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Mobilization of ionophore antibiotics and glyphosate after a rainfall simulation on agricultural soils amended with poultry litter



Marcos Navarro^{a,b,1}, Lucas L. Alonso^{a,b,*,1}, Alberto L. Capparelli^c, Damián J.G. Marino^{a,b}

^a Centro de Investigaciones del Medioambiente (CIM), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Buenos Aires, Argentina

^b Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Buenos Aires, Argentina

^c Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Buenos Aires, Argentina

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ABSTRACT

Poultry litter (PL) is a majority waste of the intensive avian production, commonly used as an organic amendment in agricultural soils. We studied the input of pollutants from the PL, as inorganic P and ionophore antibiotics (IPA), and the influence on soil pollutants (GLP and AMPA) in real systems, after a rainfall simulation on an agronomic amended soil with PL at two residence times. Physicochemical parameters were altered in the runoff after the amendment. PL from commercial farms present a preliminary load of monensin and salinomycin. The mobility of IPA by surface runoff (0.8–31%) and leaching (0.4–38%) was determined, with monensin showing the maximum losses in both processes at both residence times. PL amendments act as a pollution diffuse source of IPA. Moreover, the amendment enhanced the mobility of GLP and AMPA in soils. Maximum losses of GLP in runoff increased from 0.56% to 9.84% in soil with PL treatment. The results were related to the amounts of P released in the surface runoff. Strategies for reducing the animal wastes and their antibiotic content must be investigated regarding the productive practice involving these residues, as water and soil conservation are proven to be a key asset in the sustainability and success of circular economy processes. This is the first study to demonstrate the combined release of pollutants from multiple origins, after the amendment with poultry litter on real agricultural soils.

1. Introduction

Poultry litter (PL) is a majority waste of the intensive avian production and constitutes one of the most worrying issues for agricultural producers worldwide. In Argentina, over 6,700,000 tons of PL are generated annually (Maisonnave et al., 2015). The residue is primarily composed of bedding material, chicken excreta and animal waste. The nitrogen, phosphorus and organic matter levels of the PL provide exploitable characteristics for its application as an organic amendment in agricultural soils, adding value to the residue as a part of a circular economy strategy. Due to the time and space requirements, the application of treatments such as composting is difficult to conduct in real practice, so poultry litter is commonly applied fresh/raw (Riera et al., 2014).

The material is usually applied in doses from 5 to 10 ton ha^{-1} , according to the crop needs (Almada et al., 2016). However, depending on

its composition and previous treatments (addition of salts, composting), substantial amounts of nutrients can be released from the litter application through surface runoff (Schroeder et al., 2004). Phosphorus is a key element in nutrient management, and its loss through runoff processes causes a variety of problems, from economic disadvantages to environmental damage, such as eutrophication of aquatic systems.

These amendments can also function as a pollution diffuse source of veterinary antibiotics (Furtula et al., 2010; Sun et al., 2013). The confinement and overcrowding conditions to which animals are submitted at intensive animal production systems, have demanded the usage of antibiotics to prevent the rapid spread of diseases (Chapman et al., 2010). Ionophore polyether antibiotics (IPA) are one of the most extensively used families in avian production, which act mainly as coccidiostats (Lekshmi et al., 2017), and can also act as growth promoters (EFSA, 2008). IPA are administered throughout the life cycle in doses ranging from 70 to 125 mg kg⁻¹ of dry food (European Union

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^{*} Corresponding author at: Centro de Investigaciones del Medioambiente (CIM), Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Buenos Aires, Argentina.

E-mail address: lucasalonso@quimica.unlp.edu.ar (L.L. Alonso).

¹ Equal contribution.

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Commission, 2003; European Union Commission, 2008). After the ingestion, IPA are not completely absorbed in the intestine of birds (Gallus domesticus), and up to 80% of the administered compound can be excreted in their parental form and therefore be found in PL (Biswas et al., 2012; EFSA, 2008). These compounds could be released into the soil after application of the PL and be consequently mobilized by surface runoff or percolation into the environment, reaching water bodies such as rivers or lakes (Sarmah et al., 2006; Sun et al., 2013). IPA have been previously characterized as environmental risk pollutants (Hansen et al., 2009). Recent studies for IPA in Argentina demonstrated the extent of their environmental dynamics, with monensin being detected in rivers (with flows up to $320 \text{ m}^3 \text{ seg}^{-1}$) far from productive facilities and even at the Paraná River Delta (Alonso et al., 2019). The mobility of IPA by runoff and percolation processes after simulated rain events on soil has been previously reported (Kim et al., 2010; Sun et al., 2013). Soil characteristics as organic matter can also affect the dynamics of the IPA: either through the retention of the compounds or their degradation potential (Kim et al., 2010; Doydora et al., 2017). The reported range of soil sorption coefficients (as $logK_{oc}$) for these compounds is 2.9–4.2 for LAS, 1.9-3.8 for MON and 1.9-3.2 for SAL (Mooney et al., 2020).

