AGRONOMY SCIENCE AND BIOTECHNOLOGY

RESEARCH ARTICLE

Glyphosate and aminomethyphosphonic (AMPA) contents in Brazilian field crops soils

Francis Giard[1], Marc Lucotte[1,*], Matthieu Moingt[1] and Avner Gaspar[2]

[1]Université du Québec à Montréal, GEOTOP et Institut des Sciences de l'environnement, Succ. Centre-ville, C.P. 8888, H3C 3P8, Montréal, Québec, Canada. [2]Universidade Federal do Oeste do Pará, Rua Vera Paz Av. Vera Paz, s/n, Bairro Salé, 1° Pavimento, Unidade Tapajós, Santarém, Brazil, CEP 68035-110 . *Corresponding author, E-mail: lucotte.marc_michel@uqam.ca

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ABSTRACT

Because of a lack of direct measurements, the presence and persistence of glyphosate and its main metabolite aminomethylphosphonic acid (AMPA) in agricultural soils of Brazil remains unknown. This paper aims at reporting glyphosate and AMPA contents in Brazilian field crop soils at the country scale from southern states to eastern Amazon. Brazilian field crop farmers are among the highest users of glyphosate-based herbicides (GBH) in the world. Soybean and corn field crop soils from 17 sites were collected at two depths (i.e. 0-20 cm and 20-40 cm) in 2016 and 2018. The study area encompasses three regions of Brazil: southern Brazil, central-west Brazil and eastern Amazon, all having in common intensive, conventional, large-scale grain farming. ßGlyphosate and AMPA contents were measured using a GC-ECD following soil extraction. Both chemicals were ubiquitously detected in soils cultivated under various agricultural practices ranging from ploughing to no-till ones. Average measured glyphosate and AMPA contents were 0.08 ± 0.09 µg/g and 0.17 ± 0.16 µg/g respectively with maximum values of 0.57 µg/g and 0.98 µg/g. Glyphosate plus AMPA contents in the top 40 cm of soils presented cumulated amounts exceeding the annual glyphosate inputs via GBH. This is interpreted as a multiannual persistence of these chemicals in Brazilian agricultural soils. Downward migration of glyphosate and AMPA is also suspected with regard to the vertical distribution of these chemicals along with deeper soil horizons. This study highlights the backlash of conservation agriculture as far as glyphosate and AMPA presence in agricultural soils are concerned. These compounds persistence in Brazilian soils appear to be longer than what is usually reported in the literature, especially so for tropical environments. The worldwide concern about the ubiquitous presence of glyphosate and AMPA in the environment needs a broader screening in Brazilian field crop soils since the majority of the available data comes from Argentina, Europe and to a lesser extent North America.

Keywords: Glyphosate, AMPA, field crop, weed management, Brazil, persistence.

INTRODUCTION

Glyphosate (N-phosphonomethyl glycine) is the active ingredient of glyphosate-based herbicide (GBH), the most successful systemic, non-selective herbicide of its time. GBH importance for agriculture has been compared to what penicillin has been for medicine (Powles 2010). The first GBH formulation was commercialized in 1974 by Monsanto Co. (Duke & Powles 2008). Twenty years later, in 1994, 56 million kg of the active ingredient (a.i.), the glyphosate, were used worldwide. After the commercialization of glyphosate-resistant crops (GR) in 1996 and the expiration of the patent in 2000, generic GBH flooded the market dropping its price and spreading its use all over the world (Benbrook 2016, Denardin et al. 2012, Duke & Powles 2008). In 2014, GBH consumption reached nearly 826 million kg a.i. which represents an increase of almost 15 folds over 20 years (Benbrook 2016).

Brazil makes no exception to GBH usage in industrial agriculture. Historically, this country initiated a large movement towards conservation agriculture by adopting no-till farming in order to face strong soil erosion issues they encountered (Denardin et al. 2012). This practice required greater herbicide usage which led to the present intensive GBH use (Denardin et al. 2012). In 2014, Brazil's GBH consumption represented 23 % of the world consumption with 194 million kg. It is mainly justified by Brazil's soybean production reaching 95.5 Mt in 2014, equivalent to 30 % of the worldwide production. Of that amount, 93 % was GR soybean (Benbrook 2016). Brazil's soybean production market share kept going up reaching 37 % of the world market in 2019 with 126 Mt (SoyStats 2020).

Glyphosate biodegradation is well documented as two main pathways have been identified. The first one is by cleavage of a C-P bond releasing sarcosine and phosphates. The second one, which is known as the predominant one in agricultural soils, happens along with the cleavage of a C-N bond leading to aminomethylphosphonic acid (AMPA) formation (Cecilia & Maggi 2017). AMPA can then be used as a source of carbon, nitrogen and phosphate for bacteria (Kanissery et al. 2019, Li et al. 2015). Although biodegradation leading to AMPA is considered the main process (Cecilia & Maggi 2017), it has recently been suggested that abiotic chemical degradation could also be of some importance in the presence of birnessite (Li et al. 2015). Glyphosate photodegradation is another degradation pathway but has been considered of limited importance in natural conditions (Bento et al. 2016).

