tables (2×2) were used for each analyte and a Fisher's exact test of independence performed. A spatial-variation analysis of the pesticides in rainfall was conducted that included the three different categories over the entire region and the 4 provinces studied along with one analysis involving the annual accumulated-rainfall categories (High Zone, HZ, at >1000 mm·yr $^{-1}$; Medium Zone, MZ, at 900–1000 mm mm·year $^{-1}$; and Low Zone, LZ at <900 mm mm·yr $^{-1}$). The Spearman correlation coefficient (Conover, 1999) was employed for the entire data above the LOD to evaluate the correlation between analytes in both the rainfall ($n = 112$) and the soil ($n = 58$) matrices. The correlation between the matrices was analyzed by grouping the median concentrations of the different sites ($n = 7$). Site MJ was not considered owing to a lack of soil analyses and available published data. All the tests were set at a significance level of 0.05 and the statistical analyses performed by means of the INFostat™ software.

Meteorologic information from each rainfall was obtained from the Argentine Ministry of Agroindustry (MINAGRI) and was then correlated with the herbicide concentrations. The regional-climate information, such as wind patterns and annual accumulated rainfall, was also used to analyze the dynamics of the compounds. All the maps were constructed by means of the QGIS v.2.2.0 software.

3. Results and discussion

3.1. Analytical parameters

The analytical method used was linear within the interval studied (*i. e.*, 1–1000 $\mu\text{g}\cdot\text{L}^{-1}$) for all the analytes with an $r > 0.993$ (critical value = 0.549, 95%, $n = 10$). The LOD and LOQ for the rainwater and for the soils (in parentheses) with respect to both GLP and AMPA were 0.5 and 1 $\mu\text{g}\cdot\text{L}^{-1}$ (2 and 5 $\mu\text{g}\cdot\text{kg}^{-1}$), respectively; whereas for ATZ the corresponding values were 0.1 and 0.2 $\mu\text{g}\cdot\text{L}^{-1}$ (0.2 and 0.5 $\mu\text{g}\cdot\text{kg}^{-1}$), respectively. An analysis of the overall recovery for both liquid and solid samples, including the electrospray-ionization-source matrix effect, performed on the isotopically labelled standards gave values for rainwater of $93 \pm 5\%$ for [^{13}C , ^{15}N]GLP and $90 \pm 7\%$ for [^5D]ATZ, quantified for all the samples ($n = 112$). For the soils, the recoveries were $80 \pm 10\%$ for [^{13}C , ^{15}N]GLP and $92 \pm 5\%$ for [^5D]ATZ. Those matrix effects, measured through the ion suppression on the basis of the characteristics of the samples analyzed, were in agreement with Taylor (2005) for this type of analytical methodology. These results are in accordance with

the requirements stated by the SANCO (2009) regulation for the analysis of pesticide residues.

