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Occurrence and levels of glyphosate and AMPA in shallow lakes from the Pampean and Patagonian regions of Argentina

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HIGHLIGHTS

- We measured herbicide concentrations in lakes from the Pampa and Patagonia region.
- Glyphosate residues were detected only in the agriculture impacted Pampa region.
- Glyphosate is more frequent in sediment and water than in particulate matter.
- Glyphosate and AMPA were seldom detected together.

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ABSTRACT

Glyphosate (N-(phosphonomethyl)glycine) is a broad-spectrum systemic herbicide used to kill weeds that compete with commercial crops. In Argentina, the use of glyphosate-based herbicides increased dramatically (up to ~200,000 tons on 2012) since the introduction of glyphosate-resistant crops, such as transgenic soy and resistant corn, and the adoption of non-till practices in the 1990's. Sallow lakes within the Pampa region may be potentially impacted by continuous herbicide usage. We surveyed 52 shallow lakes from the Pampa region (Buenos Aires Province, Argentina) to assess the occurrence and concentrations of glyphosate and its main degradation product (AMPA). For comparison, we also sampled 24 shallow lakes from an area with no agricultural use of glyphosate (Northern Patagonia). Glyphosate and AMPA were analyzed by UPLC-MS/MS ESI (±) in lake water, suspended particulate matter (SPM), and sediment samples. Within the Pampa region, glyphosate residues were detected in >40% of samples. Glyphosate residues were detected more frequently in sediment and surface water than in SPM samples. The mean (maximum) concentrations of glyphosate were 2.11 (4.52) $\mu g\ l^{-1}$ for surface water; 0.10 (0.13) $\mu g\ l^{-1}$ for SPM and 10.47 (20.34) $\mu g\ kg^{-1}$ for sediment samples, respectively. Whereas, mean (maximum) concentrations of AMPA were 0.84 and (0.90) $\mu g\ l^{-1}$ for surface water; 0.07 (0.07) $\mu g\ l^{-1}$ for SPM; and 22.53 (32.89) $\mu g\ kg^{-1}$ for sediment samples. The herbicide was not detected in samples from the Patagonian region. To our knowledge, this is the first study reporting the occurrence and concentrations of the herbicide in freshwater lakes of Argentina.

1. Introduction

Glyphosate (N-(phosphonomethyl)glycine) is a broad spectrum, nonselective herbicide. Glyphosate-based formulations have become the dominant herbicides on a global scale. They were initially adopted for the eradication of unwanted weed species, but more recently they are increasingly being used as desiccants on agriculture crops (Cuhra et al., 2016). The Argentine agricultural production depends to a large extent on a technological package that combines no-till farming (NTF) practices and glyphosate for the production of glyphosate-resistant (GR) crops, mostly soybean, maize and cotton, which together occupy 23 million hectares. The massive adoption of glyphosate for agricultural production in Argentina can be traced back to 1996, when the first GR soybean was authorized for commercial production. Since then, the Ministry

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of Agro-industry and the National Commission of Agricultural Biotechnology (CONABIA) have authorized the production of new GR soybean (5), maize (17) and cotton (3) varieties. Glyphosate use in Argentina has increased dramatically since its introduction, reaching approximately 200,000 tons in 2012, and representing 80% of total commercialized herbicides (CASAFE, 2012; Primost et al., 2017). In addition to the overwhelming adoption of NTF practices, the use of glyphosate has been favored by the price drop due to the expiration of its patent in 2000 and the increasing number of glyphosate manufacturers. Glyphosate-based herbicides (GBH) are mainly applied over summer and winter crops, as well as during the fallow period (Johnson et al., 2002; Pérez et al., 2017). Besides its use in agriculture and silviculture, glyphosate is also used for the maintenance of public spaces (parks, gardens) and for aquatic weed control (Held et al., 2016; Kogan and Alister, 2010; Tasker, 1995). In fact, the ubiquitous occurrence of glyphosate in wastewater has been interpreted as an indication that non-agricultural uses of glyphosate may substantially contribute to the total burden to surface waters (Poiger et al., 2017).