Even though glyphosate is considered slightly hazardous (Class III), its heavy use has instigated numbers of studies on its impact on human health, non-target ecosystems and agricultural yield. Many studies agree on the GBH potential to disrupt the endocrine system (Gasnier et al. 2009, Richard et al. 2005, Thongprakaisang et al. 2013), alter cerebral functions (Peillex & Pelletier 2020) and has a significant effect on breast cancer development (Thongprakaisang et al. 2013). The International Agency for Research on Cancer (IARC) categorized glyphosate as probably carcinogenic to humans by its positive association with non-Hodgkin lymphoma (IARC 2017). Embryonic and placental cells sensitivity to glyphosate have also been reported (Benachour et al. 2007). Adverse glyphosate effects are also known on non-target environment like other mammals, fishes, amphibians, arthropods and birds (Evans et al. 2010, Oliveira et al. 2007, Peillex & Pelletier 2020, Relyea 2005). On top of that, glyphosate can adversely impact crop yields. Glyphosate mechanism does not only affect plants but also fungi and bacteria which alter microbial activity and affect nutrient cycles (Helander et al. 2012, Martinez et al. 2018). Smedbol *et al.* (2019) reported that both glyphosate and AMPA have repercussions on GR soybean by altering stomatal conductance, chlorophyll content

and biomass.

Numerous studies on glyphosate and AMPA residues have been published showing the omnipresence of these chemicals in water, soil, sediments, grains or humans (Aparicio et al. 2013, Bøhn et al. 2014, Gillezeau et al. 2019, Primost et al. 2017). Argentina is one of the most active countries in the monitoring of glyphosate and AMPA occurrence in agricultural soils. However, to our knowledge, Brazilian studies on these chemicals in agricultural soil remain scarce. Other studies from Brazil rather focus either on glyphosate effects on microbiota (Araújo et al. 2003), on GR soybean (Bohm et al. 2014), on its mineralization (Bonfleur et al. 2011) or its presence in groundwater (Olivo et al. 2015). Knowledge of glyphosate and AMPA contents in agricultural soils is a pressing need to properly address the environmental hazard of these products (Maggi et al. 2020). Indeed, Maggi *et al.* (2020) recognized scarcity of site-specific data as a limit for benchmarking their world glyphosate and AMPA environmental hazard model.

This study aims at filling this lack of information for Brazil. To do so, we present the first broad assessment of glyphosate and AMPA contents in field crop soils across Brazil from southern states to eastern Amazon. It extends from Rio Grande do Sul state in southernmost Brazil through Santa Catarina, Paraná, São Paulo and Mato Grosso states and up to Pará state in Eastern Amazon. As glyphosate and AMPA persistence and mobility is a matter of debate and can differ between regions, we bring elements of clarification on factors affecting them in Brazilian soils. A special attention is given to field crop practices and agricultural innovation for GBH reduction.

MATERIAL AND METHODS

Study Area

The study area encompasses three regions of Brazil; southern Brazil (Rio Grande do Sul, Santa Catarina, Paraná and São Paulo states), central-west Brazil (Mato Grosso state) and eastern Amazon (Pará state) (Figure 1). These regions all have in common intensive, conventional, large-scale grain farming. They belong to the vast and diverse agribusiness going on in Brazil.

Details on each sampling sites are given in Table 1. Southern Brazil is represented by sites #1 to 9 and are part of the former Atlantic Forest biome. An effort was made to include the central-west Brazil for its fast-moving pioneer front. As such, two sites (10 and 11) from one single farm in Sinop (Mato Grosso state) were sampled. This region lies at the border of Amazonian and Cerrado biomes. The fast-expanding soybean cultivation region in eastern Amazon was sampled in the Santarém vicinity (Pará state) and was represented by sites #12 to 17.

Sampling

Two sampling campaigns were conducted to cover the wide study area. The first one occurred after soybean harvest, between April and June 2016, in the eastern Amazon (Pará state). The second campaign was realized between June and July 2018 in central-west and southern Brazil during intercrop season. In the eastern Amazon, samples were collected in ploughed soils, according to the most frequent cultivation practice in that region. In southern and central-west Brazil, we preferentially chose innovative farming practices successfully keeping adequate yields while trying to reduce GBH use. Owner's willingness to share their GBH use was a crucial criterion

for selecting a sampling site. These criteria resulted into the sampling of five types of alternative practices; direct seeding mulch-based cropping system (DMC), Agro-silvo-pastoral system (ASP), Agro-pastoral system (AP), no-till system (NT) as well as organic farming (OF). Ploughing was also used on organic site #2. Even though site #1 was following DMC management, the yearly GBH input was similar to what is usually sprayed in conventional field crop farms in Brazil. Regardless of the farming practice, our study sites were mainly in a soybean and corn rotation. Because of the increasing market price of soybean, this crop was sowed at least two consecutive years on sites #1, #4, #6, #7 and #8. Pará sites were sampled on bare soils. ASP and AP sites were covered with *Brachiaria* (fodder) and DMC site #1 with *Crotalaria* when sampled. All other sites were covered with wheat, oat or forage turnip.

Table 1. Sampling sites of the 2016 and 2018 campaign and agronomical data.