3.2. Herbicides in rainwater in the pampas region

3.2.1. Spatial patterns

The analysis of the rainfall data from the different regions ($n = 112$) indicated detection frequencies ($>LOD$) $>80\%$ for GLP and ATZ (*i. e.*, 81.3% and 80.4%, respectively). Previous studies involving different regions in the USA for this environmental matrix have reported similar detection ranges for both compounds, between 61 and 100% for GLP and 69 and 94% for ATZ (Vogel et al., 2008; Chang et al., 2011; Coupe et al., 2000; Farenhorst and Andronak, 2015). These results reveal the ubiquitousness of these herbicides in the atmosphere (Majewski et al., 2014). In the present study, 65% of the GLP and 51% of the ATZ were detected at concentrations above the LOQ. Further analysis revealed that Córdoba was the province with the highest frequency of detections of AMPA (42%; Table 2), but that value was strikingly the lower than those of other studies, where AMPA and GLP were detected at similar frequencies with both at above 70% (Battaglin et al., 2014). Fig. 2, depicts the spatial distribution of the concentrations of GLP and AMPA in rainwater. The regional mean and median concentrations for GLP were $5.5 \pm 11.3 \mu\text{g}\cdot\text{L}^{-1}$ and $1.29 \mu\text{g}\cdot\text{L}^{-1}$, respectively. The maximum concentration of GLP (at $67.3 \mu\text{g}\cdot\text{L}^{-1}$) was measured at Site IT in the province of Córdoba, where the value recorded was significantly higher than those found elsewhere (Table 2) as well as being higher than those reported for weekly samples by Farenhorst and Andronak (2015), at $16.9 \mu\text{g}\cdot\text{L}^{-1}$, and by Quaghebeur et al. (2004), at $6.2 \mu\text{g}\cdot\text{L}^{-1}$. That in Argentina, common doses of GLP are approximately $12 \text{L}\cdot\text{Ha}^{-1}\cdot\text{yr}^{-1}$ (CASAFE, 2013) in contrast to the doses of $0.5\text{--}2.0 \text{L}\cdot\text{Ha}^{-1}\cdot\text{yr}^{-1}$ in the aforementioned countries is also notable, with those being at least, some 5 times lower. The metabolite AMPA was detected in 33.9% of the total samples, with 34.2% having concentrations above the LOQ. The mean and median concentrations were $1.5 \pm 1.8 \mu\text{g}\cdot\text{L}^{-1}$ and $0.75 \mu\text{g}\cdot\text{L}^{-1}$, respectively. The maximum concentration observed in the present work was $7.91 \mu\text{g}\cdot\text{L}^{-1}$, higher than the value reported by Chang et al. (2011) for the United States of $0.97 \mu\text{g}\cdot\text{L}^{-1}$. These results of levels and frequencies of AMPA evidence wind erosion as a main source of these compounds for the atmosphere since the presence of the metabolite is restricted to microbiological degradation in soil (Grunewald et al., 2001).

For ATZ, the mean and median concentrations in rainwater were $0.93 \pm 3.36 \mu\text{g}\cdot\text{L}^{-1}$ and $0.22 \mu\text{g}\cdot\text{L}^{-1}$, respectively. The provinces can be arranged in the following ascending order on the basis of the median values recorded: Buenos Aires = Santa Fe < Entre Ríos

< Córdoba (Table 2). The maximum concentration measured of ATZ in rainwater, at $26.9 \mu\text{g}\cdot\text{L}^{-1}$, was above that previously reported for the USA of $19 \mu\text{g}\cdot\text{L}^{-1}$ (Vogel et al., 2008). Although ATZ is a compound that can undergo photochemical degradation, the rate of degradation in the atmosphere is low; and therefore that herbicide has a great tendency to be transported over medium-to-long distances (Fenner et al., 2007). This capability is reflected in a ubiquitousness of ATZ in the atmosphere, as observed in the detectable ATZ levels in polar regions, both in precipitations (Unsworth et al., 1999) and in the lakes (Muir et al., 2004). In view of such evidence, the detection of this herbicide in 80% of the samples at concentrations exceeding the LOD at all sites—even at those with low agricultural influence, such as La Plata (LP), with no differences between the sites except for MA—is hardly surprising. The lower concentrations of ATZ compared to GLP may result from differences such as the applied volumes—*i. e.*, GLP:ATZ, 10:1 (CASAFE, 2013)—or to the degree of removal from the atmosphere. The vapor pressure of 0.039 mPa (PPDB, 2017) for ATZ, compared to GLP and AMPA which compounds are considered non-volatile (EU, 2002; U.S.EPA, 1993), indicates a major concentration in the vapor phase of ATZ herbicide (Pankow, 1994), which phase is less efficiently swept away than the particle phase (Majewski et al., 2014; Goolsby et al., 1997).