Glyphosate inhibits the 5-enolpyruvyl-shikimate-3-phosphate synthase (EPSPS), an enzyme of the shikimic acid pathway responsible for the synthesis of aromatic amino-acids. Thus, the synthesis of proteins needed for plant development and growth is compromised. Under field conditions, glyphosate is degraded (mostly through microbial activity) to aminomethylphosphonic acid (AMPA) and CO_2. Reports of glyphosate half-life in soils and surface waters range from 2 to 215 days and from 2 to 91 days, respectively. AMPA has a longer half-life in soil (60–240 days) whereas its half-life in aquatic environments is similar to that of glyphosate (Battaglin et al., 2014).

There is growing evidence on acute and chronic toxic effects of glyphosate and GBH on different target organisms (i.e. algae, microorganism, invertebrates, amphibians, fish, birds) (Pérez et al., 2011 and references therein). However, concentrations of glyphosate assayed in toxicology experiments are typically orders of magnitude higher than those reported in aquatic environments. Despite the need for accurate identification and quantification of glyphosate residues, a number of methodological pitfalls (need of specialized training, expensive equipment, use of hazardous chemicals) (Annett et al., 2014) pose serious constrains on routine field assessments. Moreover, under real-world conditions, the likelihood of glyphosate and AMPA detection, as well as their measured concentrations, are influenced by a number of factors beyond the researcher's control, such as source, variation in spatial and temporal application, hydrology, water movement pathways and degradation rate (Coupe et al., 2012). As a result, systematic assessments of glyphosate concentrations in lakes are scarce (but see McMurry et al., 2016), and for most part of the world, virtually non-existent.

Over 75% of the cultivated area and production of oilseeds and cereals in Argentina is located in three provinces (Santa Fe, Córdoba and Buenos Aires), which together encompass a large proportion of the South American Pampean plains (Ministry of Agro-industry). This large region (>600,000 km^2) harbors one of the largest wetland areas of South America (Diovisalvi et al., 2015). The occurrence of glyphosate and AMPA have been reported in the water and sediments of streams from rural and suburban basins within the provinces of Buenos Aires (Aparicio et al., 2013; Lupi et al., 2015; Mac Loughlin et al., 2017), Santa Fe (Ronco et al., 2016) and Córdoba (Bonansea et al., 2017), but their occurrence in lakes has not yet been assessed. Numerous permanent or semi-permanent lakes occupy wet lowlands of the Pampean landscape. These shallow lakes (locally called "lagunas") are typically polymictic and eutrophic, with highly variable water residence time (Quirós, 2005). Lakes are sensitive ecosystems that integrate the effects of stressors in the watershed (Adrian et al., 2009; Williamson et al., 2014, 2009). Due to the continued agriculturalization process (Quirós et al., 2006), most shallow Pampean lakes may be susceptible to pesticide contamination through surface run-off, leaching, direct overspray and/or spray drift (Annett et al., 2014).

The aim of this study is to assess the occurrence and concentration of glyphosate and AMPA in the water and sediment of shallow Pampean and Patagonian lakes. Patagonian lakes were selected from areas with no reported agricultural use of GBH, but where other uses (i.e., weed control along highways and railroads, gardening and weed control in residential areas, parks, golf courses, etc.) could not be ruled out. Herbicide residual concentrations were analyzed in relation to limnological variables and land-use descriptors of the surrounding areas. To the best of our knowledge, there is no previous information on the levels of glyphosate and AMPA for South American shallow lakes.

2. Materials and methods

2.1. Area of study

The Pampa region, one of the largest flatlands in the world, includes the center-east part of Argentina, most of Uruguay and the southernmost Brazilian state, Rio Grande do Sul. The Buenos Aires Province has an area of 307,000 km^2 at the core of the Pampa Plain. Its gentle slope is only interrupted by two mountain ranges: Ventania and Tandilia. Buenos Aires is under a temperate climate, with warm-temperate summers and cold winters. There is a precipitation gradient that ranges from 1,000 mm $year^{-1}$ in the Northeast to 400 mm $year^{-1}$ in the Southwest (Viglizzo and Frank, 2006; Volpedo, 2013). The poorly developed drainage area results in a large wetland, comprising large numbers of natural and man-made water bodies: shallow lakes, rivers, creeks, lagoons, and reservoirs (Iriondo, 2004; Volpedo, 2013).