Site #	State	Latitude	Longitude	Climat[1]	Soil type[2]	Practice	Crop	Yearly GBH input (g a.i./ha)	Last GBH input (g a.i./ha)	Time between last GBH input and sampling (month)
1	PR	-23.18	-51.98	Cfa	Red Distroferic Latosol	DMC	Soybean	8060	1860	3
2	SC	-25.70	-53.55	Cfa	Eutrophic Haplic Cambisol	Organic	Corn	0	0	>48
3	SC	-26.69	-53.51	Cfa	Eutrophic Litic Neosol	DMC	Soybean	1860	797	9
4	SC	-26.70	-53.52	Cfa	Eutrophic Litic Neosol	DMC	Soybean	2126	797	9
5	SC	-26.41	-53.08	Cfa	Brown Dystrophic Latosol	DMC	Soybean	1063	1063	9
6	SC	-26.41	-53.17	Cfa	Brown Dystrophic Latosol	DMC	Soybean	3189	1063	7
7	RS	-28.38	-52.75	Cfa	Red Distroferic Latosol	DMC	Soybean	1329	1329	9
8	RS	-28.37	-52.74	Cfa	Red Distroferic Latosol	DMC	Soybean	2658	1329	9
9	SP	-23.61	-48.40	Cfa	Red Dystrophic Latosol	DMC	Corn	3564	1944	3
10	MT	-12.08	-55.27	Aw	Red-Yellow Dystrofic Latosol	AP	Soybean	908	454	10
11	MT	-12.09	-55.26	Aw	Red-Yellow Dystrofic Latosol	ASP	Soybean	3608	1123	6
12	PA	-2.69	-54.92	Am	Yellow Dystrofic Latosol	Till	Soybean	882	882	6
13	PA	-2.66	-54.68	Am	Yellow Dystrofic Latosol	Till	Soybean	882	882	6
14	PA	-2.69	-54.92	Am	Yellow Dystrofic Latosol	Till	Soybean	882	882	6
15	PA	-2.73	-54.64	Am	Yellow Dystrofic Latosol	Till	Soybean	882	882	6
16	PA	-2.69	-54.50	Am	Yellow Dystrofic Latosol	Till	Soybean	882	882	6
17	PA	-2.71	-54.58	Am	Yellow Dystrofic Latosol	Till	Soybean	882	882	6

PR: Paraná, SC: Santa Catarina, RS: Rio Grande do Sul, SP: São Paulo, MT: Mato Grosso, PA: Pará, Cfa: Warm temperate fully humid hot summer, Aw: Equatorial savannah with dry winter, Am: Equatorial monsoon, [1](Kottek *et al.*, 2006), [2](Embrapa Solos, 2020).

At the 11 sites from southern and central-west Brazil, a set of three replicates was taken at an approximative distance of 100 m from each other. Two soil replicates were taken from each 6 Amazonian sites. Soil samples were retrieved from 0 cm to 20 cm depth and from 20 cm to 40 cm depth. Sampling was realized by digging a 20 cm wide hole with a shovel down to 40 cm in order to form a vertical column in which the desired horizon could be sampled. Once the hole dug, for each depth horizon, approximately 50 mL of soil was taken every 5 cm and then pooled in a single pot to be mixed and resampled in order to fill a 50 mL polypropylene falcon. The soil sampling in the Amazon region included a third depth category from 40 cm to 60 cm. Data on agricultural practices were obtained by semi-structured interviews either with the owner or his farm manager/agronomist. Details on GBH sprayed at least one

year before the sampling campaign were compiled (herbicide brands, periods of applications, application rates and number of applications). Crop rotation, fertilization and practices were also registered. Some of the GBH commercial names were missing, which was a problem to determine the quantity of active ingredient (i.e glyphosate) applied in the field. When missing, the average concentration of the products sprayed in other nearby sites was used. Also, agronomic information from the eastern Amazon campaign were representative of the Santarém regional average rather than site specific.