3.2.2. Temporal patterns

Although the volumes of herbicide applied differed as a function of the annual crop cycles (especially soybean; cf. Table 1), no significant differences were observed among the median concentrations of GLP, AMPA, and ATZ in rainwater, measured in the campaigns involving “high” and “low” herbicide application according to Marino and Ronco (2005). Nevertheless, the current agricultural practices furthermore involve the use of herbicides for not only weed control but also a chemically induced fallow, thus implying a continuous input throughout the annual cycle (DP, 2015). The resulting regularity of spraying produces a continuous movement via the atmosphere through primary drift, in addition to supplying the soil with the herbicide to an extent where a pseudo-persistence of GLP in different soils of Argentina was observed (Primost et al., 2017; Soracco et al., 2018). As discussed in the following section and alluded to in the Introduction, soils constitute another significant source of atmospheric herbicides via wind erosion: indeed, even during a high-application season, transport to the atmosphere via wind erosion can contribute some 20–40% of the atmospheric herbicides; whereas in weeks without any application this contribution becomes as high as 50–100% (Chang et al., 2011).

Table 2

Summary of GLP, AMPA and ATZ concentrations in rainwater and soil samples both for the Pampean Region as a whole and for each individual province.

Rainwater (n = 112)																
Area ($\mu\text{g}/\text{L}$)	Pampean Region			Buenos Aires			Córdoba			Santa Fe			Entre Ríos			
	GLP	AMPA	ATZ	GLP	AMPA	ATZ	GLP	AMPA	ATZ	GLP	AMPA	ATZ	GLP	AMPA	ATZ	
% DF	81	34	80	72	40	75	72	42	94	97	23	60	81	31	100	
Media	5.49	1.53	0.93	3.39	1.69	0.2	11.18	2.10	2.10	3.50	0.75	0.17	2.26	0.75	0.30	
Mín	0.50	0.75	0.10	0.75	0.75	0.10	0.50	0.75	0.10	0.75	0.75	0.10	0.75	0.75	0.10	
Max	67.28	7.91	26.9	30.06	7.71	0.49	67.28	7.91	26.9	47.78	0.75	0.49	7.69	0.75	0.77	
Mdn	1.24	0.75	0.22	0.99	0.75	0.10	3.18	1.30	0.36	1.21	0.75	0.10	0.75	0.75	0.28	
Soil (n = 58)																
Area ($\mu\text{g}/\text{kg}$)	Pampean Region			Buenos Aires			Córdoba			Santa Fe			Entre Ríos ^a			
	GLP	AMPA	ATZ	GLP	AMPA	ATZ	GLP	AMPA	ATZ	GLP	AMPA	ATZ	GLP	AMPA	ATZ	
% DF	41	22	32	9	–	23	87	60	47	50	–	25	100 ^a	100 ^a	–	
Media	125	297	13	216	<LD	12	97	297	14	214	<LD	–	2299 ^a	4204 ^a	–	
Mín	28	80	4	184	<LD	6	28	80	4	104	<LD	<LD	–	–	–	
Max	323	732	66	248	<LD	17	233	732	66	323	<LD	7	–	–	–	
Mdn	102	223	7	216	<LD	12	67	223	5	214	<LD	–	–	–	–	

^a Primost et al. (2017).