Fifty-two shallow Pampean lakes were sampled in order to assess the occurrence and concentrations of glyphosate and AMPA in Buenos Aires lentic environments. The lakes were chosen based on their social (drinking water), cultural (recreational), economic (tourism, cropland irrigation), environmental (biodiversity) and scientific relevance. Sampling campaigns were carried out between September 14th and December 2nd, 2015 (i.e., spring in the Southern Hemisphere).

Although glyphosate is used all year round with different purposes, by focalizing the field sampling to springtime we aimed at maximizing the chances of herbicide detection: glyphosate is used as a major component for chemical fallow in the pre-sowing period (INTA, 1997a, 1997b, 1997c), as a desiccant for preharvest in winter crops like wheat and barley (AHDB-HGCA, 2008; Monsanto, n.d.) and as a selective herbicide over glyphosate resistant crops. In addition, 24 lakes located in non-agricultural areas of Northern Patagonia lakes were sampled during November 2016 (Fig. 1, and Table SM-1 in the Supplementary Material, SM).

2.2. Sampling

Water temperature, pH (Orion pH-meter), conductivity (Hach conductometer), dissolved oxygen concentration (DO; YSI 5000 m), turbidity (Hach turbidimeter 2100 P) and Secchi disc depth were measured *in situ.* Sub superficial water samples for physical, chemical and biological determination were taken from each lake. Sampling sites were typically ~1 m deep. Samples for herbicide determinations were collected concurrently and stored according to standardized methodologies. Three environmental compartments were analyzed: dissolved fraction (i.e., water), suspended