In addition to the contribution of substances from the poultry litter, it is important to evaluate how its application has an impact on contaminants already present in the receiving soil. PL application increases nutrient species in soils, as dissolved organic matter (DOM) and phosphorus species (Dutta et al., 2012; Tewolde et al., 2020). The ability of phosphates to desorb agricultural pollutants as glyphosate and AMPA (GLP) has been demonstrated in several types of soils (Gimsing et al., 2004; Padilla and Selim, 2019), and has been reported to have significant more weight than DOM (Okada et al., 2016). This effect was observed on Argiudol soils from Argentina, where glyphosate desorption phenomena have been reported after chemical fertilization with inorganic P (Sasal et al., 2015). Glyphosate has been reported as a soil pollutant in multiple regions from Argentina (Primost et al., 2017; Alonso et al., 2018; Castro Berman et al., 2018), which is the third largest producer of genetically modified soybeans, with more than 55 million tons produced annually.

Therefore, the present work emerges considering the reported use of poultry litter as organic amendment in several crops and its generation under antibiotic-dependent systems, the magnitude of the amendment practice, and the lack of studies with focus on the potential situation regarding multiple environmental consequences of the practice. The objective was to study the loss of phosphorus, the input of ionophore antibiotics into soils and their mobility by runoff of leaching processes, and the subsequent effect on the mobility of soil pollutants, as glyphosate and its metabolite aminomethylphosphonic acid (AMPA), after the simulation of a rainfall event on a real agricultural soil amended with commercial poultry litter.

2. Materials and methods

2.1. Runoff simulation

Poultry litter was provided by a local poultry farm from Entre Ríos province, with no specific preliminary treatment. Rainfall simulation trials were conducted in agricultural fields from the INTA's Agricultural Experimental Station of Paraná, Entre Ríos, which were never exposed to poultry litter or any other animal amendment. The studied soil was Aquic Argiudol, of the Tezanos Pinto series (Table 1), with an A horizon of 18 cm (SiSINTA, 2021). Before application of poultry litter, soybean plants and stubble were removed from the surface.

The experimental design of the study is detailed in Table 2. Before the trial, soil samples were collected (Initial soils, n = 3) for GLP and AMPA analysis. Plots were divided into unamended soils (UA-soils) and soils amended with poultry litter (PL-soils). The UA-soils consisted of 3 random plots that were kept unamended to contrast the influence of the practice on soluble phosphorus, GLP and its metabolite AMPA. For PL- Table 1

Physicochemical parameters of the studied agricultural soil (Tezano Pinto series).

01	gaille carbon %	рн	Clay %	Silt %	Sand %
Aquic Argiudoll 2.6	65 ^a	5.7 ^b	27.60	30.70	67.90

^a Loss of ignition, corresponding to the Ap horizon

^b Soil pH was determined using a 10 mL distilled water and 10 g soil (SAMLA, 2004)

soils, two independent sets of plots from the agricultural field were tested at 24 (n = 9) and 72 h (n = 9) after PL application. Plots of 1 m² were randomly selected for each treatment, and PL (46% moisture) was applied on the soil surface (PL-soils) in a scaled amount according to reported conventional practice application rate (5 ton ha⁻¹) assuming a minimal dose scenario (Almada et al., 2016).

Prior to the trials, PL was fractionated in 3 parts for the corresponding ionophore transport study: one fraction was kept unchanged (Control), and the other 2 were fortified with monensin (MON), salinomycin (SAL) and Lasalocid (LAS) at 0.1 mg kg⁻¹ (C1) and 1 mg kg⁻¹ (C2). Both concentrations were selected to simulate real loads of IPA according to preliminary reports (Furtula et al., 2009; Sun et al., 2013).

A portable simulator (Fig. 1a) was selected to perform rainfall simulations (Irurtia and Mon, 1994). The device was located perpendicular to the ground surface. Once positioned at the center of each 1 m² plot, the simulator delimited a 0.25 m x 0.25 m work area. This device allowed applying constant rainfall intensity between 10 and 130 mm h⁻¹ on each plot (Sasal et al., 2015). A rainfall of 120 mm h⁻¹ was established, reflecting a worst-case scenario as reported by Kim et al. (2010) at 115 (mm h⁻¹), which also allowed each entire test (24 and 72 h) to be carried out in a single day. A running time of approximately 2 h per plot was achieved. Rain was simulated with dechlorinated tap water.

2.2. Solvents and reagents

All solvents used in chemical and chromatographic analysis were HPLC grade and all inorganic salts were analytical grade (JT Baker-Mallinckrodt Baker Inc., USA). A Sartorius Arium TM water purification system (Sartorius AG, Göttingen, The Netherlands) was used to obtain ultrapure water. Analytical standards of the studied IPA (MON, SAL, and LAS), GLP and AMPA, isotopically labeled glyphosate- 2^{-13} C, 15 N (GLP- 2^{-13} C, 15 N), and 9-fluorenylmethyloxycarbonyl chloride (FMOC-Cl) were purchased via Sigma Aldrich, St. Louis, MO, USA.