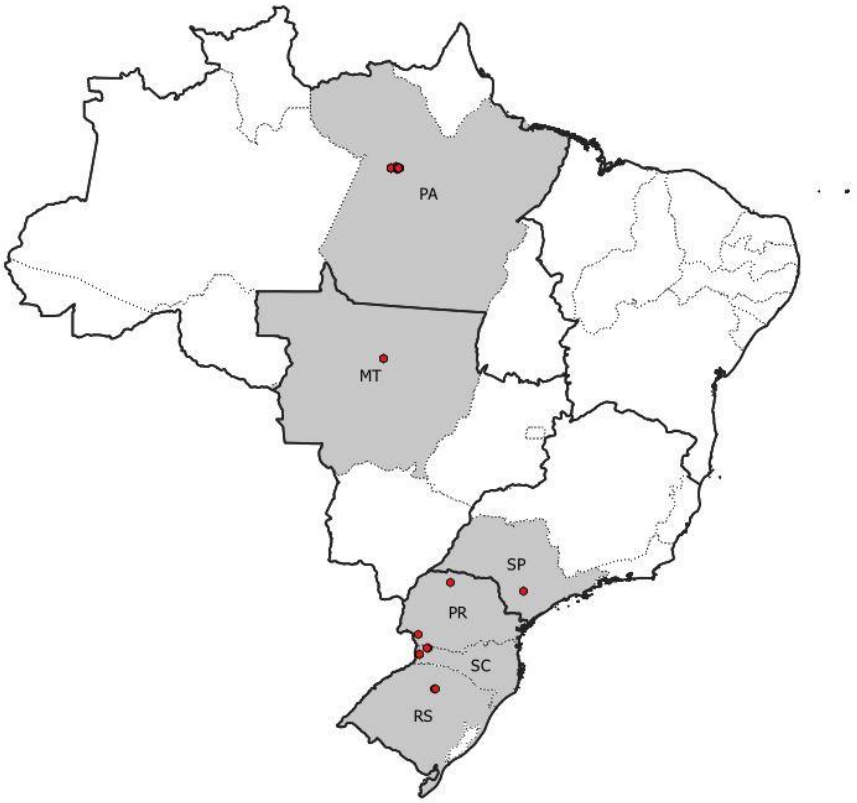

Figure 1. Map of soil sampling in various industrial field crop regions of Brazil from the 2016 and 2018 sampling campaign. Red dots represent the sampling sites, Brazilian states are represented by two letters: RS: Rio Grande do Sul, SC: Santa Catarina, PR: Paraná, SP: São Paulo, MT: Mato Grosso, and PA: Pará.

Glyphosate and AMPA measurements

Samples were kept frozen until they were freeze-dried. Coarse debris were removed manually and the samples were grinded in preparation for the extraction. Then, 5 g of soil samples was combined in a 50 mL falcon with 20 mL nanofiltered water and 20 mL of an extracting solution described by Alferness and Iwata (1994) made of 1.00 % NH_4OH and 1.36 % KH_2PO_4. Falcons were tumbled 30 minutes at 200 rpm in a tube rotator and centrifuged 20 minutes at ≈ 3500 rpm. 2 mL supernatant of each sample was filtered with 0.2 µm nylon filter (InnoSep^{TM} SF25) and transferred to a 2 mL tube. Finally, 40µL of the filtered supernatant was moved to an injection vial with 20 µL of 2-Amino-3-phosphonopropionic acid (APPA) as an internal standard.

For each series, one of the samples supernatants was designated to act as a control matrix. Five vials were prepared with the designated matrix in the same way

as the samples but with an addition of standard glyphosate (0.25 µg/mL) and AMPA (0.50 µg/mL) in a 0; 10; 20; 30; 40 µL gradation. Then, the liquid content of all vials was evaporated to dryness under nitrogen flow. Afterwards, samples and controls were derivatized by adding 500 µL of 2,2,2 trifluoroethanol (TFE) and 1000 µL of trifluoroacetic anhydride (TFAA) to the vials and then placed on a heating plate for an hour at 100°C. Once cooled down to room temperature, samples and controls were again evaporated to dryness under nitrogen flow. Samples were finally dissolved in 1 mL isopropyl acetate prior to injection (1 µL). The injection was made in a Varian CP 3800 gas chromatograph coupled with an electron capture detector (GC-ECD). It was carried out using hydrogen as carrier gas with a flow of 1.6 mL/min in a Rxi-5Sil MS column (Restek, Pennsylvania, USA) (30m x 0.25 mm x 0.25 µm). Injector and detector temperatures were respectively held at 280°C and 300°C. The total runtime of an injection was 31.8 minutes. The program starts at 70°C for 0.8 min and then increased at a 5°C/min rate up to 130°C and held for 5 minutes. Then, a 60°C/min heating rate was held to reach 250°C and maintained for 15 minutes. Glyphosate and AMPA peaks were identified on the resulting GC-ECD chromatograms and then integrated.

The controls were used to plot the calibration curves by using their glyphosate and AMPA integrals as a function of their known glyphosate and AMPA levels. The five-points linear equation (r^2 > 0.92 and r^2 > 0.90 for glyphosate and AMPA, respectively) from the calibration curves allowed the conversion of each samples' integrals into glyphosate and AMPA content. The limit of detection (LOD) and the limit of quantification (LOQ) were determined based on the method described in Mocak *et al.* (1997). The calculated LOD and LOQ were 0.02 µg/g and 0.05 µg/g and 0.03 µg/g and 0.09 µg/g for glyphosate and AMPA, respectively.

Statistical analysis

Position indicators such as mean, median and quartiles were used to get hints about the data distribution and to produce box plots to ease sample distribution comparison. The non-parametric Wilcoxon-Mann-Whitney test (U-test) was conducted on the glyphosate and AMPA content to test if, whether or not, differences could be observed in terms of depth and location. Because variables are not normally distributed, this test was preferred over student t-test.

RESULTS AND DISCUSSION

The presence of glyphosate and AMPA was detected in almost every sampled farm soil regardless of the agricultural practices. As such, 16 out of the 17 sampled sites presented glyphosate contents over the LOD and all of them had AMPA content over the LOD. The average glyphosate content for the 17 sites analyzed in this study was 0.08 ± 0.11 (µg/g) and 0.06 ± 0.06 (µg/g) in the 0-20, 20-40 cm horizons, respectively, and was 0.14 ± 0.10 (µg/g) in the 40-60 cm horizon for the 6 sites where it was sampled. For AMPA, the average content was 0.23 ± 0.21 µg/g and 0.16 ± 0.10 µg/g in the 0-20, 20-40 cm horizons, respectively, and was 0.08 ± 0.07 µg/g in the 40-60 cm horizon for the 6 sites where it was sampled. Maximum glyphosate contents of 0.57 µg/g, 0.19 µg/g and 0.38 µg/g and AMPA contents of 0.98 µg/g, 0.38 µg/g and 0.20 µg/g in the 0-20, 20-40 and 40-60 cm horizons respectively contributed to spreading the span of the results (Figure 2). Glyphosate and AMPA contents reported in this study are of the same order of magnitude as most values reported for field crop soils around the world with the exception of some studies from Argentina (Table

2).

