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Evidence for soil pesticide contamination of an agroecological farm from a neighboring chemical-based production system

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ABSTRACT

The global chemical-based agriculture (*CBA*) production system brought social and environmental consequences such as the contamination of soils, waters, bottom sediments and food, as well as negative effects on non-target species. As an alternative, a new paradigm emerged: agroecology-based agriculture (*ABA*), based on ecosystem services and the reduction of chemical inputs. More and more establishments have adopted this form of production; however, they are located next to crops to which pesticides are applied. The objective of this work was to study, through the spatio-temporal characterizations of pesticides in soils, how an *ABA* production system can be affected by the *CBA* fields around it. Two sampling campaigns were conducted and soil samples were obtained from "La Aurora", an agricultural establishment located in the Argentine pampa and recognized by the FAO for its agroecological practices, and from neighboring fields with *CBA* productions. The samples were tested for 19 herbicides (including 3 metabolites) and 3 fungicides by UPLC-MS/MS, of which we detected glyphosate and its metabolite AMPA, 2,4-D, atrazine, acetochlor, metsulfuron-methyl, desethyl-atrazine, epoxiconazole, and tebuconazole. Three or more pesticides co-occurred in 93% and 32% of the *CBA* and *ABA* samples, respectively. Glyphosate and AMPA, with the highest detection frequency, also accounted for 90% of the total pesticide load in both systems. The maximum concentrations (μg kg^{-1} dry weight) in the CBA/ABA fields, respectively, were glyphosate (1268.92/98.93), AMPA (2919.17/114.01), followed by 2,4-D (38.52/31.12), and epoxiconazole (13.35/18.41). No significant temporal differences were found in glyphosate concentration within each establishment, corroborating its pseudo-persistence in *CBA* establishments, and establishing it in *ABA* field. Moreover, glyphosate was found in the *ABA* field more than 300 m from the limit with the CBA fields. Glyphosate and AMPA concentrations are in the order of those reported to cause sublethal and lethal effects in soil organisms. These results highlight the mobility of pesticides, as the *ABA* establishment is affected by its surroundings where pesticides are used, even at sites far from the interface between them. Given their higher detection frequencies and environmental concentrations in comparison to the other pesticides, glyphosate and AMPA are proposed as environmental tracers of conventional agroproductive activities.

1. Introduction

World food production is continually adopting the latest advances in agricultural (bio)technology, like the development of genetically modified organisms (GMOs), the use of pesticides, no-till (or zero tillage) and the introduction of computerized machinery. With this way of

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production, the cultivated area worldwide of biotech crops increased 110 times in just 21 years of commercialization of these new technological developments (ISAAA, 2016).

Argentina is the third country, after the United States and Brazil, with the largest area cultivated with GMOs in the world, reaching 23.6 million ha planted in 2017 (ISAAA, 2017). This expanse represents 61% of the area cultivated with extensive monocrops during the 2017/2018 agricultural cycle(July 1, 2017 - June 30, 2018) in Argentina (MAGyP, 2019). Out of the total cultivated GMOs, the majority corresponds to soybeans (77%), followed by corn (22%) and cotton (1%) (ISAAA, 2017). As a result of the tendency towards monoculture practices and the increasing use of the previously mentioned biotechnological tools, chemical control to combat weeds, pests and diseases has intensified, as well as the use of synthetic fertilizers to replenish nutrients (FAO, 1990; Sarandón and Flores, 2014). According to the latest official information reported in Argentina, the use of pesticides increased by 900% since the approval of the first transgenic event in 1996, with 317 million kg or L of active ingredients being used in 2012, and showing an increasing trend in use (CASAFE, 2012).

The conventional production system, also known as *chemical-based agriculture* (*CBA*), has brought socio-cultural and environmental problems as consequences (Leguizamón, 2014; Rauchecker, 2019). The use of pesticides, together with intensive mechanical practices, can result in the loss of natural habitats, and consequently alter the biodiversity associated with them (Benton et al., 2003; Sharma et al., 2018). The harmful effects of these compounds on beneficial species, for example, insects and arthropods that provide ecological services and functions such as biological control of pests and pollination, or oligochaetes and microorganisms responsible for nutrient recycling and maintaining soil structural properties, has been reported (Benamú et al., 2010; Pelosi et al., 2014; Evans et al., 2018; Sharma et al., 2018; Wołejko et al., 2020).

Glyphosate (GLP) is the most extensively used pesticide worldwide and in Argentina, accounts for 62% of the pesticides sold in the country (CASAFE, 2012). GLP is a broad-spectrum, systemic and post-emergent herbicide, applied to GM crops resistant to it for weed control in no-tillage systems (Okada et al., 2016; Primost et al., 2017). Due to its physicochemical properties, it binds strongly to soil components, with reported half-life of up to 197 days, conditioned by soil type, climate conditions and microbial activity. The main degradation product is the aminomethylphosphonic acid (AMPA), which in turn degrades more slowly than glyphosate in soils, with a half-life range from 60 to 240 days (Giesy et al., 2000). Moreover, Primost et al. (2017) has classified both molecules as pseudo-persistent in Argentinian soils. The increase in pesticide use is due to, not only the larger expanse of cultivated area, but also to the development and spread of pesticide resistance by some pests and pathogens, which consequently leads to the use of higher doses and/or the release of new active ingredients and formulations (Sarandón and Flores, 2014).

Once released into the environment, the fate of every compound is variable, as pesticide dynamics fundamentally depend on their physicochemical properties and weather conditions, as well as soil properties (Azcarate et al., 2015; Okada et al., 2016). Concentrations of some of these compounds have been reported in surface waters, soils and sediments (Ronco et al., 2016; Mac Loughlin et al., 2017; Etchegoyen et al., 2017; Van Bruggen et al., 2018; Silva et al., 2019), in food (Mac Loughlin et al., 2018), and in rainwater and air particulate matter (Chang et al., 2011; Alonso et al., 2018). Concurrently, there is evidence to the adverse effects they cause on non-target species, and, ultimately, pose a risk for biodiversity (Van Bruggen et al., 2018; Iturburu et al., 2019; Trudeau et al., 2020).

Agroecology emerged in the 1970s as a new approach and paradigm in Agricultural Sciences in Latin America, and has been gaining strength on account of the environmental, social and productive problems caused by the conventional system (Altieri, 2017; Sarandon and Marasas, 2017). Different from organic agriculture, that adopts specific measures such as prohibition of certain agrochemicals in order to meet the certification requirements, the agroecological practices seek the stability and sustainability of the agrarian system by strengthening ecological processes or functions, thus resulting in a decrease or elimination of chemical inputs (Gurr et al., 2016; Altieri, 2018). The agro-biodiversity (genetic, specific, and structural), when just maintaining the key necessary components, can provide functional ecological services such as pests and pathogens regulation, nutrient cycling (decomposition of organic matter and maintenance of soil fertility), control of erosion (vegetation cover), pollination, among others (Altieri, 2018).

In Argentina, there are no official reports of the number of *agroecological-based agriculture* (*ABA*) systems, since only organic certified crops are registered nationally, representing 0.1% of the total extensive production (SENASA, 2019; MAGyP, 2019). However, the growth of the ABA production (Sarandon and Marasas, 2017) is reflected on its addition as a type of agricultural practice in the National Agricultural Census carried out in 2018 (INDEC, 2020 - Data is still in the analysis stage).