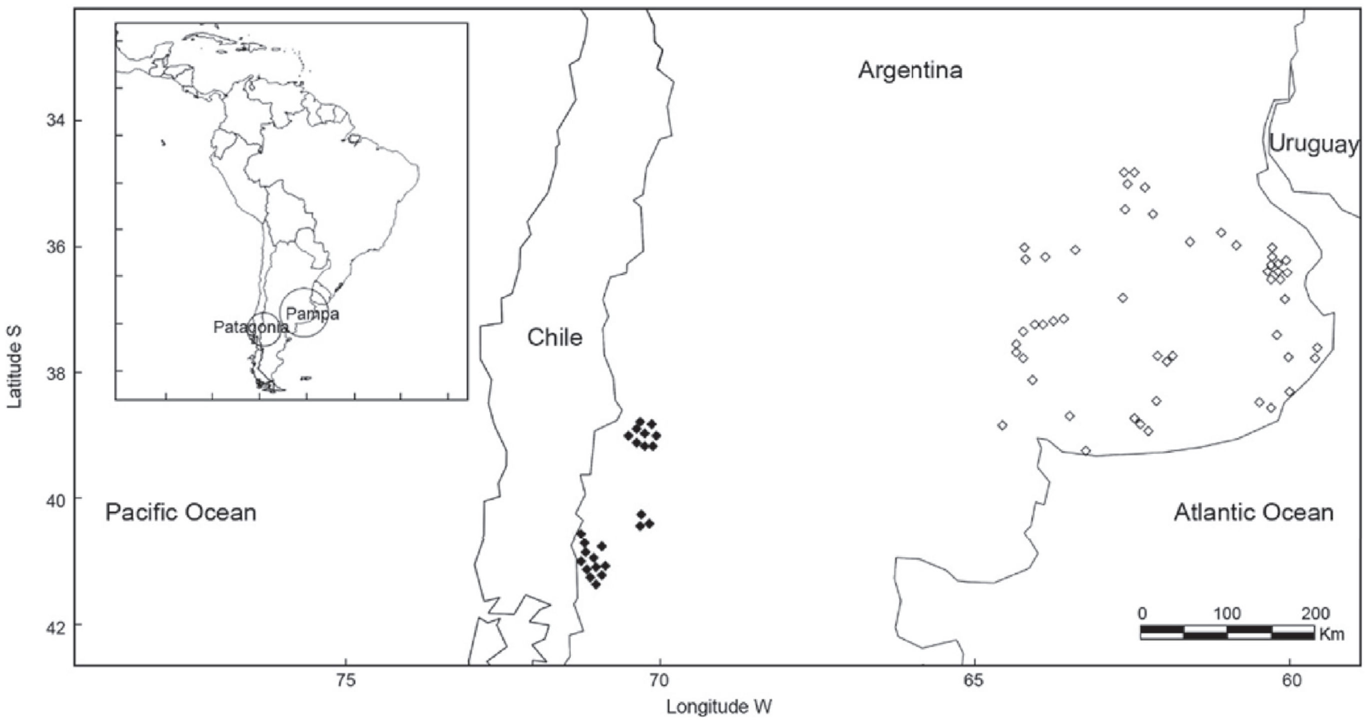

Fig. 1. Map of the study area showing the geographical distributions of Pampean (open diamonds) and Patagonian (solid diamonds) shallow lakes (for geographic coordinates see Table SM-1). Inset: the study area within South America.

particulate matter -SPM- (GF/F filters) and sediments (APHA/AWWA/WEF, 2012; Iwatsubo and Groat, 1999).

2.3. Chemical and physical analyses

Water analyses were performed following APHA (1992): suspended particulate matter (SPM) by drying to constant weight at 103–105 °C precombusted and weighted GF/F filters (method 2540D); particulate organic matter (POM) was estimated as the weight difference between dry and ignited SPM filters (method 2540E); total phosphorus (TP, unfiltered water) and total dissolved phosphorus (TDP, GF/F filtered water) by the Ascorbic Acid Method (method 4500-P-E); total organic nitrogen (TON, unfiltered water) and total dissolved organic nitrogen (TDON, GF/F filtered water) by semi-micro-Kjeldahl method (method 4500-Norg-C); chlorophyll-*a* concentration (Chl-*a*) by the Monochromatic Spectrophotometric Method (Lopretto and Tell, 1995); dissolved organic carbon (DOC) was measured with a Shimadzu TOC-L high temperature analyzer (GF/F filtered water). The mean DOC concentration resulting from each DOC measurement corresponds to the average of 2–4 injections of 400 μL (coefficient of variation (CV) < 2%).

2.4. Glyphosate and AMPA analyses

Analyses were performed using high-performance liquid chromatography and mass spectrometry (HPLC-MS) after derivatization with 9-fluorenylmethoxylcarbonyl chloride (FMOC-CL; Sancho et al., 1996). 10 μL of isotopically labeled glyphosate standard (1 $\mu g\, l^{-1}$) was added to 1 mL of sub-superficial water samples. Then, samples were derivatized by adding 50 μL (40 mM) sodium tetraborate (pH 9) followed by 1 mL of FMOC-CL solution in acetonitrile (1 $mg\, mL^{-1}$) addition. The solution was kept overnight in the dark at room temperature (Ibáñez et al., 2005). GF/F filters, containing suspended matter, were extracted by adding 3 ml of phosphate solution (0.1 M K_2PO_4), shook, sonicated 15 min twice and centrifuged (Miles and Anson Moye, 1988). 60 μL of isotopically labeled glyphosate standard (1 $\mu g\, l^{-1}$) was added to 1 mL of the extract. Then, derivatization with FMOC-CL and overnight was followed as in water samples (Ronco et al., 2016). Wet sediment samples were homogenized and 5.0 g of dry weight subsamples were transferred to centrifuge tubes (50ml) (Ibáñez et al., 2005). 100 μL of isotopically labeled glyphosate standard (20 $\mu g\, l^{-1}$) was added. Samples were extracted by adding 25 ml of phosphate solution (0.1 M K_2PO_4), shook manually, sonicated 15 min twice and centrifuged (Miles and Anson Moye, 1988). One milliliter of the extract was used for derivatization with FMOC-CL as in water samples. All derivatized samples were finally extracted with 3 ml dichloromethane, shook and centrifuged. After that, the aqueous phase was injected into the LC-ESI-MS/MS for HPLC-MS determination.