As suggested by Okada *et al.* (2016), total extracted glyphosate (TEG) was calculated by converting AMPA content into glyphosate equivalent using molecular weights and adding it to the measured glyphosate content, all horizons combined together. To compare TEG with the applicated glyphosate, we converted the glyphosate application rate from g/ha into g/m^3 over a 0.4 m depth at SB and CWB sites and 0.6 m depth at EA sites. Then, bulk density data corresponding to soil type, geographical proximity and agricultural conditions were used to convert the data from g/m^3 into µg/g (Denardin et al. 2014, Durigan et al. 2017). After those calculations, TEG content was higher than the amount of glyphosate spayed during the last GBH application in 100% of the samples. In 91% of the samples, TEG was higher than the yearly glyphosate application. In the organic farming sites, glyphosate and AMPA contents were above the LOD even though the last GBH application was done four years prior our sampling.

U-test ran over the whole data set revealed no difference in glyphosate or AMPA content between 0-20 cm and 20-40 cm depth. However, there were some significant differences within the dataset itself. As such, Eastern Amazonian sites exhibited AMPA contents significantly higher in the 0-20 cm horizon with respect to its 20-40 cm one (ρ=0.01). The 40-60 cm horizon of that same region showed glyphosate content significantly higher with respect to its 0-20 cm horizon (ρ=0.04) but not with its 20-40 cm one (ρ= 0.14). Also, AMPA content in 20-40 cm horizon was significantly lower in eastern Amazonian soils with respect to southern (ρ=0.0001) and central-west (ρ=0.031) Brazilian soils. On the opposite, glyphosate content observed in this same horizon (20-40 cm) was higher in the Eastern Amazon region compared to southern Brazil with a near significant ρ-value (ρ=0.054).

Usage of GBH by field crop farmers in Brazil is one of the highest in the world, ranging on average from 5 kg a.i./ha to 9 kg a.i/ha per year (Fernandes et al. 2018). Argentinian farmers surpass their Brazilian colleagues with 11 kg a.i./ha to 16 kg a.i./ha sprayed on average in 2014 (Vazquez 2014). For their part, US farmers use, on average 1.1 kg a.i./ha (Benbrook 2016), EU farmers a maximum of 4.32 kg a.i./ha (Silva et al. 2017) and Canada farmers from 0.25 kg a.i./ha to 4.32 kg a.i./ha. Although inconvenient to compare ranges to averages, these statistics give an insight of the GBH application rate around the world. In the present study, we purposefully included agricultural sites with relatively low-GBH applications in our sampling effort, i.e. DMC, ASP and AP farming systems (table 1). As such, we selected field crop sites with average annual GBH input of 1.69 kg a.i./ha, which is below the Brazilian average but, still, around that of the United States one.

Glyphosate and AMPA occurrence and content

With such an intense use of GBH around the world, it is not surprising to see growing observations of the ubiquity of glyphosate in agricultural soils (Aparicio et al. 2013, Lupi et al. 2015, Okada et al. 2018, Primost et al. 2017). In agreement with the scientific literature, quantifiable glyphosate and AMPA contents were measured on almost every site sampled in this study regardless of the agricultural practices employed. Considering the fact that 96 % of the Brazilian soybean production was genetically modified in 2019 (SoyStats 2020), the latter statement might seem obvious, but glyphosate and AMPA content and occurrence measurements had not previously been documented in Brazilian soil. To our knowledge, the only glyphosate content study in Brazilian soil was published by Bohm *et al.* (2014). Their results, along with those of Primost *et al.* (2017) for Argentina, stand out of the global

literature for being particularly high. In fact, most measurements of agricultural soil glyphosate and AMPA contents reported in the literature range between their LOD and 1 µg/g and rarely exceeds 1.5 µg/g (Table 2). Primost *et al.* (2017) explained their high values with record high yearly GBH applications. However, given the relatively low GBH application rate of our sites, the similarity of our data to the global literature raises some questions about the invoked positive correlation between GBH application rate and the glyphosate content in soils (Peruzzo et al. 2008, Primost et al. 2017). Indeed, site#1 was characterized with a GBH input similar to the most intensive one sampled by Primost *et al.* (2017). Still, glyphosate detected was under our LOQ and AMPA was 0.98 µg/g which is 39 times lower than what Primost *et al.* (2017) reported. Furthermore, Soracco *et al.* (2018) and Alonso *et al.* (2018), observed low glyphosate content in soils while their study area in Argentina also experienced intensive GBH spraying throughout their experiment.