The expansion of *ABA* systems is still in an initial stage, which means that these systems will be immersed in an environment of conventional systems where pesticides are used. Given their close proximity, and taking into consideration the complexity of pesticide dynamics in the environment, it is relevant to assess the reach of these agrochemicals in these scenarios, as they can alter the ecological functions in agroecological plantations. Therefore, the objective of this work was to study, through the spatio-temporal characterizations of pesticides in soils, how an *ABA* system can be adversely influenced by the pesticide applications in the *CBA* crop fields around it.

2. Materials and methods

2.1. Study area

The study area is located in Benito Juárez, in the south of the Province of Buenos Aires, Argentina. The region is a landscape of soft to moderately undulating plains, with slight depressions of the "Pampa Deprimida Occidental Sector" sub-region, in a well-drained hillside position, developed in loessic sediments on a calcareous crust of regional extension, non-saline, non-alkaline, on slopes of 1% (INTA, 2002). The climate is mesothermal humid (temperate), with average annual precipitations between 800 and 900 mm. The annual average temperature is 13.8 °C, with an average maximum and minimum temperature of 21.4 °C and 6.9 °C, respectively (INTA, 2014). The soil of the region is a typical Argiudol. The main use of the land is livestock production and extensive agriculture, with the less suitable soils used for raising cattle, and the intermediate to good ones dedicated to agriculture (Cerda et al., 2014). The selected study system is an extensive *ABA* and livestock production farm adjacent to conventional agricultural fields with a *CBA* production system.

2.1.1. ABA: Agroecological-based agriculture

The agroecological farm “La Aurora” has a total surface of 650 ha, of which 15 ha are not agriculturally exploited,186 ha correspond to low grounds, 152 ha to hills, and 297 ha to agricultural soils, in turn divided into 14 plots (Fig. 1). In 1997, an agroecological transition process began, which involved strengthening rotation, maximizing carbon fixation, increasing the surface area of crop associations with legumes (biological nitrogen fixation), enriching soil organic matter, improving the animals’ diet and the use of their manure to balance nutrients in the soil, among others. This *ABA*-management succeeded in reducing the use of agrochemicals, with the last herbicide application in 2011 (Table 1) (Iermanó, 2015; Cerdá et al., 2014). In 2016, “La Aurora” was recognized by the FAO as one of 52 worldwide agroecological farm, for having demonstrated that productive agriculture without agrochemicals is not only possible, but also profitable (FAO, 2016).

The plots that have agricultural aptitude are planted with annual crops, winter greens and pastures. The main winter crops are wheat

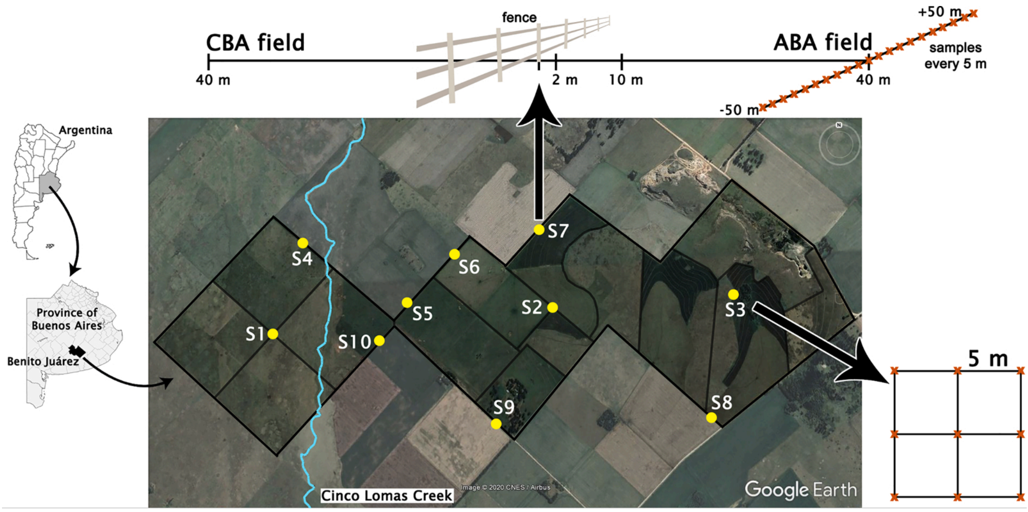

Fig. 1. Geographic location of the “La Aurora” (*ABA* field), in a darker shade, surrounded by *CBA* fields, in a lighter shade, in Benito Juarez, Province of Buenos Aires, Argentina. The 14 parcels in which the ABA field is subdivided are shown. Sampling sites are shown with yellow dots. Graphical representation of the sampling methodology for border sampling sites, shown with S7, and center sites (>300 m), shown with S3. The transect is only shown in for the 40 m distance in the *ABA* field, but the same procedure was applied for the other distances (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Table 1
Land use in the *ABA* (Agroecological Based Agriculture) field for each campaign, and registry of pesticide applications until 2011, when the last application occurred.

Site	Last application (year)*	Land Use	
		C1 (July-winter)	C2 (November-Spring)
S1-ABA	n.p.a.	Pasture (cattle)	Pasture (cattle)
S2-ABA	2,4D - Dicamba (2011)	Sorghum	Sorghum (cattle)
S3-ABA	2,4D- Dicamba- Metuslfuron Methyl (2011)	Natural Field	Natural Field
S4-ABA	n.p.a.	Pasture	Pasture
S5-ABA	Metsulfuron methyl (2010)	Tillage	wheat + clover
S6-ABA	n.p.a.	Pasture + oat + *Vicia sp.* (cattle)	Pasture + oat + *Vicia sp.* (cattle)
S7-ABA	2,4 D Amina-Dicamba (2011)	Oat + *Vicia sp.*	Oat + *Vicia sp.*
S8-ABA	2,4D- Dicamba- Metuslfuron Methyl (2011)	Clover (cattle)	Clover
S9-ABA	Dicamba (2010)	Corn	Corn harvested
S10-ABA	n.p.a.	Tillage	wheat + clover

n.p.a. : no pesticide applications since 2006.
* Personal records on pesticide applications and management practices provided by the farmer and owner of the “La Aurora”, Juan Khier.

(*Triticum aestivum* L.), barley (*Hordeum vulgare* L.), and oats (*Avena sativa* L.), all in consortium with legumes such as red clover (*Trifolium pratense* L.) or *Vicia* sp. During the summer, the crops are forage sorghum (*Sorghum bicolor (L.) Moench*), graniferous sorghum (*Sorghum sudanense (Piper) Stapf*), and corn (*Zea mays*). In general, saved crop seeds are used for new plantings. During each crop rotation, cattle are introduced into these plots in order to feed on the stubble and fertilize the soil. As previously mentioned, due to soil restrictions, there are plots dedicated exclusively to livestock farming, but no plot is exclusively arable.