An Agilent 1100 liquid chromatograph model was used for detection and quantification of GLY + AMPA, with ESI ionization source operating in negative mode, coupled to an Agilent model VL single quadrupole mass spectrometer (Agilent Technologies Inc., Miami, FL, USA). Chromatographic separation was performed in a C18 X-SELECT ™ column (75 mm × 4.6 mm and 3 mm pore size, from Waters Corp., Milford, MA, USA) using methanol and nanopure water gradient, with NH_4Ac as ionization additive, according to the methodology described by Ronco et al. (2016). Glyphosate and AMPA were quantified by means of an external calibration curve ranges from 0 to 200 $\mu L^{-1}$and through a measurement of the area under the chromatographic peaks after considering the dilution effected on each tree matrices and the recovery of each compound. The software use for the system operation was Aligment ChemStation LC-MSD (Rev.10A.02).

Pesticide-residual-grade dichloromethane, HPLC grade acetonitrile and methanol were all obtained from J. T. Baker (USA). The 9-fluorenylmethyl chloroformate (FMOC-Cl) for HPLC derivatization, standards of glyphosate (99%), AMPA (98.5%), glyphosate-2^{13}C,^{15}N (99 atom % ^{13}C, 98 atom % ^{15}N; ^{13}C, ^{15}N-GLY) were acquired from Sigma Al-drich (St. Louis, MO, USA). A Sartorius Arium water purification system (Sartorius AG, Göttingen, The Netherlands) was used to obtain nanopure water. Potassium phosphate dibasic (K_2HPO_4), and ammonium acetate (NH_4Ac) (all analytical grade) were obtained from Merck (Darmstadt, F.R. Germany).

Quality controls for glyphosate and AMPA were ensured by using procedural and instrumental blanks duplicates and certificated reference material (Ich, 2005). Linearity, reproducibility, precision, accuracy, detection and quantification limits (DL & QL), matrix effect and recovery were accordingly tested (SANTE/EU, 2015). Glyphosate and its environmental metabolite AMPA were analyzed. Linearity, precision, accuracy, detection and quantification limits (DL & QL) were acceptable and in agreement with the methodological validation by Ronco et al. (2016).

When the concentration of glyphosate was below the detection limit it was set to zero, when it was between detection and quantification limit it was replaced with the value of detection limit. The total glyphosate + AMPA was calculated as the sum of glyphosate and AMPA concentrations for each compartment. The percentage of AMPA (%AMPA) was calculated as the percentage of AMPA concentration in total glyphosate + AMPA concentration in each compartment.

2.5. Land cover/land use characterization

A land cover classification was developed based on a time series of 24 EVI image products covering the period from January 2015 to January 2016. Each image corresponds to a 16-day composite EVI (Enhanced Vegetation Index) from MODIS-Terra product MOD13Q1 V006, with pixel size of 250 m. The study region is covered by two product tiles (h12v12 and h13v12) which were mosaicked before stacking. An initial clustering on 10 classes was performed using the Iterative Self-Organizing Data Analysis Technique (ISODATA) algorithm (Ball and Hall, 1967; Biehl and Landgrebe, 2002). We interpreted the EVI time signature of each class by means of landscape observations via Google Earth (https://www.google.com/earth/) and assign it to a land cover/land use class. The initial classes were regrouped into: cropland, grassland, vegetated wetland, wetland with open water or exposed substrate, and water. Urban areas were added as a mask from MODIS Land Cover Type product (MCD12Q1, Land Cover Type = 3). Lake polygons were extracted from the Water Bodies vector shapefile published by Instituto Geográfico Nacional (http://www.ign.gob.ar/sig#descargas), and 5 km buffer area was defined for each studied lake. Land use/land cover data was extracted within buffer areas and class pixel numbers were converted to percentages. Image processing was done using MultiSpecW32 software (http://engineering.purdue.edu/~biehl/MultiSpec/); QGIS (http://www.qgis.org) and R (https://cran.r-project.org/), were used for GIS processing and lake attribute data organization.