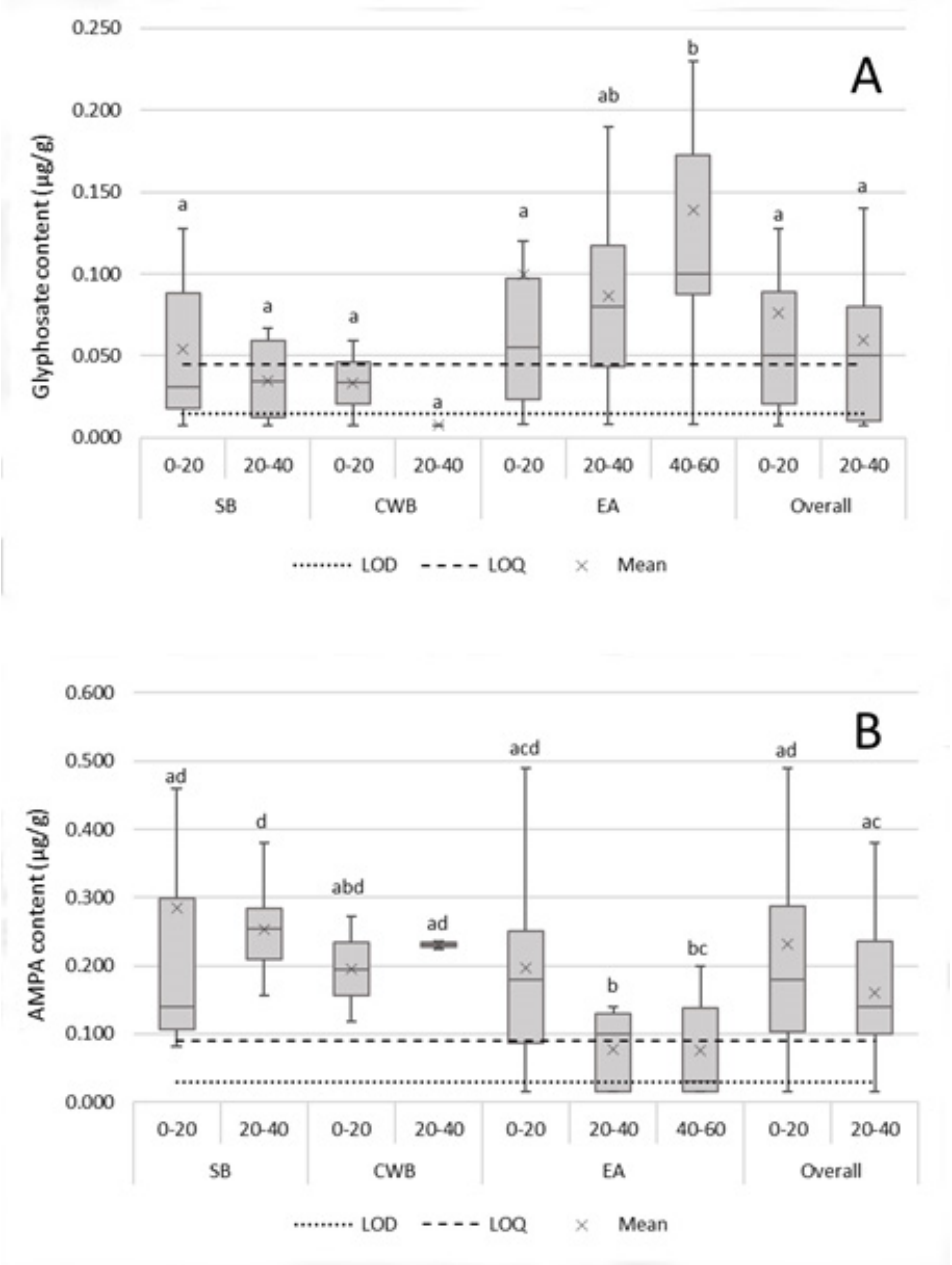

Figure 2. Box plot representing the regional and overall (A) glyphosate content (µg/g) and (B) AMPA content (µg/g) measured in 0-20 cm, 20-40 cm and 40-60 cm depth horizons (cm). SB: Southern Brazil, CWB: Central-West Brazil, EA: Eastern Amazon.

Table 2. Glyphosate and AMPA content measured in field crop agricultural soils around the world.

				Glyphosate (µg/g)			AMPA (µg/g)		
Articles	Country	Crop	Practices	Min	Max	Mean	Min	Max	Mean
Aparicio *et al.* (2013)	Argentina	soybean/wheat	na	0.03	1.50	0.40	0.30	1.05	0.69
Primost *et al.* (2017)	Argentina	soybean/corn/wheat	no-till	nd	8.11	2.30	na	38.94	4.20
Peruzzo *et al.* (2008)	Argentina	soybean	no-till	nd	4.45	na	na	na	na
Lupi *et al.* (2015)	Argentina	soybean/barley	Na	<LOD	0.25	na	<LOD	0.16	na
Alonso *et al.* (2018)	Argentina	soybean/corn	na	0.03	0.32	0.13	0.08	0.73	0.30
Soracco *et al.* (2018)	Argentina	corn/soybean	till/no-till	0.01	0.06	na	0.02	0.90	na
Okada *et al.* (2018)	Argentina	soybean/corn/wheat	till/no-till	0.00	1.22	0.18	0.00	7.35	0.78
Barwald Bohm *et al.* (2014)	Brazil	soybean	no-till	nd	nd	6.00	na	na	9.67
Candela *et al.* (2010)	Spain	wheat	no-till	<LOD	0.46	na	<LOD	0.22	na
Silva *et al.* (2017)	E.U.	wheat/barley/corn/oats	na	0.05	0.60	na	0.05	0.62	na
Scribner *et al.* (2007)	U.S.A.	corn/soybean	na	0.00	0.48	na	0.00	0.96	na
Humphries *et al.* (2005)	Canada	canola	na	<0.03	1.67	na	<0.15	0.40	na
Maccario (2020)	Canada	soybean	till/no-till, GR	0.01	0.47	0.07	0.02	1.09	0.30
Maccario (2020)	Canada	soybean	till/no-till, IP	0.01	0.45	0.06	0.02	1.16	0.26
Maccario (2020)	Canada	soybean	till, organic	0.01	0.15	0.04	0.02	0.24	0.06