2.3. Sampling and extraction methods

Sampling started at the beginning of the runoff process, collecting water in a graduated tank (mm) at regular intervals of 5 min until constant runoff, which was accomplished after three equal and consecutive volume measurements, indicating that the basic soil infiltration rate was achieved (Sasal et al., 2015).

General parameters as pH and electric conductivity (EC) were determined in situ with the Lutron® multi-parameter probe (YK-2001PH and YK-200PCT). Runoff water collected on each plot was divided into 2 fractions. The fraction destined for IPA analysis was stored into 500 mL amber glass bottles with 1% of MeOH to avoid microbial degradation (Alonso et al., 2019), and were stored at -20 °C until further analysis. The other fraction was separated for GLP and AMPA, dissolved reactive phosphorus (DRP) analysis and total suspended solids. DRP was determined by the colorimetric procedure, according to American Public Health Association APHA, 1998. For the total suspended solids, 100 mL of runoff water were filtered in situ through a pre-weighed 0.45- μ m pore size, nylon filter (diameter, 47 mm), which were placed in a desiccator for 24 h for drying, and weighed to determine the weight (Mac Loughlin et al., 2020).

PL samples from each treatment were collected before rainfall

Table 2

Experimental set-up for each chemical group and residence time.

	24 h				72 h			
Physicochemical	-	PL-soil $(n = 9)$			UA-soil (n =	PL-soil $(n = 9)$		
parameters in runoff					3)			
Ionophore antibiotics (IPA)	-	Control (n = 3)	C1	C2	-	Control (n = 3)	C1	C2
			(n = 3)	(n = 3)			(n = 3)	(n = 3)
Glyphosate (GLP) and aminomethylphosphonic acid	Initial soil (n = 3)	PL-soil $(n = 9)$			UA-soil (n =	PL-soil $(n = 9)$		
(AMPA)					3)			

PL-Soil: Poultry litter amended soil; UA-soil: Unamended soil.

C1: 0.1 mg kg⁻¹ of monensin (MON), lasalocid (LAS) and salinomycin (SAL).

C2: 1 mg kg⁻¹ monensin (MON), lasalocid (LAS) and salinomycin (SAL)

simulation. Soil samples were taken at different depths after the simulation. Integrated fractions at surface (0–2 cm) and sub-surface level (2–20 cm) were collected at five points from the plot (Fig. 1b), adapting the design by Kim et al. (2010). Each soil fraction was homogenized in-situ and kept at -20 °C until further analysis. Dry weight of soil and PL was measured at 105 °C until constant mass, and organic matter content was determined by loss on ignition at 430 °C (SAMLA, 2004).

For runoff samples, the extraction method was adapted from Sun et al. (2013). Briefly, 7.5 mL of McIlvaine buffer (pH=7; 10 mM Na2EDTA) and 2.5 mL of MeOH were added to 30 mL of the water sample, followed by two ultrasound cycles (10'). Hexane (5 mL) was added to the tubes and after 30 min shaking and 10 min centrifugation, the organic layer was transferred to a glass tube. The procedure was repeated twice, and the combined hexane extracts were evaporated to dryness under N2 stream and were reconstituted with 0.5 mL of MeOH. Prior to LC-MS/MS analysis, the extracts were added 0.5 mL of a 5 mM Na2EDTA solution and then filtered by 0.22 µm (Alonso et al., 2019). For soils and PL, a similar method was applied, starting with 3 g of the solid samples instead (Sun et al., 2013). Surrogate samples from the different matrices were analyzed to evaluate the analytical recovery and matrix effect. Matched-matrix solutions were surrogated with known concentrations of IPA to assess the matrix effect. The recoveries of IPA in each analyzed matrix, ranged between 56% and 82% (PL); 89-94% (runoff water) and 67-81% (soils), in the same order as reported by other authors (Sun et al., 2013; Arikan et al., 2016).

For GLP and AMPA analysis in soils, PL and runoff waters, precolumn derivatization was applied with FMOC-Cl. 5 g of solid samples were spiked with [¹³C,¹⁵N] GLP. The analytes were extracted according to Primost et al. (2017), adding 25 mL of a 0.1 M K₂HPO₄ solution, followed by 3 cycles of ultrasound extraction of 10 min each. The extracts were centrifuged, and a 2-mL aliquot was adjusted to pH = 9 with Na2B4O7 (40 mM) and added with 2 mL of a FMOC-Cl ACN-solution (1 mg mL^{-1}) and left overnight. For water samples, a 2 mL aliquot was treated equivalently to the soil extracts. Standard solutions and reagent blanks were prepared under equivalent operational conditions for calibration and quantification purposes. Finally, derivatized samples were extracted with 5 mL of dichloromethane, centrifuged, and the aqueous supernatant filtered through a membrane of 0.22-µm pore size before LC-MS/MS analysis. For GLP and AMPA, the isotopically labeled GLP was used as an internal standard for the evaluation of the global recovery within each sample, with average values of $81 \pm 4\%$ and 78 \pm 5% for water and soil samples, in agreement to previous studies (Primost et al., 2017; Alonso et al., 2018).