2.1.2. CBA: chemical-based agriculture

The fields neighboring “La Aurora” currently rotate their crops between soy, sunflower or corn during the summer, and wheat, rapeseed, or barley during the winter. Unlike the *ABA* field, these *CBA* establishments do not have any livestock activity. As the latter’s production is carried out in a conventional way, agrochemicals are used during the

Table 2
Land use in the *CBA* (Chemical-Based Agriculture) fields for each campaign, and pesticides used for each crop.

Site	C1 (July-winter)	C2 (November-spring)	Pesticide Applieda (month)*		
			Fallow	Growing	
			Herbicides	Herbicides	Fungicides
S4-CBA	Wheat	Wheat	Glyphosate, metsulfuron-methyl (April-June)	Glyphosate, metsulfuron-methyl, 2,4-D (September-October)	Epoxiconazol, tebuconazole (October-December)
S5-CBA **S6-CBA** **S10-CBA**	Chemical fallow	soybean	Glyphosate, metsulfuron-methyl, 2,4-D (May-October)	Glyphosate, acetochlor (December-January)	Epoxiconazole (January-April)
S7-CBA	Chemical fallow	Barley	Glyphosate (April-June)	Metsulfuron-methyl, dicamba (July-September)	Epoxiconazol, tebuconazole (July-November)
S8-CBA	Chemical fallow	Wheat	Glyphosate, metsulfuron-methyl (April-June)	Glyphosate, metsulfuron-methyl, 2,4-D (September-October)	Epoxiconazol, tebuconazole (October-December)
S9-CBA	Chemical fallow	Chemical fallow	Glyphosate, metsulfuron-methyl, 2,4-D (May-October)		

* Based on surveys carried out with producers in the province of Buenos Aires, regarding the crops and pesticides applied (DP, 2015).

pre-sowing period (chemical fallow with herbicides), and at growth stages (pesticides and fertilizers).

2.2. Sampling

Two sampling campaigns were carried out, **C1** during the winter (July 2016) and **C2** in the spring (November 2016), in order to evaluate temporal variations in environmental pesticide concentrations as a consequence of the different application frequency and rates (DP, 2015), in accordance with production cycles (Table 2). Ten sampling sites were selected according to the spatial extent and surrounding *CBA* fields. Of these, 3 locations were in the middle of the *ABA* field (S1 to S3), more than 300 m from the *CBA-ABA* borders, and 7 locations were in the border area between *CBA* and *ABA* fields (S4 to S10). At each site, subsurface soil samples from the first 10 cm were collected (Bento et al., 2016). The location of the sampling sites and a scheme of the sampling methodology is summarized in Fig. 1.

For sites S1-S3, which were in the ABA farm more than 300 m from the CBA borders, samples were taken every 5 m on a 10 m by 10 m grid, as shown for S3 in Fig. 1, and combined to create a composite sample. At the border sites (S4 to S10), samples were taken at different distances from the fence that divides the fields: on the *CBA* side, at 40 m from the fence, and on the *ABA* side at 2, 10 and 40 m from the fence, as exemplified with the S7 in Fig. 1. At each distance, moving perpendicularly 50 m to each side, subsamples were collected every 5 m; then combined to obtain one sample (approximately 1 kg) for each distance from the fence. Therefore, in each campaign, 3 samples were taken from the middle of the *ABA* farm (S1-S3), 7 from the *CBA* fields (S4-S10), and 21 samples from the agroecological side at different distances from the border with the conventional fields (7 sites × 3 distances).

The distances from the border were chosen based on the recommendations of the farmer and the agroecological field advisor, who observed less growth of their crops at a distance of up to 40 m from the *CBA* field.

In each sampling campaign, the crop present in the *ABA* (Table 1) and *CBA* (Table 2) production lots was recorded, so as to be able to associate pesticide concentrations results in the soil samples with the crop being grown.

2.3. Pesticides studied

The pesticides analyzed consisted of 16 herbicides: 2,4-D (2,4-dichlorophenoxy acetic acid), acetochlor, ametryn, atrazine, chlorimuron, dicamba, diclosulam, glyphosate (GLP), flurochloridone, imazapic, imazapyr, imazaquin, imazethapyr, metolachlor, metribuzin, metsulfuron-methyl; 3 herbicides metabolites: aminomethylphosphonic acid (AMPA), desethyl-atrazine, desisopropyl-atrazine; and 3 fungicides: tebuconazole, epoxiconazole, metconazole.

2.3.1. Sample analysis

The soil samples were homogenized, ground and sieved through 2 mm mesh. A sub-sample (1 g) was taken and dried until constant weight at 105 °C to determine moisture content and express pesticide concentration as μg kg^{-1} dry weight (dw).

Herbicides and fungicides were extracted by employing the *QuEChERS* (Quick, Easy, Cheap, Effective, Rugged and Safe) procedure with modifications proposed by Masiá et al. (2015) and Mac Loughlin et al. (2017). The procedure stated in brief: 5 *g* of wet soil were weighted in a 50 mL polypropylene tube, spiked with isotopically labeled atrazine (atrazine-D_5, purchased from Sigma Aldrich) as internal standard, so as to have a nominal concentration of 100 μg L^{-1} at instrumental analysis, and then 10 mL of nanopure water were added, the tubes were shaken, and left to stand for 5 min. Then, 15 mL of acetonitrile were added, and two 15-minutes sonication cycles were performed. The extraction salt mixture (2 *g* NaCl and 6 *g* anhydrous $MgSO_4$) was added and vigorously shaken manually for 1 min, then centrifuged 10 min at 3000 rpm. Of the supernatants, 1 mL was filtered through a 0.22-μm pore size nylon filter and transferred into a chromatographic vial for instrumental analysis.

For the extraction and analysis of glyphosate and its environmental metabolite AMPA, the procedure proposed by Aparicio et al. (2013) was followed. All the samples were spiked with isotopically labeled-glyphosate (glyphosate-2-^{13}C,^{15}N, 99 atom% ^{13}C, 98 atom% ^{15}N, purchased from Sigma Aldrich) as internal standard, in order to achieve a 100 μg L^{-1} nominal concentration at instrumental analysis. In short, 5 *g* of soil was weighed into a 50 mL polypropylene tube and extracted with 25 mL of a 100 mM K_2HPO_4 solution at pH = 9. Three sonication cycles of 15 min each were applied and, then, samples were centrifuged at 3000 rpm for 10 min. Of the supernatants, 1 mL was derivatized with a 1 mg mL^{-1} solution of 9-fluorenylmethyl chloroformate (≥99.0%, for HPLC derivatization, Sigma Aldrich) in acetonitrile, leaving it to react overnight in the dark. A clean-up was performed by adding dichloromethane. Finally, the aqueous phase was filtered through a 0.22-μm nylon filter prior to instrumental analysis.

2.3.2. Instrumental analysis

Instrumental analysis was performed with a Waters Acquity Ultra Performance Liquid Chromatography (UPLC) system coupled to a Quattro Premier XE tandem quadrupole mass spectrometer (MS/MS), with an electrospray ionization (ESI) source. High purity nitrogen was used as the nebulizer and drying gas, and argon was used as the collision gas. For the analysis of glyphosate and AMPA, the UPLC was equipped with a C_{18} Acquity UPLC BEH column (1.7 μm, 50 × 2.1 mm), operating at a flow of 0.50 mL min^{-1}, with a methanol-nanopure water gradient, both solvents 5 mM NH_4Ac. For the chromatographic separation of the rest of the herbicides and fungicides, a C_{18} column (1.7 μm, 100 × 2.1 mm) was used, at a flow of 0.3 mL min^{-1} with acetonitrile/methanol-nanopure water gradient (previously conditioned with formic acid). The ESI ionization source operated in positive mode for all compounds, except for 2,4-D and dicamba, for which the source was used in negative mode. The software MassLynx v4.1 and the TargetLynx package were used for data analysis.