na: not available, GR: Glyphosate resistant, IP: Identity preservation.

Our sampling campaign did not include a large enough number of AP, ASP and organic sites to statistically assess the dynamics of glyphosate and AMPA contents between those sites and the DMC sites. It seems that the GBH application rate is not sufficient to explain glyphosate and AMPA contents in soils. Other factors like runoff intensity and degradation rates should be considered. By taking into account tens of soil variables, GBH and fertilizer application rates, irrigation, glyphosate and AMPA kinetics and soil adsorption, Maggi *et al.* (2020) were able to model degradation recalcitrance of glyphosate and AMPA around the globe. Their work shows clearly Brazilian soils as significantly recalcitrant to glyphosate and more so AMPA degradation. This could lead to long-term persistence of these chemicals in Brazilian soils.

Glyphosate and AMPA persistence in Brazilian soils

The concept of persistence is a source of misconception among the scientific community. At the Stockholm Convention on persistent organic pollutants, the United Nations agreed to define persistence as a chemical trait acquired when the half-life of a compound is over 6 months in soils, 2 months in water or 6 months in sediments (United Nations Environment Program, 2001). Although practical to legislate and classify, this definition is arbitrary. The International Union of Pure and Applied Chemistry (IUPAC) rather defines persistence as « the residence time of a chemical species in a specifically defined compartment of the environment » (Greenhalgh 1980). With that said, the half-life of a chemical compound should not be considered as a constant trait but changing with soil environment.

As such, glyphosate and AMPA half-lives in soils are highly variable between studies. Very short half-life of 9 days for glyphosate and 32 days for AMPA have been reported in a reduced tillage, loam topsoil from Denmark (Simonsen et al. 2008)

while other longer glyphosate half-life of 210 and 1000 days have also been estimated respectively in Finnish clay soil and Danish sand soil (Borggaard & Gimsing 2008, Laitinen et al. 2006). Most studies agree that AMPA half-life in soils is longer than that of glyphosate. However, Bergström *et al.* (2011) showed that under high clay and high organic matter content, AMPA could be degraded faster than glyphosate. Glyphosate degradation kinetics fits a bi-exponential model or two-compartment kinetic model (Bento et al. 2016, Okada et al. 2017, Zablotowicz et al. 2009). The short soluble phase straight after spraying is characterized by a fast dissipation rate. Then, as glyphosate gets adsorbed to iron and aluminum oxides in soil, the dissipation rate declines with time (Borggaard & Gimsing 2008, Candela et al. 2010, Okada et al. 2017). At this point, glyphosate degradation is strongly dependent on its slow desorption (Zablotowicz et al. 2009). Once adsorbed, glyphosate traces could persist almost one year in soil (Okada et al. 2017). In fact, Okada *et al.* (2016) have identified the adsorption coefficient as the major factor defining glyphosate persistence. Primost *et al.* (2017) pointed out a "pseudo-persistence" behavior of glyphosate content in soil. In the latter study, expected glyphosate and AMPA contents were estimated based on the GBH application rate and frequency. The observed glyphosate and AMPA soil contents often exceeded the estimated one, which led the authors to conclude that a continuous replenishing of the degraded glyphosate occurred, defining the "pseudo-persistence" concept. Accordingly, following the UNEP (2001) definition of persistence, Maggi *et al*. (2020) showed that glyphosate might not be persistent (<6 months) in 73% of the croplands worldwide. But, for the other 27%, glyphosate can persist 12 to 24 months and even longer in certain parts of the world, which includes Brazil. For its part, AMPA could persist up to 20 years in a large portion of the worldwide cropland (Maggi et al. 2020).

Calculated TEG content in our samples were systematically above the glyphosate input from last GBH spraying event, even if, sampling was realized on average 180 days after the last GBH spraying (Table 1.). In addition, a large proportion of our samples revealed TEG contents above the total annual glyphosate application. Even if our method was not designed to measure residence time, our observations suggest that a fraction of TEG would not only reside over 6 months in Brazilian soils but even over one year. The slow full dissipation of TEG in Brazilian soils is consistent with Maggi *et al.*'s findings (2020) and progressively leads to the relatively long-term accumulation of glyphosate and AMPA in agricultural soils. The latter phenomena could be related to specific soil acidity which increases adsorption power of the soil matrix. Indeed, most of our sites were classified as dystrophic soil. These soils are known to have low base saturation which is a variable closely and positively related to pH (Kabala & Łabaz 2018). On top of that, glyphosate content above LOD was measured in the organic agriculture soils even if the last GBH spraying event took place at least 4 years earlier. Indeed, GBH spray drift or glyphosate and AMPA runoff could be in cause but it is not the first time that long-term residence of glyphosate and AMPA is reported. Simonsen *et al.* (2008) measured detectable glyphosate content after almost two years without any GBH application in a reduced tillage system in Denmark. Caution is also needed when claiming « pseudo-persistence ». Indeed, replenishing of glyphosate is likely to occur considering the heavy GBH usage but the possibility of a strong persistence, as our results suggest should not be neglected.