2.4. Instrumental analysis

The analysis of IPA, GLP and AMPA was carried out with a Quattro Premier XE Tandem Quadrupole Mass SpectrometerTM (Waters) equipped with an electrospray-ionization source, set in the positive mode. The mass spectrometer was set to operate in multiple reaction monitoring (MRM) mode. Sodium adducts of IPA were selected as precursor ions $[M+Na]^+$ (Alonso et al., 2019). The optimized conditions for the chromatographic analysis of IPA, GLP and AMPA were previously optimized

and reported by Alonso et al. (2019) and Primost et al. (2017).

Parameters as linearity, reproducibility, detection, and quantification limits (LOD and LOQ, respectively) were tested accordingly. The ratio between the chromatographic areas of two mass transitions and the retention times were selected as analytical criteria (SANTE, 2019). Quantification was conducted with external calibration curves for the most abundant mass transition for each pollutant (Primost et al., 2017; Alonso et al., 2019).

2.5. Data analysis

The software MassLynx v4.1 and the TargetLynx package were used for data analysis. Since the concentration data did not follow a normal distribution, nonparametric tests (Kruskal-Wallis test and pairwise comparison) were applied for the statistical analysis of the data set. A Spearman correlation coefficient test was employed to evaluate the relations between concentration of nutrients and pollutants in runoff water and soils (at both depths). All the tests were set at a significance level of 0.05 and the statistical analyses performed by means of the INFOSTATTM software.

3. Results and discussion

3.1. Physicochemical characteristics of the runoff

A comparative analysis was performed between the water quality parameters in the collected runoff regarding the application of the PL (UA-soils vs. PL-soils) at the 72-h residence time (Table 3). Specific information for each plot is supplied in the Supplementary Material. An increase in the pH (p = 0.0008), EC (p = 0.0433) and DRP (p = 0.0034) values was observed when PL was applied. The variation of pH and EC is consistent with the contribution of slightly alkaline materials from the PL (Table 3). As for DRP, the levels found in the runoff from PL-soils were even higher than the concentration (2.03 mg L^{-1}) reported for soils amended with a rate of 7 ton ha⁻¹ of PL in Georgia, USA (Schroeder et al., 2004). Suspended solids in the runoff were not affected by the amendment (p > 0.05). Application of PL enhances the water retention capacity of soils as the local Aquic Argiudoll, but reduces rainwater infiltration, which can lead to higher runoff flows and soluble P losses, which can be transported by runoff and reach nearby surface water bodies (Lamelas et al., 2019).

No significant differences were found between pH, EC and DRP within 24 h and 72 h residence times of the PL. Schroeder et al. (2004) reported a decrease in the P losses from PL amendments at least 30 days after the application. The median DRP concentrations quantified (Table 3) in runoff water of PL-Soil were 4.0 mg L⁻¹ (24 h) and 3.6 mg L⁻¹ (72 h), both higher than the level reported by Sasal et al. (2015) in runoff (2.6 mg L⁻¹) collected 24 h after the application of an inorganic fertilizer (100 kg ha⁻¹ of calcium triple superphosphate) on the same studied soils. The PL-soil mixture constitutes a long-lasting source of P, that releases the nutrient over longer periods of time and multiple rainfall events (Kleinman and Sharpley, 2003). Several approaches like alum addition and composting have been reported as



Fig. 1. a Portable rainfall simulator. The main parts of the device are indicated in the side boxes. b Individual plot (left) and the area delimited by the rainfall simulator (right). The circles represent the site of the sample collected in the plot.

efficient methods to prevent the risk of P losses (Wang et al., 2015; Saleem et al., 2018).

Moreover, the application rate of poultry litter is commonly calculated based on nitrogen supply, reaching values four times greater than those used in the present work (over 20 ton ha^{-1} of fresh PL), according to the proper regulatory limit of micropollutants as Cu and Zn (Lamelas et al., 2019). In this scenario, the P input is oversupplied, and applications of fresh PL can lead to even greater P losses, decreasing water quality and causing environmental effects such as eutrophication (García-Albacete et al., 2012). Other environmental consequences of the mobilization of soluble phosphorus species involve competition of sorption sites from soils, enhancing pollutants desorption and therefore, their transport from soils into runoff or the soil column (Sections 3.2.2.1 and 3.3.2).

3.2. Input and mobility of ionophore antibiotics

3.2.1. Poultry litter

The studied PL, collected from a local farm from Entre Rios, showed mean residual concentrations of MON and SAL (Figs. 2, 3a, 3b) of 9 \pm 15 $\mu g~kg^{-1}$ and 1219 \pm 1473 $\mu g~kg^{-1},$ respectively (the LOD of both MON and SAL was 0.5 μ g kg⁻¹). As for LAS, initial levels in the PL were

Table 3

General parameters analyzed in poultry litter, runoff water and soils from each treatment after rainfall simulation. Complete results are detailed in **Table A** in Supplementary Materials.