2.3.3. Quality control and quality assurance

The performance of each analytical method was carried out by quantifying isotopically labeled glyphosate and atrazine in each sample, using their recovery as a quality criterion. At the same time, blank reagents and random duplicate samples were performed. Pesticide quantification was performed by means of an external standard calibration curve, in a range of 0−200 μg L^{-1}.

At least two transitions were used for each analyte, with the transition of higher abundance used for quantification (Q) and the second used for confirmation (q). Subsequently, the Q/q area ratio in the positive samples was used in comparison to the standard as a criterion to identity the pesticide (Furlong et al., 2001), accepting a deviation no greater than 20% from the Q/q ratio of the standard (SANTE, 11945/, 2015). The limits of detection (LOD) and quantification (LOQ) were calculated from the signal-to-noise ratio (S/N), applying times 3 and 5 as factors, respectively. Recovery, linearity, precision, matrix effect, LOD and LOQ were evaluated in accordance with the criteria established by SANTE, 11945/, 2015.

Percentage recoveries for isotopically labeled standards ranged from 60% to 110% for atrazine-D_5, and 80%–100% for glyphosate-2-^{13}C,^{15}N. These factors were considered to correct the concentration in each individual soil sample. The LOD and LOQ obtained for the *QuEChERS* procedure ranged from 0.01–7.8, and 0.03 to 30.4 μg kg^{-1}, respectively. With regard to glyphosate and AMPA, LOD and LOQ were 2 and 4 μg kg^{-1}.

2.4. Data analysis

Descriptive statistics (median, minimum and maximum ranges, detection frequency) were performed with concentrations above the

LOD, and concentrations below LOQ (detectable, non-quantifiable) were replaced by the mean value between corresponding LOD and LOQ. Statistical analyses were performed only on glyphosate and AMPA concentrations, with concentrations below LOD were replaced by LOD/2. (Etchegoyen et al., 2017; Antweiler, 2015). The percentage AMPA (% AMPA) was calculated for each soil sample as the ratio of AMPA concentration to the sum of glyphosate and AMPA concentration, AMPA= [AMPA/(Glyphosate + AMPA)]*100 (Battaglin et al., 2014; Silva et al., 2018). Since the concentration data did not follow a normal distribution (Shapiro-Wilk test), nonparametric tests were used for its analysis. Wilcoxon–Mann–Whitney test was used to assess significant differences in concentrations between production systems, and for temporal variations within each system. For spatial analysis, the Kruskal-Wallis test was employed; if differences were statistically significant, multiple *a posteriori* comparisons were performed according to the guidelines proposed by Conover (1999). The relationship between compounds, where concentrations were above the LOD, each production system was analyzed using Spearman correlations. For all tests, the level of significance was set at $p < 0.05$. Statistical analysis was performed using InfoStat (version 2020I) and STATISTICA (Stat Soft, Inc. 2001; version 7).

3. Results and discussion

3.1. Detection, mass load and relative proportion of occurrence of the studied pesticides

Recovery values, LOD and LOQ were consistent to those published by other authors (Aparicio et al., 2013; Primost et al., 2017; Masiá et al., 2015) and in accordance with the ranges accepted by the SANTE regulation, 11945/, 2015 for the analysis of pesticide residues.

Only 9 of the 22 analyzed pesticides were found above LOD: 5 herbicides: 2,4-D, atrazine, acetochlor, glyphosate (GLP), metsulfuron-methyl; 2 metabolites: desethyl-atrazine and AMPA; and 2 fungicides: epoxiconazole and tebuconazole. The detected pesticides were in agreement to those reported for registered applications in *CBA* according to regional official surveys (DP, 2015) for crops observed at the time of sampling (cf.Table 2). Regarding the co-occurrence of these compounds, mixtures of 3 or more pesticides were found in 93% and 32% of the *CBA* (maximum 6), and *ABA* (maximum 5) soil samples, respectively. The analysis of pesticides in European soils that receive direct applications shows that co-occurrence is common (Silva et al., 2019). However, this study shows that this pattern was repeated in agroecological soils with no pesticide application.

Fig. 2 shows the pesticide detection frequencies, which were always higher in *CBA* than in *ABA*, with all pesticides detected in the *ABA* farmalso detected in the *CBA* fields, but not the other way around. For example, metsulfuron-methyl and acetochlor were only found at the *CBA*. The herbicide GLP and its environmental metabolite AMPA exhibited the highest detection frequencies in both production systems, with a 100% occurrence of the pair in the *CBA* samples, and 91%% and 54% for GLP and AMPA in the *ABA* samples, respectively. These results of the *CBA* fields are similar to those reported for soils in the European Union (Silva et al., 2019), where GLP and AMPA also proved to be the most detected compounds. In Argentina, the occurrence of GLP and AMPA detected for the *CBA* are comparable to those reported by other authors for conventional fields (Aparicio et al., 2013; Primost et al., 2017). Distinctly, the detection frequencies of GLP and AMPA in the ABA soils were 25% and 75%, respectively, higher than those reported by Aparicio et al. (2013) in fields without target applications: 25% GLP and 75% AMPA.

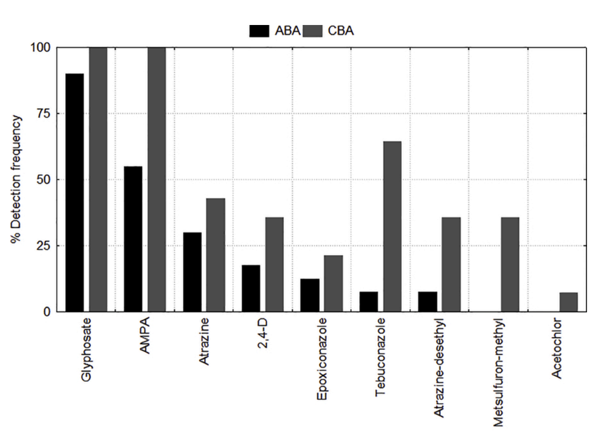

Fig. 2. Detection frequency of the pesticides analyzed by production model. (*CBA*: chemical-based agriculture; *ABA*: agro-ecological-based agriculture).

Additionally, by analyzing the profiles of the quantified pesticides, it is observed that GLP and AMPA represented 90% of the total mass load on average in both production systems (Table 3), in accordance to trends published for soils in Europe by Silva et al. (2019), and in other environmental matrices, such as sediments, in Argentina (Mac Loughlin et al., 2017). This result shows the ubiquity of GLP and AMPA in agroproductive soils from the region, both where the herbicide is sprayed (Primost et al., 2017; Soracco et al., 2018), as well as in agroecological soils. The results of both detection frequency and mass load are consistent with the market data available, with glyphosate being the most widely used pesticide in Argentina, representing 62% of the commercialized pesticides, and an average use of 200 million liters according to the last available report, published in 2012 (Woodburn, 2000; CASAFE, 2012).