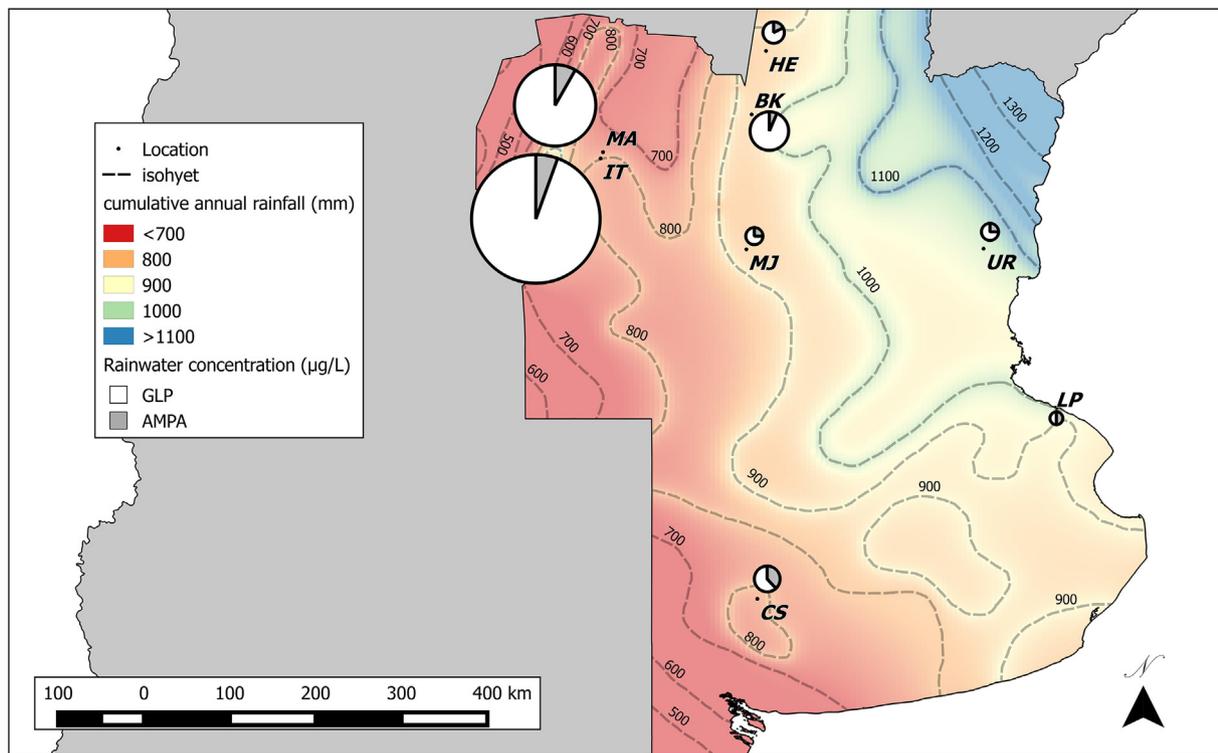


Fig. 2. Relative concentration of GLP and AMPA in rainfall at each sampling site. Of diameters proportional to \log_{10} of the median concentration ($\mu\text{g}\cdot\text{L}^{-1}$) of GLP (white) + AMPA (gray), the pie charts denote the relative levels of the two herbicides in rainwater at the indicated monitoring sites. The annual accumulated precipitation isohyets of the pampas region are indicated by the broken lines. Categories: High Zone (blue to green), HZ, at $\geq 1000\text{ mm}\cdot\text{yr}^{-1}$; Medium Zone, MZ (green to yellow), at $900\text{--}1000\text{ mm}\cdot\text{yr}^{-1}$; and Low Zone (orange to red), LZ at $< 900\text{ mm}\cdot\text{yr}^{-1}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Soil as the source of herbicides in the atmosphere

The overall herbicide-detection frequencies in soils obtained in this work were 41% for GLP, 22% for AMPA, and 32% for ATZ. These results are of particular relevance since soils act as an emission surface, both for the airborne (Tao et al., 2008) and particle-loaded parental compounds and metabolites such as AMPA (Bento et al., 2017). The GLP and AMPA contained within the top centimeters of soil are susceptible to wind erosion and subsequent atmospheric transport. Silva et al. (2018) estimated the GLP and AMPA removal through the action of wind erosion to be some $1900\text{ mg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ for soils with GLP and AMPA concentrations below $0.5\text{ mg}\cdot\text{kg}^{-1}$ and up to $3000\text{ mg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ for soils with higher concentrations.