Sampling plot	Unit	Poultry litter (PL)	Unamended (UA)-soils	Poultry Litter	· (PL)-Soils
Time	h		_	24	72
n	_	3	3	9	9
рН	UpH	$\begin{array}{c} 7.9 \\ \pm \ 0.02 \end{array}$	$\textbf{6.20} \pm \textbf{0.01}$	$\textbf{6.9} \pm \textbf{0.3}$	$\textbf{6.5} \pm \textbf{0,1}$
Electrical conductivity (EC)	$\substack{\mu S \\ cm^{-2}}$	$\begin{array}{c} 7700 \\ \pm \ 200 \end{array}$	138 ± 21	294 ± 171	250 ± 80
Total phosphorus	mg g ⁻¹	17 ± 1			
Dissolved reactive phosphorus (DRP)	mg L ⁻¹	_	0.47 ± 0.06	$\textbf{3.8} \pm \textbf{1.5}$	3.7 ± 1.4
Total suspended solids (TSP)	$\begin{array}{c} mg \\ L^{-1} \end{array}$	-	$\textbf{0.07} \pm \textbf{0.04}$	-	$\begin{array}{c} 0.08 \\ \pm \ 0.03 \end{array}$
Soil organic matter (SOM)	%	60 ± 2	$\begin{array}{c} 2.7\pm0.2\\ (02\text{ cm})\end{array}$	7.7 ± 0.6 (0–2 cm) 4.9 ± 0.2 (2–20 cm)	6.4 ± 0.7 (0–2 cm)

below the LOD (1 μ g kg⁻¹). These results agreed with previously reported low degradation rates on these biosolids, where both IPA were persistent for over 3 years (Biswas et al., 2012) and MON being less affected than SAL (Dolliver and Gupta, 2008; Sun et al., 2014). Quantified concentrations of IPA in the studied PL were of the same order of magnitude as found in commercial farms from Canada (Furtula et al., 2009) and USA (Biswas et al., 2012; Sun et al., 2014). These results characterize PL as an environmental source for these pollutants, and ionophore levels that may vary geographically according to each poultry practice (Furtula et al., 2009). Particular attention is drawn to the difficulty of acquiring litter without the presence of these xenobiotics to, for example, develop different environmental studies (Furtula et al., 2009, 2010; Biswas et al., 2012). The intra-variability among replicates (33-71%) for quantified concentrations of MON and SAL in PL agreed with the range (23-97%) reported by Furtula et al. (2009). This variability is also explained by the heterogeneity characteristics of the solid matrix and the small mass considered for the chemical analysis.

3.2.2. Surface runoff

3.2.2.1. Concentrations of IPA in surface runoff. For the IPA analysis, PLsoils were subdivided in 3 categories: Control, C1 and C2 (Section 2.1). The results of IPA in the runoff water are shown in Fig. 2. The 3 studied IPA were detected in the runoff, with MON and SAL being detected at

both treatments, after 24 and 72 h residence time. As expected from PL levels, runoff concentrations of SAL from C1 and C2 plots showed no differences from the control plots, and the mean concentrations of SAL at 24 and 72 h in runoff were 4.3 \pm 2.5 $\mu g \ L^{-1}$ and 3.8 \pm 1.3 $\mu g \ L^{-1}.$ For MON, C2 mean concentrations in the runoff at 24 (1.5 \pm 1.4 μg $L^{-1})$ and 72 h (0.7 \pm 0.4 µg L⁻¹) were higher than the Control samples of each time (p < 0.05). The mobility of LAS was affected by residence time, being detected at C1 only at 72 h, meanwhile the response at 72 h on surface runoff agreed with the expected spiked concentration on PL: C2 $(0.040 \pm 0.014 \ \mu g \ L^{-1}) \qquad > C1 \qquad (0.004 \pm 0.002 \ \mu g \ L^{-1}) \qquad > Control$ (<LOD). It is noteworthy that its presence in runoff increased over a short period of residence time (from 24 to 72 h), since other authors reported that a decrease in antibiotic losses started a week after the manure application (Barrios et al., 2020). Also, Sassman and Lee (2007) reported an inverse correlation of LAS sorption coefficients (Koc) with soil pH for several organic soils, whereas in this work, the increased mobility occurred when the runoff pH was lower (Table 3). It is expected that other factors not analized in the present study (DOM, clay content) play a major role in LAS sorption and desorption equilibriums in a real soil scenario (Sassman and Lee, 2007; Swan, 2012); .

The concentrations of MON in runoff water were positively correlated with SAL concentrations (Table B and C in Supplementary Materials), and both were significantly correlated with EC and DRP, at 24 h after the application of PL. Conversely to the 24 h results, MON concentrations mobilized by runoff at 72 h were not related to any of the other measured parameters. The solubility of MON depends on its chemical speciation (anion, protonated and sodium/potassium adduct), and it is affected by multiple interrelated physicochemical parameters, therefore even a slight pH decrease (as observed at 72 h) could have influenced its equilibrium in the runoff (Sun et al., 2016). At 72 h, SAL instead, was still correlated to EC and DRP, and was the only IPA that maintained a positive association with the concentration of soluble phosphorus at both times, which agreed with the reported capacity of phosphates to desorb SAL from PL (Ramaswamy et al., 2012).