In the case of fungicides, the frequency of detection of tebuconazole in *CBA* fields was higher than reported by Silva et al. (2019) in the European Union (60%*versus* 12%), while epoxiconazole was detected at similar levels (22 *versus* 24%). Regional comparisons are limited since there are few works in Argentina about multiresidue analysis of pesticides in soils (with the exception of GLP and AMPA). Nevertheless, atrazine, tebuconazole, metsulfuron-methyl, acetochlor, GLP, and AMPA were reported in surface waters of the same present study region (De Gerónimo et al., 2014; Okada et al., 2018), reflecting the regional relevance of the detected pesticides. The reach and ubiquity of the pesticides used in chemical-based systems in the Pampas region, imply a scenario comparable to that observed in other continents such as the North America and the Europe, showing the general consequences of the *CBA* system, regardless of the country under consideration (Battaglin et al., 2014; Farenhorst and Andronak, 2015; Silva et al., 2019).

3.2. Pesticide in soils related to management in studied agricultural systems

The frequency and concentrations obtained from the pesticides detected, separated by production system and by sampling campaign are shown in Table 3. As a general trend, an increase in the co-occurrence of pesticides was observed in **C2**. In **C1**, at least 3 pesticides were found in 85% and 27% of the *CBA* and *ABA* samples, respectively; while in **C2**, both values increased, reaching 100% and 35% of the samples in each agroproductive system.

For *CBA* fields, GLP and AMPA were detected in every sample analyzed in both **C1** and **C2**. The frequency of detection of 2,4-D, atrazine, metsulfuron-methyl and epoxiconazole increased in the second campaign for both systems, while tebuconazole decreased from C1 to C2 in the CBA samples (Table 3). As indicated in Table 2, most CBAfields did not have crops at the time of **C1** and were under chemical fallow based on GLP, 2,4-D and metsulfuron-methyl. The detection of herbicides and the highest degree of co-occurrence of residues in **C2**, might be a consequence of the adding post-sowing spraying of these pesticides in agreement with the application schedule for the crops present in *CBA* (Table 2*)*. Atrazine is commonly associated with crops such as corn and

Table 3
Median concentration, minimum-maximum range (min-max), and detection frequency (%) of the studied pesticides, differentiated by campaign and production system (ABA: agroecological-based agriculture; CBA: chemical-based agriculture). The limits of detection (LOD) and quantification (LOQ) of each pesticide are detailed. All concentrations are expressed in µg kg-1 dry weight (dw).

			C1 (July-Winter)		C2 (November-Spring)	
Pesticide	*LOD*	*LOQ*	*ABA*	*CBA*	*ABA*	*CBA*
Glyphosate (GLP)	2.00	4.00	**26.96** (8.52–98.93) 100%	**237.68** (65.42–383.12) 100%	**32.24** (LOD-47.77) 82%	**580.2** (86.75–1268.92) 100%
AMPA	2.00	4.00	**15.46** (LOD-48.29) 44%	**758.73** (455.9–1787.58) 100%	**51.93** (LOD-114.01) 64%	**1423.99** (707.43–2919.17) 100%
2,4-D	4.40	14.90	**21.91** (LOD-31.12) 11%	**25.49** (LOD-38.52) 29%	(LOD-LOQ) 23%	(LOD-LOQ) 43%
Atrazine	0.01	0.04	**0.38** (LOD-1.16) 22%	**0.45** (one sample) 14%	**0.08** (LOD-2.12) 36%	**0.07** (LOD-0.28) 71%
Desethyl-atrazine	0.07	0.37	(LOD-LOQ) 17%	(LOD-LOQ) 71%	<LOD	<LOD
Metsulfuron Methyl	0.09	0.29	<LOD	<LOD	<LOD	**3.46** (LOD-5.02) 71%
Acetochlor	0.15	0.49	<LOD	**0.53** (one sample) 14%	<LOD	<LOD
Epoxiconazole	0.60	1.80	**2.96** (LOD-4.73) 11%	**9.96** (one sample) 14%	**1.2** (LOD-18.41) 14%	**11.65** (LOD-13.35) 29%
Tebuconazole	0.47	1.50	<LOD	**1.91** (LOD-11.07) 71%	(LOD-LOQ) 14%	**1,27** (LOD-1.97) 57%

<LOD concentration below detection limit.

sorghum (DP, 2015). Therefore, its detection, along with its desethylated metabolite, was unexpected since the presence of such crops was not registered in the surrounding *CBA* fields and no application registers were observed from 2006 to date in *ABA* (Table 1 y Table 2). The presence of this compound could be a consequence of older applications in *CBA* fieldsand its high persistence and stability in the environment, with a half-life in soils of up to 4 years (de Albuquerque et al., 2020). There is evidence of the presence of atrazine in soils from the same studied region, and the relevance of its atmospheric transport and wet deposition (Alonso et al., 2018). The opposite was observed for metsulfuron-methyl, which is applied both for chemical fallow and for post-seeding maintenance of the present crops in *CBA* fields (DP, 2015). Furthermore, applications of the herbicide are registered in *ABA* farm-during 2010 and 2011 (Table 1). However, it was only detected during the second sampling campaign in the *CBA* fields. This result is consistent with other studies in soils from the south of the Province of Buenos Aires, that evidence its lower half-life (38–51 days; Bedmar et al., 2006), its low adsorption (Zanini et al., 2009), and its consequent leaching potential (Azcarate et al., 2015) and mobilization towards surface water bodies (De Gerónimo et al., 2014).

In the case of fungicides, there are regular applications at the growing stage for all the crops registered in *CBA* fields. The main active ingredients used are epoxiconazole, for which higher median concentrations were observed, and tebuconazole, this being the most frequently fungicide detected in *CBA* sites. Spraying of fungicides takes place between July and November for barley, and between October and December for wheat, while for soy crops it is between January and April (cf.Table 2). The input of pesticides in the *CBA* crops is then reflected in the presence of these compounds in the *ABA* establishment (no applications of fungicides registered from 2006), where the maximum concentration of epoxiconazole was detected (cf.Table 3), evidencing the influence of the chemical-based system practices on the agroecological field.