2.6. Statistical methods

Non-parametric Spearman's correlations were performed to relate the levels of herbicide residues to environmental variables (geographical and morphometric variables, limnological parameters, land cover descriptors). The relationship between glyphosate + AMPA concentration in sediments (for non-zero values) vs. lake area (log transformed) was investigated using linear regression. The Normal distribution of data was verified using the Shapiro-Wilk test.

3. Results

3.1. Water physicochemical variables

Most limnological variables showed overlapping ranges for both set of samples (i.e. Pampean and Patagonian lakes). However, maximum values of chl-*a*, nitrogen, phosphorus and DOC were one order of magnitude higher in the Pampean lakes (Table 1). Within the Pampean region, similar ranges of physicochemical-variables were observed for the seven watersheds analyzed (Table SM-1).

3.2. Land use/land cover characteristics

Within the Pampean region, cropland was the major land cover descriptor in five out of seven watersheds (Table 2). Its percentage coverage, decreased with latitude ($r = 0.7032$; $P_{value} < 0.0001$) and longitude ($r = 0.5769$; $P_{value} < 0.0001$), while the percentage of grassland coverage increased with latitude ($r = -0.6862$; $P_{value} < 0.0001$) and that of vegetated wetland increased with both latitude ($r = -0.7720$; $P_{value} < 0.0001$) and longitude ($r = -0.5912$; $P_{value} < 0.0001$). A northeast-southwest (NE-SW) gradient was observed, with higher cropland coverage and less grassland and/or vegetated wetland coverage in the NE region of the Buenos Aires Province (Fig. 2). On the other hand, urban development was observed in more than half of the sampled lakes (Table SM-2).

Table 1
Summary statistics of environmental variables for the Pampean and Patagonian sets of lakes.

	Pampean Lakes (n = 52)				Patagonian lakes (n = 24)			
	Mean	SD	Max	Min	Mean	SD	Max	Min
Water temperature (°C)	18.5	5.1	30	6.5	16.7	2.1	20.7	13
DO ($mg\,l^{-1}$)	10.24	2.6	20	5	9.47	1.89	11.32	5.3
PH	8.76	0.31	9.40	8	8.24	0.99	10.33	5.64
Conductivity ($mS\,cm^{-1}$)	7.97	27.79	202.10	0.32	0.85	1.45	4.58	0.02
Secchi disc depth (cm)	29	29	140	7	26	19	46	4
Turbidity (NTU)	88.67	76.60	363	2.71	13.99	30	151	1.01
SPM ($mg\,l^{-1}$)	116.8	142.5	788.4	6.7	41.6	100.4	456	1.5
POM ($mg\,l^{-1}$)	40.80	47.60	344	6.70	12.79	19.34	83	1.5
DOC ($mg\,l^{-1}$)	93.23	176.30	1010	1.63	16.84	24.03	112.60	0.99
Chl-a ($\mu g\,l^{-1}$)	87.8	152.2	981.1	1.6	8.8	8.9	35.4	0.01
TON ($\mu g\,N\,l^{-1}$)	5063.0	1474.4	10830.4	2856.0	535.5	218.4	941.2	201.2
TDON ($\mu g\,N\,l^{-1}$)	3790.1	1072.2	7235.2	1926 4	348.2	212.5	765.2	123.2
TP ($\mu g\,P\,l^{-1}$)	766.1	876.3	4538.0	46.1	154.6	242.1	898.9	14.1
TDP ($\mu g\,P\,l^{-1}$)	560.4	804.0	4139.6	0.1	80.8	197.4	892.9	0.1

Abbreviations: DO: dissolved oxygen, SPM: suspended particulate matter, POM: particulate organic matter, DOC: dissolved organic carbon, Chl-*a*: chlorophyll-*a*, TON: total organic nitrogen, TDON: total dissolved organic nitrogen, TP: total phosphorus and TDP: total dissolved phosphorus. SD: standard deviation.

Table 2
Average coverage (percentage) of each land cover descriptor within the defined 5 km buffer area of each lake (see text for details). The values are averages of all lakes within each watershed, as defined by Subsecretaría de Recursos Hídricos de la Nación Argentina (https://www.mininterior.gov.ar/obras-publicas/info-mapas.php).