The GLP and AMPA levels detected in soils of the provinces of Buenos Aires, Córdoba, and Santa Fe (Fig. 1), were not significantly different, having an average concentration of $125 \pm 87\text{ }\mu\text{g}\cdot\text{kg}^{-1}$ (along with a maximum of $323\text{ }\mu\text{g}\cdot\text{kg}^{-1}$). These concentrations of GLP are within the range observed previously for the southeast region of Buenos Aires by Aparicio et al. (2013) at $35\text{--}1502\text{ }\mu\text{g}\cdot\text{kg}^{-1}$, but are one-eighteenth of those of the soils of the province of Entre Ríos, as reported by Primost et al. (2017), at $2299 \pm 476\text{ }\mu\text{g}\cdot\text{kg}^{-1}$. These differences between the quantified levels could be related to the bias inherent in the sampling design within the framework of the proposed objectives. Both in the present study and in Aparicio et al. (2013) the soils sampled were associated with different types of crops, whereas Primost et al. (2017) studied exclusively soybean fields, which plants in particular have a greater requirement for GLP.

The mean overall concentration of ATZ in soil was $13 \pm 17\text{ }\mu\text{g}\cdot\text{kg}^{-1}$, along with a maximum of $66\text{ }\mu\text{g}\cdot\text{kg}^{-1}$ in Córdoba. No differences were observed between the concentration of ATZ in those soils from Córdoba and the soils from Buenos Aires; where corn production is concentrated in both those provinces thus producing a higher requirement for ATZ (MINAGRI, 2017). No data, however, were available from Entre Ríos,

and only a single positive value was detected among the different soil samples from Santa Fe.

3.4. Relationships between herbicide concentrations in soil and rainwater

In rainwater, a significantly positive correlation ($r = 0.66$) was observed between the values for GLP and AMPA. In addition, this correspondence was also observed in soil ($r = 0.88$), as has been reported for other environmental matrices by Primost et al. (2017). Since soils are the only source of AMPA for leaching into the atmosphere (Majewski et al., 2014), the correlation between the concentration of this metabolite and the levels of GLP in rainfall is an indicator of the key role of soil as an emission source in addition to primary drift (Chang et al., 2011). Nevertheless, significant positive correlations between those two compounds and ATZ in rainfall ($r = 0.46$ and $r = 0.47$ respectively) were observed, evidencing the combined use of the two herbicides in agricultural protocols (Ghida Daza and Urquiza, 2014).

A comparison between the concentrations for all the herbicides found in rainwater versus the corresponding levels in the local soils of the different study sites, in particular, revealed no significant correlations between the compounds measured in those two environmental matrices. In view of this finding, we could infer that soils are a source of these compounds for the atmosphere; but that lack of correlation prevents the definition of a local atmospheric fingerprint, with wind erosion and volatilization furthermore having a significant role in the dynamics of those herbicides. Moreover, the higher adsorption of GLP and AMPA to the finest particles of soils ($< 10\text{ }\mu\text{m}$) increases the off-site airborne transport (Bento et al., 2017).

3.5. Herbicides in rainfall as a consequence of climate factors

Exploring the climatic variables recorded for each rainfall—the precipitation volume of maximum temperature and wind speed—we

recorded no correlations between each variable and the concentrations of GLP, AMPA, and ATZ. Furthermore, no significant association between the concentrations of the three herbicides occurred, as recorded by Waite et al. (2005). Owing to the negligible vapor pressure of both compounds, as mentioned by Majewski et al. (2014), we accordingly expected that the detection of GLP and AMPA would be related mainly to the dynamics of atmospheric recharge of particulate material and therefore to the frequency of precipitations rather than the climatic conditions at the time of sampling. Nevertheless, when evaluating the accumulated annual precipitation isohyets, an association between median concentrations of GLP and AMPA and annual precipitation volumes was observed.