3.3. Glyphosate and AMPA as most relevant pesticides in soils of agroproductive systems

3.3.1. Occurrence and concentrations of GLP and AMPA

Considering that GLP and AMPA were the most detected analytes, and that they represented over 90% of the total mass load of the quantified pesticides, a spatio-temporal analysis for both compounds and a correlation analysis between them were carried out. When comparing the agricultural systems studied, it was observed that the median concentrations of both the herbicide and its environmental metabolite were higher ($p < 0.001$, $n = 62$ for both compounds) in the *CBA* than in the *ABA* system (Fig. 3). Different studies reported GLP and

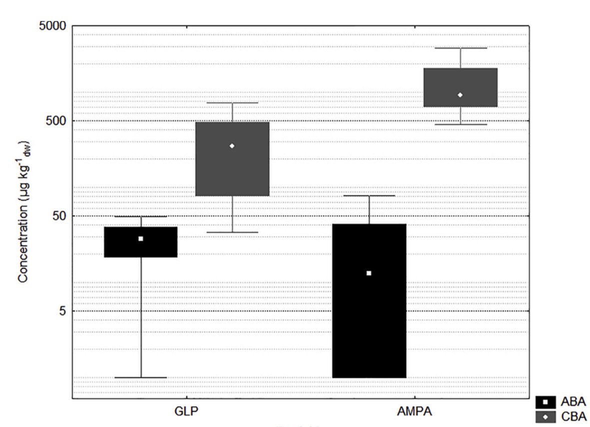

Fig. 3. Concentration of glyphosate (GLP) and AMPA in soils from each establishment (*ABA*: agroecological-based agriculture; *CBA*: chemical-based agriculture). Concentration (µg kg-1 dw) is plotted on the y-axis on a logarithmic scale for each pesticide displayed on the x-axis. In the box plots, the marker indicates the median, the box the 25% and 75% percentiles and the whiskers the non-outlier range.

AMPA concentrations in agroproductive *CBA*-type soils from Argentina, in concentrations of the same order of magnitude as those found in the *CBA* fields of this work (Aparicio et al., 2013; Lupi et al., 2015; Primost et al., 2017; Alonso et al., 2018; Soracco et al., 2018; Okada et al., 2018). Until now, no concentrations of pesticides have been reported in real scale agroecological fields of the country. However, in non-agricultural fields (without application registers in over 10 years) immersed in productive locations, Aparicio et al. (2013) reported maximum concentrations of 41.4 μg kg^{-1} for GLP and 43.2 μg kg^{-1} for AMPA, approximately less than half of those found in the *ABA* field of the present study. In addition, Lupi et al. (2015), who assessed an area separated from the agricultural field with GLP applications by a live windbreak, detected GLP and AMPA at concentrations of 2.0 and 5.6 μg kg^{-1}, respectively, even without having received direct application. In the present study, the concentrations found in the agroecological field were up to 20 times higher than those, with a maximum of 98.93 μg kg^{-1} dw of GLP, and 114.01 μg kg^{-1} dw of AMPA.

The most probable mechanisms by which pesticides may mobilize to the agroecological field are subsurface runoff and atmospheric transport (Chang et al., 2011; Lupi et al., 2019), which includes the primary drift from the application spray (Jensen and Olesen, 2014), and secondary processes from wind-blown soil particles. The latter gains relevance due to the high affinity of GLP and AMPA for adsorption processes on agricultural soils (Okada et al., 2016; Lupi et al., 2019), as they can be transported by the particulate material generated by wind erosion or during soil tillage (Gill et al., 2006; Bento et al., 2017).

Currently, the physical separation between the fields of study is just a wire fence. Research on the subject indicates that windbreaks mitigate spray drift from *CBA* fields, and have been proven effective in protecting non target areas, organisms and crops (Ucar et al., 2001; Baker et al., 2018). Moreover, planted tree belts can reduce the transport of pesticide in dust particles (Zaady et al., 2018). This demonstrates the relevance of management strategies such as the use of windbreaks to minimize pesticide drift from conventional fields. However secondary drift can reach large distances. Previous studies have demonstrated the association of these compounds to fine particles (Bento et al., 2017; Ramirez Haberkon et al., 2020), followed by mobilization by atmosphere, from the spray zone, and then return to the soil by means of wet or dry deposition (Chang et al., 2011; Farenhorst and Andronak, 2015). From the Pampas region of Argentina, Alonso et al. (2018) detected GLP and AMPA in 80% of the rainwater samples, even in places far away from crops.

3.3.2. *Spatio-temporal variation of glyphosate and AMPA concentrations*

No statistically significant differences were observed between sampling campaigns in the GLP concentrations within each agricultural system model (*CBA*: $p = 0.0973$ $n = 14$; *ABA*: $p = 0.2109$, $n = 48$) (Fig. 4). These results are in accordance with that described by Primost et al. (2017) for *CBA* systems, where GLP was characterized as pseudo-persistent in soils as a consequence of spraying frequencies that are between 5–7 times per year. It is important to note that this was also observed in the agroecological system studied, where use of this herbicide was not part of their agricultural practice since 2006 (Table 1).

Regarding the concentrations of AMPA, there were significant differences between the campaigns within each system (*CBA*: $p = 0.0379$, $n = 14$; *ABA*: $p = 0.0194$, $n = 48$), with the highest median concentration in **C2** for both systems (Fig. 4). This can be explained by the glyphosate sprays that occurred in the *CBA* system between sampling campaigns, as evidenced by higher median and maximum concentrations of GLP in *CBA*-**C2** (cf.Table 3), and an increase in the degradation rate, of up to 30 times greater degradation of GLP to AMPA at higher temperatures and humidity (seasonality) due to the microbial activity in the soil (Bento et al., 2016), regardless of the further degradation of AMPA.

Lastly, the median concentrations of AMPA were significantly higher than those of GLP for both sampling campaigns in *CBA* fields(**C1**: $p = 0.0006$, $n = 14$; **C2**: $p = 0.0111$, $n = 14$; Fig. 4a). These trends were also

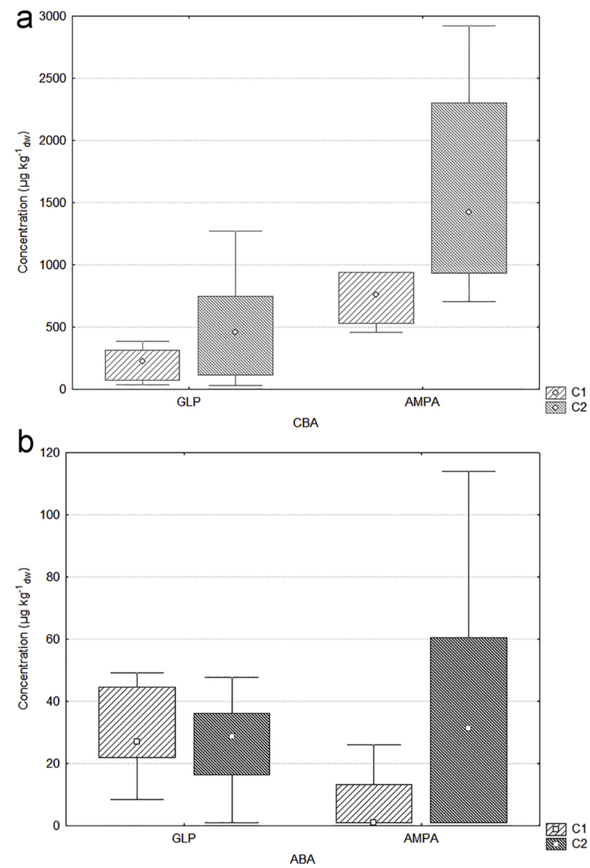

Fig. 4. Comparison of glyphosate (GLP) and AMPA concentrations from the two agricultural systems in the two sampling campaigns. **a)***CBA*: chemical-based agriculture. **b)***ABA*: agroecological-based agriculture. Concentration (μg kg-1 dw) is plotted on the y-axis for each pesticide displayed on the x-axis. In the box plots, the marker indicates the median, the box the 25% and 75% percentiles and the whiskers the non-outlier range.

found by other authors (Okada et al., 2018; Silva et al., 2018), who proposed that the dissipation of AMPA in soils that received frequent applications is less than that of glyphosate in the same environmental conditions, due to its longer half-life (Battaglin et al., 2005; Bento et al., 2016).