Watershed Id./Watershed[a]	Number of lakes	Cropland	Grassland	Land use/land cover percentage (%)		Water	Urban/ Residential
				Vegetated wetland	Wetland with open water or exposed substrate		
48- Rio Salado of Buenos Aires	20	78.6	4.2	2.3	4.6	8.1	2.2
49- Channelted area to the south of the Rio Salado	5	66.5	15.9	7.5	5.1	4.9	0.1
50- Streams of the south east of Buenos Aires	3	48.8	16.2	13.3	8.4	11.2	2.0
51- Streams of the south of Buenos Aires	9	47.3	20.2	10.8	3.6	15.8	2.3
61- Rivers and minor streams with Atlantic slope between the south of Buenos Aires and the Chubut river	1	32.0	31.1	26.8	3.2	4.8	2.0
96- Region without drainage of San Luis, Cordoba, La Pampa and Buenos Aires	4	16.2	33.0	24.1	5.9	19.8	1.0
98- Shallow lakes region of the southwest of Buenos Aires	10	0.1	07	779	59	15.4	0.0
Total lakes	52						
Mean land use/land cover classes		41.4	17.3	23.2	5.3	11.4	1.4

[a] According to Subsecretaría de Recursos Hídricos de la Nación Argentina.

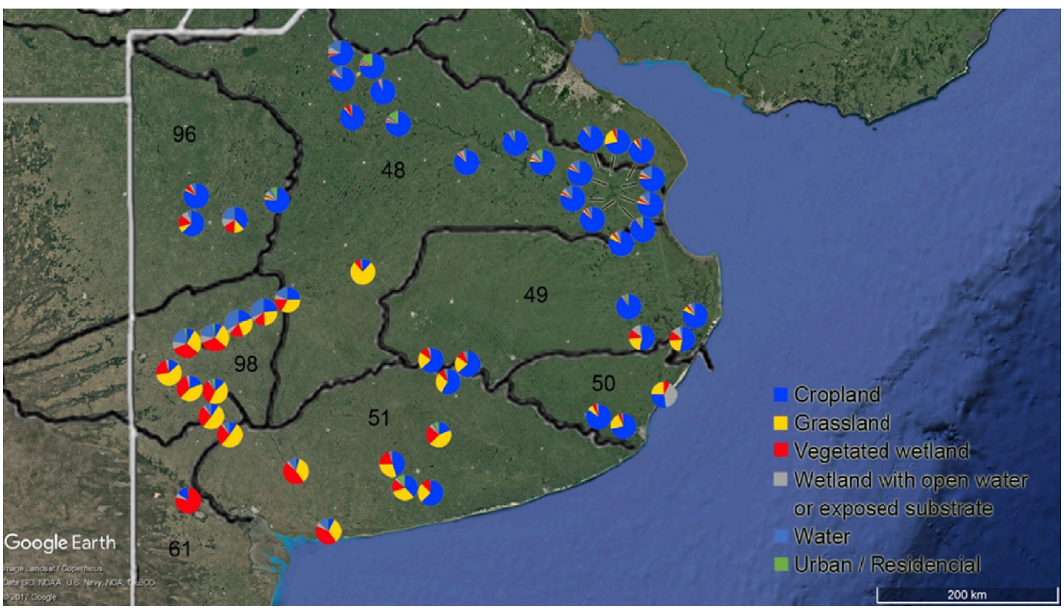

Fig. 2. Geographical location and land cover descriptors for the 5km buffer area of each Pampean lake. Each pie graphs shows the relative coverage for each lake. The numbers correspond to the watershed codes (as in Table 2) according to the Subsecretaría de Recursos Hídricos de la Nación Argentina.