Glyphosate and AMPA contents along with soil depth

Glyphosate and AMPA are reported to usually accumulate in the first 5 cm or 10

cm of soil (Lupi et al. 2015, Okada et al. 2016, Soracco et al. 2018). The mobility of both chemicals towards deeper horizons appears limited by the strong adsorption of glyphosate to soil matrix. Okada *et al.* (2016) identified clay content and cation exchange capacity (CEC) as the major factors influencing glyphosate adsorption. AMPA adsorption capacity might be as strong as that of glyphosate (Sidoli et al. 2016) so neither glyphosate nor AMPA should easily percolate downwards in soils. In our study, neither global TEG nor glyphosate nor AMPA contents showed significant differences between soil depths except in eastern Amazon where glyphosate content increased in deeper horizons while AMPA content remained higher in topsoil. This means that, unlike what is commonly argued, glyphosate and AMPA did migrate vertically in a relatively easy way down to 40 cm depth (60 cm depth in eastern Amazon). Even if the majority of glyphosate pool is generally measured in the surface soil horizon, many authors have observed vertical migration of glyphosate towards deeper layers to a minor extent (Candela et al. 2010, Laitinen et al. 2006, Lupi et al. 2015, Soracco et al. 2018). As glyphosate is transported in its soluble form, hydraulic conductivity and macroporosity play an important role in this migration by regulating water percolation (Soracco et al. 2018). Indeed, it has been demonstrated that rainfall events shortly after GBH spraying can lead to rapid vertical migration of glyphosate, surpassing the adsorption power of the soil matrix (Candela et al. 2010, Lupi et al. 2015, Shushkova et al. 2010). This could result in glyphosate enrichment in deeper soil horizons (Lupi et al. 2015) like we observed in the eastern Amazon sites. The most accepted explanation for soluble glyphosate vertical migration is by preferential solute transport through macropores (Borggaard & Gimsing 2008, Candela et al. 2010, Laitinen et al. 2006, Soracco et al. 2018). Translocation by roots degradation (Laitinen et al. 2006), higher hydraulic conductivity (Soracco et al. 2018, Villarreal et al. 2020) and factors decreasing glyphosate adsorption such as higher soil pH and phosphate content (Borggaard & Gimsing 2008, Okada et al. 2016) are other invoked processes enhancing vertical migration of glyphosate. As glyphosate progresses downward into the soil, the bioactivity of microfauna decreases and so does the glyphosate degradation into AMPA (Bento et al. 2016, Bergström et al. 2011, Cecilia & Maggi 2017).

Eastern Amazon compared to southern Brazil

While two years separate the sampling campaigns in Eastern Amazon and the other Brazilian sites, caution should be the rule while comparing both regions as many factors could interfere from year to year. Yet, having data on such a wide latitudinal gradient is interesting because the annual precipitation and temperature are variables known to influence the dynamics of both chemicals in soils (Bento et al. 2016, Kummu & Olli 2010, Peruzzo et al. 2008). The U-test did confirm significant glyphosate and AMPA content differences between eastern Amazon and southern Brazil soils in the 20-40 cm horizon but not in the 0-20 cm horizon. Glyphosate content in the 20-40 cm was greater in eastern Amazon soils while AMPA content was greater in southern Brazil soils. The fact that glyphosate and AMPA contents differed in deeper horizons but not in topsoil was unexpected and no clear interpretation was found to explain this observation. Distinctive subsoil microbial activity could be a part of the explanation as soil microbial activity is dependent upon soil temperature, moisture, organic matter or O_2 availability (Bento et al. 2016, Cecilia & Maggi 2017). Brazilian data on these variables in relation with soil depth would be needed to support this hypothesis. That said, further research with corresponding sampling time on the agricultural agenda would be better suited to

verify the glyphosate and AMPA dynamics throughout Brazilian agricultural regions.

CONCLUSIONS

This study is the first broad-scale assessment of glyphosate and AMPA contents in field crop soils of Brazil. It highlights the backlash of conservation agriculture as far as glyphosate and AMPA presence in agricultural soils are concerned. It also lays the foundation of further research on the issue of the dynamics of these ubiquitous chemicals in field crop regions of Brazil. Glyphosate and AMPA persistence in Brazilian soils appear to be longer than what is usually reported in the literature, especially so for tropical environments.

Accumulation in topsoil has not been observed as both chemical species migrated relatively freely through soil horizons at least down to 40 cm depth. The worldwide concern about the ubiquitous presence of glyphosate and AMPA traces in the environment needs a broader screening in field crop soils of Brazilian agricultural regions as the majority of the available data comes so far from Argentina, Europe and to a lesser extent North America.

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