The spatial variation of GLP and AMPA was studied considering *CBA* as a "source" close to *ABA* and analyzing the soils samples at different distances from said source. The GLP concentrations (Fig. 5a) showed significant differences between the source and the different distances within the *ABA* farm for both sampling campaigns, but no significant differences were observed between the samples obtained from the *ABA* system. The same trend was found for AMPA in **C1** (Fig. 5b). On the other hand, during **C2** a gradient was observed, decreasing in concentration as it moved away from the source.

It is noteworthy that GLP was quantified at distances more than 300 m from the *CBA* borders (S1, S2, and S3, Fig. 1), and at concentrations that did not present significant differences with respect to those found in the area near the CBA fields (Fig. 5a), showing the ubiquity of the spread of pesticides from *CBA* fields. GLP has been previously defined as pseudo-persistent pesticide in *CBA* fields in Argentina (Primost et al., 2017).The results of GLP and AMPA concentrations and detection frequencies in soils of the *ABA* farm has also show a pseudo-persistence condition. Given that agricultural formulations based on GLP represent 62% of the market, this pesticide is the most sold in Argentina (CASAFE, 2012) and that several environmental studies have frequently detected presence of this herbicide and its main metabolite in large river basins (Ronco et al., 2016), shallow lakes (Castro Berman et al., 2018),

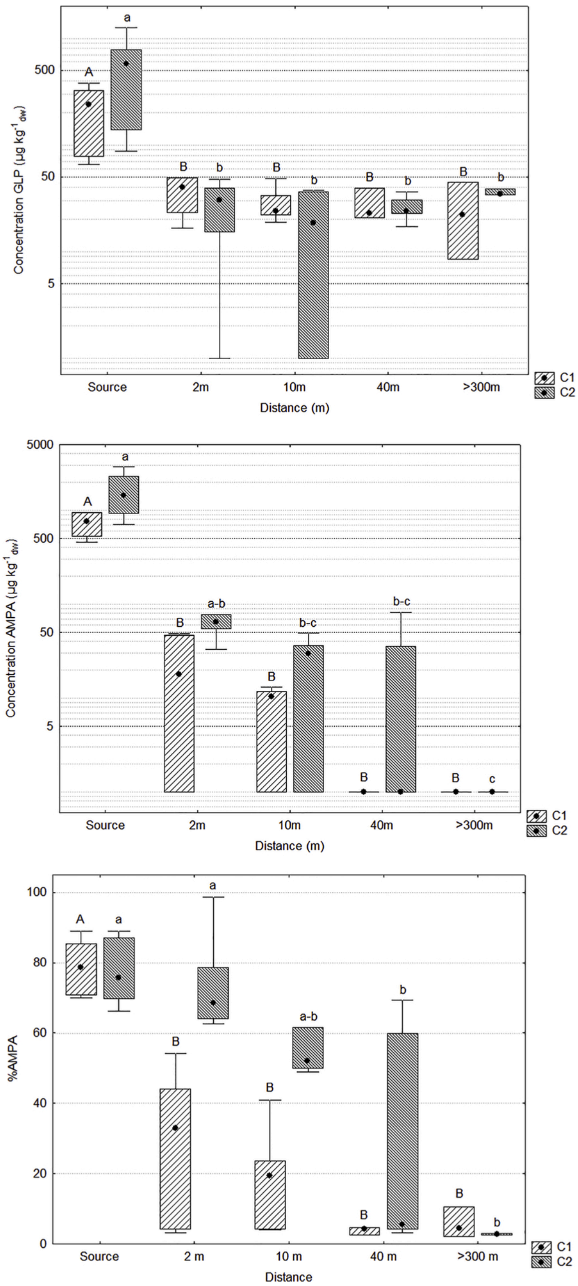

Fig. 5. Spatial distribution of **a)** glyphosate (GLP) and **b)** AMPA concentrations in soils, and **c)** %AMPA. Equal letters (uppercase **C1**, lowercase **C2**) indicate that there are no significant differences. In the figures **(a)** and **(b)**, the concentration (μg kg-1 dw) is plotted on the y-axis on a logarithmic scale, while in figure **(c)**, the %AMPA is plotted on the y-axis. Distances are plotted in the x-axis (*CBA*: source; *ABA*: 2 m, 10 m, 40 m, and >300 m from border fence). In the box plots, the marker indicates the median, the box the 25% and 75% percentiles and the whiskers the non-outlier range.

in the atmosphere (Alonso et al., 2018; Ramirez Haberkon et al., 2020), horticultural areas (Mac Loughlin et al., 2017) and a *ABA* farm, leads to them being proposed as environmental tracers of chemical-based agriculture for Argentina.

Relationships between glyphosate and AMPA were evaluated through correlation tests and %AMPA. Positive and significant correlations were observed in all cases (*CBA*-**C1**: $r = 0.82$, $p = 0.0442$, $n = 7$; *CBA*-**C2**: $r = 0.96$, $p = 0.0182$, $n = 7$; *ABA*-**C2**: $r = 0.63$, $p = 0.0369$, $n = 12$), except for *ABA*-**C1** ($r = 0.57$, $p = 0.1360$, $n = 8$). This analysis has already been performed with concentration data from soils of *CBA* fields and bottom sediments sampled from watersheds in areas of intense agricultural activity (Primost et al., 2017; Okada et al., 2018). Those same authors concluded that, in solid matrices, biotic degradation is favored over other removal processes, such as wind erosion, surface runoff and leaching, and is strongly associated with the formation of AMPA through the breakdown of GLP *in situ*. The degradation rate, measured through %AMPA (Fig. 5c), showed no significant differences between **C1** and **C2** in the *CBA* fields ($p = 0.5754$, $n = 14$). All the while, GLP was applied in *CBA* fields between sampling campaigns, and, therefore, degradation processes had already occurred at the time of sampling for **C2.**

Likewise, in **C2**, the *ABA* soils presented a positive and significant GLP-AMPA correlation, and, between sampling campaigns, there was an increase in the median concentrations of AMPA in samples up to 10 m from the border (Fig. 5b). Furthermore, %AMPA increased significatively from **C1** to **C2** in samples at 2 m ($p = 0.0179$, $n = 11$) and 10 m ($p = 0.0431$, $n = 7$) within the *ABA* system, to the point that no significant differences were detected with respect to the *CBA* field for **C2** (Fig. 5c). These results show the environmental pressure of herbicide application cycle in *CBA* crops on the neighboring *ABA* farm, as, after application, the agroecological system responded as a conventional system, by generating the metabolite AMPA in samples up to 10 m from the field boundary, with medians of %AMPA greater than 50%, as described for conventional agricultural soils in the region (Okada et al., 2018). Based on the observations of the agronomist who manages the agroecological field, and these experimental results, it can be suggested that the distance of direct influence is between 10 and 40 m.