3.2.2.2. Runoff losses in the environmental context. Runoff losses (%) were calculated as the ratio (percentage) between the mass of IPA in runoff water and the initial mass in PL. For MON, runoff losses at both times were up to 31% (24 h) and 22% (72 h) of the total mass respectively, higher than those reported by other authors. Kim et al. (2010) reported a runoff transport of 0.26%, from soils sprayed with liquid manure spiked with MON, while Dolliver and Gupta (2008) indicated a maximum transport of 2% after applying bovine manure directly on arable soils. Differences between IPA sources, application methodologies and residence time before rainfall event are influential factors on the partition of the pharmaceuticals to runoff (Doydora et al., 2015; Barrios et al., 2020), being PL application on surface soils the one exhibiting higher loss percentages.

Lower mobility percentages were registered for SAL (17%) and LAS



Fig. 2. Concentrations of salinomycin (SAL), monensin (MON), and lasalocid (LAS) in surface runoff, at 24 and 72 h. Statistically different treatments (p < 0.05) are indicated with letters (a,b) above the bars.



Fig. 3. Concentrations of salinomycin (SAL), monensin (MON), and lasalocid (LAS) in: a) the upper (0-2 cm) fraction of the studied soils, at 24 and 72 h; b) the lower (2–20 cm) fraction of the studied soils, at 24 and 72 h. Statistically different treatments (p < 0.05) are indicated with letters (a,b) above the bars.

(3.5%), reflecting maximum concentrations of 9.86 μ g L⁻¹ and 0.055 μ g L⁻¹ in runoff water, respectively. SAL was previously quantified in surface runoff from litter-fertilized soils at levels up to 9.0 μ g L⁻¹ (Sun et al., 2013). On the other hand, no further information of LAS mobilization from PL was found in the literature.

From an environmental perspective, the overall ranges of mean concentration values for MON and LAS (Fig. 2) found in runoff (0.020–1.450 μ g L⁻¹) even at C2, were within the range of IPA reported for surface water bodies of the Pampas region (0.004–4.670 μ g L⁻¹) by Alonso et al. (2019), and of the same order as other environmental concentrations reported in rivers from different countries (Lissemore et al., 2006; Bak and Björklund, 2014). The specific case of SAL is noteworthy, since a significantly higher initial load of in the PL determined higher runoff concentrations, with values up to 1 order of magnitude higher than the maximums observed in surface waters adjacent to husbandry facilities (1.150 μ g L⁻¹; Alonso et al., 2019).

3.2.3. Soils

The concentration of IPA at surface (0-2 cm; Fig. 3a) and subsurface (2-20 cm depth, "A" horizon; Fig. 3b) soils was analyzed. Most concentrations of IPA at the 2–20 cm were one or even two magnitude orders below the concentrations quantified at the 0–2 cm layer at both times. LAS was only quantified in 0–2 cm soils at C2, and under the tested conditions did not show a movement beyond 2 cm in depth, emerging at the 2–20 cm layer only at the 72 h treatment. This lower mobility of LAS is in accordance with its higher sorption coefficient range, when compared to MON and SAL. The 2–20 cm/0–2 ratio (as a percentage) of MON was up to 38% at 72 h, reaching higher values than those obtained at 24 h (Fig. 3a, b). Other authors found that MON is mobilized in the soil column to a depth of 30 cm, obtaining the maximum percentage (36.1%) at a depth of 20 cm (Kim et al., 2010). Regarding SAL, no statistical differences were found in the vertical mobility percentages between both residence times. In comparison with

the losses of SAL by leaching in the 2–20 cm soil layer, a lower proportion than MON was observed, reaching a maximum of 9% (7 μ g kg⁻¹). This range was less than the expected according to the initial concentrations in the PL and considering that SAL was previously reported on the 10–20 cm fraction of soils, at 30 μ g kg⁻¹ in soils amended with manure (Bak and Björklund, 2014).

It is important to mention that after the rainfall, no differences regarding MON and SAL concentration were found between C1 and Control plots in soils and runoff (Section 3.2.2.1). Those results indicate a close behavior of both compounds in soils, as reflected by their similar Koc range (Section 1.1). Furthermore, spiked levels of MON and SAL were masked by the preliminary load of the compounds in PL. Higher additions of the pollutants were not assayed as they would have generated non-real solid matrices.

The mobility of IPA in the soil column depends on the composition and consequently, physicochemical properties of the soil (Sassman and Lee, 2007). At the studied soil, typical pH values are in the vicinity of 5.7 (Tezanos Pinto - INTA), and thus the transport of IPA can be favored due to the prevalence of the anionic species in their speciation equilibrium (Sassman and Lee, 2007; Sun et al., 2016). Soil organic matter (SOM) is expected to play an important role in the sorption of MON. Biswas (2014) found a positive correlation between soil-sorbed MON and organic matter (%) from 74 soils (ranging between 0.1% and 3.1%). However, depending on the pH, higher amounts of SOM provided by the amendments increase DOM, which facilitate MON desorption and transport in the soil column (Biswas, 2014; Doydora et al., 2017). In the present study, %SOM increased from 2.67% before PL to 7.6% (0-2 cm) and 4.8% (2-20 cm) (Table 3), which represent a high organic-content scenario according to Yoshida et al. (Yoshida et al., 2010), and possibly explained by the fact that surface applied PL is not subjected to rapid microbial descomposition (Nyakatawa et al., 2001). Regarding SAL, it is expected that other factors have a higher influence than SOM on its sorption, such as the content of clay or sand or phosphate levels

(Section 3.2.2.1). Further studies should aim to understand specific sorption and persistence processes with regards to those levels of SOM and the resulting DOM, as another influential factor derived from the amendment.

