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

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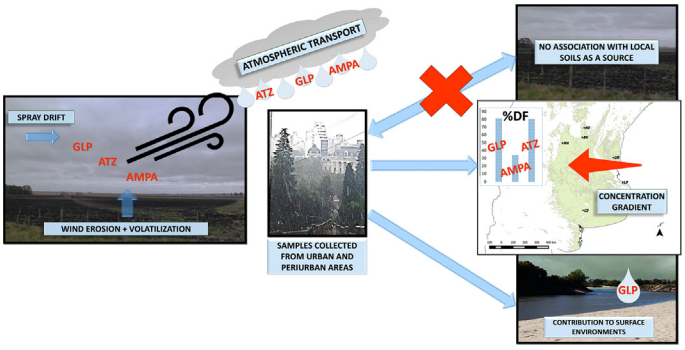
HIGHLIGHTS

- 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 1.24–67.3 $\mu g \cdot L^{-1}$ (GLP) and 0.22–26.9 $\mu g \cdot L^{-1}$(ATZ), while aminomethylphosphonic acid (AMPA) was detected at 34% (0.75–7.91 $\mu g \cdot L^{-1}$). In soils, GLP was more frequently registered (41%; 102–323 $\mu g \cdot kg^{-1}$) followed by ATZ (32%; 7–66 $\mu g \cdot kg^{-1}$) and then AMPA (22%; 223–732 $\mu g \cdot kg^{-1}$). 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 onc 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 $\mu g \cdot L^{-1}$ 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 (Grynkiewicz 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 $\mu g \cdot L^{-1}$ 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 [^{5}D] atrazine ([^{5}D] 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

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