Fig. 2 illustrates the monitoring sites, subdivided according to rainfall parameters, derived from the accumulated annual-precipitation isohyets (AAPIs). In particular, the mean concentrations of GLP in rainfall when grouped by isohyets exhibited significant differences ($p \leq 0.05$) among the three zones. LZ, corresponding to the lowest AAPI, was characterized by significantly higher GLP concentrations than those registered the other zones, while lower concentrations than those of LZ were detected in HZ at nevertheless a higher AAPI. These results agree with Messing et al. (2013) and Hill et al. (2002), where the highest concentrations of herbicides were detected at sites with lower rainfall frequencies (considering only wet deposition). AMPA displayed a similar behavior with the high zone having significantly lower median concentrations than the other two, whereas no significant differences were found between the concentrations recorded at LZ and MZ.

As for ATZ, the median concentrations evidenced a similar pattern, increasing toward the southwest; but significant differences were observed between the sites only in the medium and high zones.

3.6. The role of rainfall in the mass deposition of GLP onto the environmental surface

In view of the rainfall deposition and the calculations made by Coupe et al. (2000) and Vogel et al. (2008), we estimated the contribution of these herbicides to the surface level of the environments in the MZ isohyet (cf. Fig. 2) as the most unfavorable scenario. The annual precipitation for that zone was estimated at 950 mm, corresponding to the average value of the limiting isohyets and was therefore considered uniform over the entire surface. If then the median regional concentrations (at $1.24 \mu\text{g}\cdot\text{L}^{-1}$) are taken into account, the annual mass of GLP deposited would amount to some $11,780 \text{ mg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$. To evaluate these results, taking up as proposed by Silva et al. (2018), annual input from wind erosion provides the atmosphere with some $1940 \text{ mg}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ from soils with concentrations of GLP below $0.5 \text{ mg}\cdot\text{kg}^{-1}$. Then, from those considerations, the annual estimated deposition by rainfall indicates the extent of other sources of the herbicide for the air.

Even though runoff is expected to be the main source of these herbicides for water bodies (Messing et al., 2011; Sasal et al., 2015), under certain specific conditions—i. e., a torrential storm—the wet deposition of pesticides could exceed their contribution by runoff (Donald et al., 2005). According to the results found in our study, rainfall definitely needs to be considered as a relevant source of these pollutants for surface-level environments. As previously reported by Majewski et al. (2000) and Nations and Hallberg (1992), these results reinforce the notion of airborne levels of herbicides in urban and periurban communities, thus adding a possible exposure pathway for humans and animals in the pampas region, as was cited by Bento et al. (2017) and Battaglin et al. (2014) for other countries. In view of such implications, we propose an update of the Argentine guidelines for environmental quality by duly incorporating the herbicide criteria for ambient air.

4. Conclusions

The results of this study of herbicides in rainwater—the first such in Argentina—have demonstrated the high frequency of detection (>80%) of both GLP and ATZ along with the ubiquitouness of those compounds

in the atmosphere associated with annual precipitations. The maximum concentrations of both herbicides were higher than those detected in other countries, possibly as a consequence of the higher agronomic dosages used in Argentina. GLP, AMPA, and ATZ were detected in soils, with the concentration levels of GLP associated with soybeans being greater than with other crops. Thus, although this matrix constitutes a significant source, no association with the atmospheric concentrations was observed at the local scale. A spatial variability of the pesticide concentration was observed among the accumulated-precipitation/isohyets that was more evident for GLP and AMPA than for ATZ. Thus the atmospheric reloading of particulate material determined the concentration of both those compounds in the rainfall. Because the atmospheric deposition of herbicides through rainfall onto surface water bodies and soils as well as onto urban sites in the region might constitute a source of exposure of the population to these pollutants from the air, an inclusion of those compounds in the air-quality guidelines and in national monitoring programs is necessary. Upon additional consideration of the broader range of active substances used in the current agricultural practices nationwide, we also suggest future investigations involving the inclusion in the analyses of other pesticides that furthermore are known to become dispersed into regions outside the area of application.

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Dr. Donald F. Haggerty, a retired academic career investigator and native English speaker, edited the final version of the manuscript.

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