The application of PL in the present study, led to IPA concentrations into soil fractions corresponding to the rhizosphere, which could be uptaken by crops (Broekaert et al., 2012). Translocation could suppose a route of human exposure to these pollutants through food, which raises the need for its regulation, and must be included in quality controls and agri-food safety.

3.3. Mobilization of glyphosate and AMPA

3.3.1. Soils

Glyphosate and AMPA were not detected in PL (< 0.1 µg kg⁻¹). Both compounds were quantified in the 0–2 cm fraction of the Initial soils from the studied site, with mean (maximum) concentrations of 40.1 \pm 19.8 µg kg⁻¹ (62.7 µg kg⁻¹) and 61.8 \pm 22.3 µg kg⁻¹ (87.3 µg kg⁻¹), respectively. Concentrations of both compounds were of the same order as those previously reported by Sasal et al. (2015) for the same fields.

No interactions were found between IPA, GLP and AMPA concentrations, thus all PL-soils were treated as one group, in contrast to the UA-soils. After the rainfall simulation assays, quantifiable concentrations of GLP and AMPA were detected in both analyzed fractions of soils (Fig. 4a, b) and in runoff water (Fig. 4c). The concentrations of GLP in the surface (0–2 cm) fraction were significantly lower (p = 0.0102) than those detected in the surface soils before the rainfall. Higher mean concentrations of GLP and AMPA (Fig. 4a, b) were detected in surface soils ($22.2 \pm 7.7 \ \mu g \ kg^{-1}$ and $57.6 \pm 19.5 \ \mu g \ kg^{-1}$, respectively) than those found at the 2–20 cm layer ($10.4 \pm 2.4 \ \mu g \ kg^{-1}$ and $8.0 \pm 5.1 \ \mu g \ kg^{-1}$, respectively). In the studied real agricultural system, GLP and AMPA were retained in the upper fraction of soils rather than mobilized to subsurface layers, in accordance with the results of Okada et al. (2016). No statistical differences were observed between the residual concentrations of GLP and AMPA detected in the UA-soils and

PL-soils in both fractions. The GLP/AMPA ratio (Table 4) was calculated to analyze patterns in the distribution regarding the surface soil (0-2 cm). The ratio at the 0-2 cm fraction was similar for both soil treatments, indicating a prevalence of AMPA in the upper fraction, which Okada et al. (2018) reported as more persistent than the parent GLP. An opposite scenario was observed for the ratio GLP/AMPA at 2-20 cm, with the values > 1, indicating a higher relevance of GLP in the lower fraction. Considering the similar concentrations of GLP at 2-20 cm in both soils (UA and S+PL), the lower ratio determined for the amended soils reflects the influence of the PL in the concentrations of AMPA (Fig. 4b). The amount of P incorporated by the PL (Section 3.2) into the soil favors the desorption of AMPA when competing for sorption sites (Sidoli et al., 2016). In a larger extent, these results support with insight to the studies of Demonte et al. (2018) and Okada et al. (2018) who found a higher relevance of AMPA in groundwater from Argentina, where P fertilizers are applied besides GLP formulations as part of the chemical management in which the production model is based (Sasal et al., 2015).

3.3.2. Runoff

For surface runoff waters, higher levels of GLP (p = 0.0386) were found in water collected from PL-soils ($1.6 \pm 1.1 \ \mu g \ L^{-1}$) than in UA-soils ($0.16 \pm 0.06 \ \mu g \ L^{-1}$), in contrast to AMPA, in which case no statistical differences were detected between treatments. The ratio between runoff and initial soil concentrations are similar to those reported by

Table 4

Calculated quotient glyphosate/aminometylphosphonic acid (GLP/AMPA) for each analyzed matrix.

Matrix	UA-soil	PL-soil
GLP/AMPA (0–2 cm) GLP/AMPA (2–20 cm) GLP/AMPA runoff	$\begin{array}{c} 0.40 \pm 0.09 \\ 2.4 \pm 0.8 \\ 0.08 \pm 0.06^{*} \end{array}$	$\begin{array}{c} 0.39 \pm 0.06 \\ 1.6 \pm 0.6 \\ 0.5 \pm 0.2^{*} \end{array}$

^{*} Samples showed significant statistical differences (p = 0.0096)



Fig. 4. Concentrations of glyphosate (GLP) and its metabolite AMPA in a) the 0-2 cm fraction for both soil treatments: unamended soil (UA) and soil + poultry litter (S+PL); b) the 2–20 cm fraction for both treatments; c) the water runoff for both treatments. Statistically different treatments (p < 0.05) are indicated with letters (a, b) above the boxes.