3.4. Effects in edaphic organisms by pesticide in soils

The negative effects of pesticides on key soil organisms have been evidenced (Pelosi et al., 2016; Wołejko et al., 2020), particularly for herbicides, which can affect the trophic networks of which these organisms are part (Van Bruggen et al., 2018; Sharma et al., 2018).

There are ecotoxicological studies that report biological effects relative to concentrations of pesticides in soil (mass of active ingredient/ soil mass) (USEPA, 2020). Published effects on soil organisms for some of the quantified pesticides in the present study (atrazine, 2,4-D, epoxiconazole, and tebuconazole) were at concentrations at least 5 times higher than those reported here. However, 64% and 43% of GLP and AMPA concentrations were higher than the lowest concentration reported to generate negative effects on different organisms.

Fig. 6 details the cumulative distribution for GLP and effect concentrations for soil organisms, considering lethality and different sublethal effects. From the *CBA* fields GLP soil concentrations, it was observed that 7% of the quantified samples were above the concentration which is lethal to 50% of a population (median lethal concentration, $LC_{50} = 1130$ μg kg^{-1}) for the springtail *Folsomia candida* (Santos et al., 2012), and the Lowest Observed Effect Level (LOEL = 790 μg kg^{-1}) for cell viability in mycorrhizal arbuscular fungi (Druille et al., 2013). Furthermore, at least 50% of the concentrations found in *CBA* fields were higher than the reproductive median effective concentration (EC_{50} = 330 μg kg^{-1}) in *F. candida* (Santos et al., 2010). Effects at a biochemical level should also be considered, since more than 65% of the concentrations of the herbicide were above the LOEL (216 μg kg^{-1}) for the activity of the glutathione-S-transferase antioxidant enzyme in the oligochaeta *Eisenia hortensis* (Hackenberger et al., 2018).

For the environmental metabolite AMPA, the only soil effect concentration reported is the reproductive LOEL (1000 μg kg^{-1}) for the species *Eisenia fetida* (Dominguez et al., 2016), which, as previously stated, 43% of AMPA concentrations were above said level.

For the agroecological system studied, and to the best of our knowledge, no concentrations were observed that generate direct effects at the individual level for GLP and AMPA. However, concentrations in the surrounding *CBA* fields are capable of harming key organisms (worms, invertebrates, and fungi) in the ecosystem functions, necessary

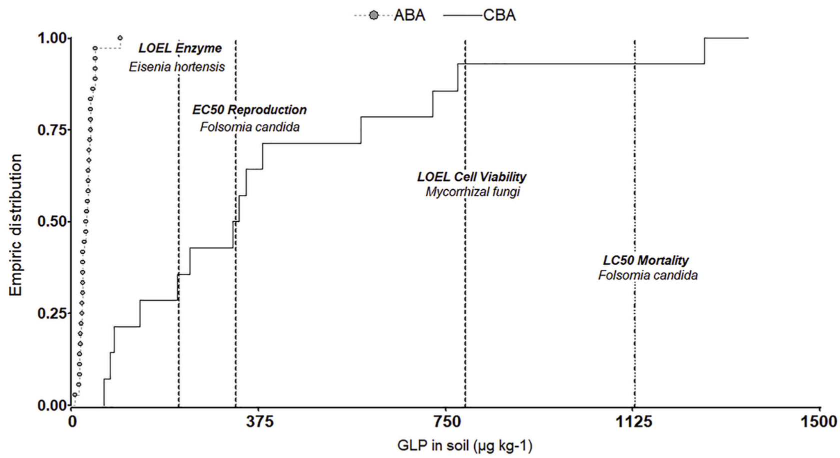

Fig. 6. Accumulated empirical distributions of glyphosate (GLP) concentrations in soils from *ABA* (agroecological-based agriculture) and *CBA* (chemical-based agriculture). The vertical lines indicate reported sub-lethal (LOEL: Lowest Observed Effect Level, and EC50: Median Effective Concentration) and lethal (LC50: Median Lethal Concentration) concentrations of glyphosate for soil organisms.

for optimal functioning of agroecological systems (Gurr et al., 2016), not only because of the aforementioned direct effects at the individual level, but also in terms of community/ecosystemic level consequences.

For instance, the absence of spontaneous vegetation (seen as "weeds" from the perspective of the *CBA* system), and therefore the absence of host plants, is considered an indirect effect of herbicides on beneficial organisms, causing a reduction in the population (Sharma et al., 2018). In Argentina, it has been detected a decrease in the abundance of beneficial predatory organisms due to the decrease of semi-natural environments (spontaneous vegetation) in areas close to wheat crops (Marasas et al., 2010).

Finally, it is worth noting the concern about the lack of information associated with the effect of pesticide mixtures, particularly due to the co-occurrence found in the *ABA* farm samples (Silva et al., 2019; Wołejko et al., 2020). It is necessary to develop ecotoxicological criteria to understand the possible effects on biota in cases like this work, where there is co-occurrence of up to 5 compounds in at least one site of both establishments, even without considering the potential presence of other pesticides as insecticides, of greater toxic effect (Pelosi et al., 2014).

4. Conclusions

The present study showed the occurrence of 9 herbicides and fungicides out of the 22 analyzed pesticides, of which there is a paucity of information for the region. This is the first report on pesticides dynamics in real conventional-agroecological scenarios. Moreover, there is sufficient evidence to affirm that pressure is being exerted to the agroecological establishment "La Aurora" by the agricultural practices carried out in the surrounding fields, as pesticides were detected there, some of which have not been applied in more than 10 years. Detection frequencies, mass loads and co-occurrence of compounds in the *ABA* field were conditioned by the actions implemented in the *CBA* fields, such as application cycles, stage and type of crop and, in at least one of the sampling campaigns, the direct impact of the applications on the *CBA* system was identified up to 10 m within the *ABA* system. Similar findings were observed in both establishments, such as the association between GLP and AMPA, and the pseudo-persistence of GLP in soils. Soil concentrations of GLP and AMPA in the *CBA* plots reached such values, up to 1268.92 and 2919.17 μg kg^{-1} dw for GLP and AMPA, respectively, in the *CBA* fields, capable of causing sub-lethal and lethal effects to organisms like springtails, oligochaetes, and to the soil microbial fauna, all of which have direct implications on the structure and function of the edaphic ecosystem. Given their higher detection frequency and environmental concentrations, the fact that they were both detected in samples taken more than 300 m from the perimeter, along with high detection and concentration records across Argentina, GLP and AMPA are proposed as environmental tracers of conventional agroproductive activity. The information presented in this work indicates that exposure to GLP must be taken into consideration in future studies focusing on agricultural biodiversity, since in Agroecology, its conservation and management are central for biological control and nutrient recycling. The studied agroecological system is reached by pesticides, both from the neighboring conventional system, and as a consequence of being located in a region dominated by the pesticides-dependent production system. In order to minimize this situation, management tools must be adopted to reduce the use of pesticides, and thus protect ecosystemic equilibriums that are the foundation of agroecological production and can be affected by the presence of these pollutants.

Declaration of Competing Interest

The authors declare no conflict of interest. This study was supported by national funds from the Universidad Nacional de La Plata and grants from the National Agency for Scientific and Technological Promotion (ANPCyT).

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