Sasal et al. (2015). The relative mobility in runoff is favorable to GLP, also reflected in the GLP/AMPAGLP/AMPA ratio (Table 4), which might have been a consequence of specific desorption mechanisms in the amended (PL) soils. Moreover, positive correlations were found between GLP and both DRP (r = 0.73, p = 0.0074) and EC (r = 0.71, p = 0.010) in runoff, which denotes the relevance of the inorganic content supplied by the PL in the sorption and the consequent input of the herbicide into the water. The loss of the GLP was calculated as the percentage in runoff with regards to the concentrations in the studied soils before rainfall. After 1 h rainfall simulations, UA-soils exhibited GLP losses up to 0.56%, while losses from PL-soils reached a maximum of 9.84% (Fig. 4c). Increased phosphate levels were previously reported as desorption promoters of GLP (Gimsing et al., 2004; Padilla and Selim, 2019), and the process was verified after chemical fertilization with industrial phosphorus-based products in Argentinean soils of the same characteristics as those studied in the present work (Sasal et al., 2015). This interaction has been widely described from chemical fertilizers, but not at the same extent for the organic amendments such as PL, this being one of the first works to report this process in Argentina. The results indicate that the mobilization of GLP could be associated with P sources independently of their nature. However, since the behavior of AMPA in runoff showed no differences between UA and PL soils, neither it was not related to the other variables studied, other factors could be involved in the GLP desorption mechanism besides the phosphonic acid moiety. Furthermore, GLP concentrations in the runoff samples were inversely correlated to the water pH (p = 0.048), in this way sorption of GLP (not AMPA, due to the absence of the carboxylic group) is also affected by pH, with desorption being higher in acidic soils (Munira et al., 2018) as the one we studied in the present work.

The results obtained in the present study were registered after a single rainfall event at each time. Therefore, if physicochemical properties of the soil are affected, resulting in lower pH conditions and high loads of P remain in the surface layer of soil, these pollutants could be released again after the next rainfall event. Moreover, long-term applications can transform these systems into permanent sources of these compounds as has been reported for DRP (Bos et al., 2021), and increase the desorption (and therefore, their mobility) of pollutants in the soil, as GLP and AMPA (Munira et al., 2018) or MON (Doydora et al., 2017). The lesser retention of these pollutants favors their transport to aquatic systems by surface runoff.

Both IPA (Alonso et al., 2019), GLP and AMPA (Primost et al., 2017; Castro Berman et al., 2018) have been previously reported on aquatic environments from agroproductives zones of Argentina. However, the application of PL in adjacent fields has not been considered as a relevant exposure source yet. Considering the extensive use of this herbicide in current agriculture, the risk of compounds mobilization after PL application should be assessed, and further research of the consequences must be addressed.

4. Conclusions

The present work comprised a field scale study, which characterized the effect of PL application on soils regarding the input and mobility of agricultural pollutants as ionophores, GLP and AMPA after a rainfall simulation. The PL modified the physicochemical characteristics of the runoff, and contributed a load of dissolved phosphorus, which affects the sorption and transport of soil pollutants. PL provided by local commercial farms showed quantifiable residual loads of MON and SAL, which were mobilized by surface runoff. MON was the most detected compound in all the studied matrices, showing the maximum losses in both processes.

A decrease in soil GLP concentrations was observed after the rainfall simulation. Inversely, an increased transport via runoff was observed when PL was added to the soil. AMPA exhibited highest concentrations at the surface layer, reflecting its strong binding to soil particles. According to the GLP/AMPA ratio, GLP was more susceptible to be transported in the runoff, and to lower soil layers. The increased concentration of soluble phosphorus is a relevant factor in the mobility of these compounds, and other parameters as pH can be also intervening.

The use of poultry litter as an organic amendment in agricultural soils is a widespread practice due to the contribution of nutrients and the material recycling, in terms of circular economy. However, the practice constitutes a diffuse source of high loads of nutrients and veterinary antibiotics and involves the release of soil pollutants that influence surface and groundwater quality, according to the environmental dynamics of each compound. In perspective, strategies for reducing the animal wastes and their antibiotic content must be investigated regarding the productive practice involving these residues, as water and soil conservation are proven to be a key asset in the sustainability and success of circular economy processes. Also, alternative production systems must be approached to preserve the usage of substances as antibiotics, as recommended by FAO and WHO. This is the first study to demonstrate the combined release of pollutants from multiple sources, after the amendment with poultry litter on real agricultural soils. Further research should aim to characterize the potential risk of combined pollutants as glyphosate and ionophore antibiotics.

Ethics approval and consent to participate

Not applicable.

CRediT authorship contribution statement

Marcos Navarro: Methodology, Investigation, Writing – original draft. **Lucas L. Alonso**: Conceptualization, Methodology, Validation, Writing – review & editing, Supervision. **Alberto L. Capparelli**: Conceptualization, Resources, Funding acquisition. **Damián J. Marino**: Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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Ethics declarations

NA.

Consent for publication

Not applicable.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agwat.2022.107963.

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