3.3. *Herbicide occurrence, levels and geographical distribution*

No herbicide residues were found in samples from Patagonian lakes. In contrast, herbicide residues were detected in 40.4% of samples from Pampean lakes. Within each Pampean watershed, at least one positive detection of glyphosate or AMPA was observed (Table 3). Glyphosate was detected in 30.8% and AMPA in 13.5% of the samples from Pampean lakes, considering all three compartments (i.e. surface water, SPM and sediment). Detection frequencies were higher for both chemicals in sediments than in the other two compartments. Glyphosate was detected in 13% of surface water, 6% of SPM and 21% of sediment samples. AMPA was detected in 4% of surface water, 4% of SPM, and 8% of sediment samples. The mean (maximum) concentrations of glyphosate were 2.11 (4.52) μg l^{-1} for surface water; 0.10 (0.13) μg l^{-1} for SPM and 10.47 (20.34) μg kg^{-1} for sediment samples, respectively. Whereas, mean (maximum) concentrations of AMPA were 0.84 and (0.90) μg l^{-1} for surface water; 0.07 (0.07) μg l^{-1} for SPM; and 22.53 (32.89) μg kg^{-1} for sediment samples.

Glyphosate and AMPA were seldom detected together in a single lake, exceptions being Lakes Chasicó and La Lujan. Moreover, over 70% of the herbicide (either glyphosate or AMPA) detections were made in only one compartment: i.e., water, SPM or sediment. La Luján was the only lake where both chemicals were found in the same compartment (sediment). September was the month with the highest number of positives detections (76%), followed by October (19%) and December (5%), no detections were registered in November (Fig. 3). Furthermore, in September Glyphosate + AMPA concentration exceeded October, November and December in one order of magnitude in the dissolved and particulate fraction.

No significant correlations were found between herbicide levels vs. geographical location, limnological variables, or land use/land cover descriptors. On the other hand, the concentration of glyphosate + AMPA found in sediments showed significant

Table 3
Concentrations of glyphosate and AMPA in each of the three compartments (water, SPM, and sediment) for each shallow Pampean lake. Ancillary information: sampling dates, lake type, and basic morphometric descriptors (area, perimeter and coastline development).

Lake	Lake ID	Sampling Date	Watershed ID[a]	Type	Morphometric Variables			Glyphosate			AMPA		
					Area (km^2)[b]	Perimeter (km)[b]	Coastline development[c]	Water ($\mu g\ l^{-1}$)	SPM ($\mu g\ l^{-1}$)	Sediment ($\mu g\ kg^{-1}$)	Water ($\mu g\ l^{-1}$)	SPM ($\mu g\ l^{-1}$)	Sediment ($\mu g\ l^{-1}$)
Chascomus	CH	17/9/15	48	Lake	30.76	32.34	1.65	–	–	–	–	–	–
La limpia	LI	14/9/15	48	Lake	6.34	14.07	1.58	–	–	–	–	–	–
El triunfo	TR	14/9/15	48	Lake	1.59	5.89	1.32	–	–	–	0.90	–	–
La Salada de monasterio	SM	14/9/15	48	Lake	5.51	14.77	1.77	–	–	-	–	–	–
Vitel	VI	14/10/15	48	Lake	15.20	22.62	1.64	–	–	–	–	–	–
Las Tablillas	TA	14/10/15	48	Lake	13.07	39.91	3.11	–	–	–	–	–	–
Barrancas	BS	14/10/15	48	Lake	9.95	21.75	1.94	–	–	–	–	–	–
Chis-Chis	CC	14/10/15	48	Lake	18.11	47.37	3.14	–	–	–	–	–	–
El Burro	BU	14/10/15	48	Lake	10.34	20.55	1.80	–	–	–	–	–	12.93
Adela	AD	14/10/15	48	Lake	24.95	59.43	3.36	–	–	–	–	–	–
Blanca Grande	BG	28/10/15	48	Lake	4.10	11040	1.59	–	–	–	–	–	–
Lobos	LO	29/10/15	48	Lake	7.30	14.14	1.48	–	–	–	–	–	–
Rocha	RC	24/11/15	48	Lake	4.60	16.30	2.14	–	–	–	–	–	–
Mar Chiquita (Junin)	MA1	24/11/15	48	Lake	71.49	141.17	4.71	–	–	–	–	–	–
Gómez	GO	24/11/15	48	Lake	61.64	118.92	4.27	–	–	–	–	–	–
Carpincho	CA	24/11/15	48	Lake	3.60	10.62	1.58	–	–	–	–	–	–
Azotea	AZ	25/11/15	48	Lake	0.20	1.85	1.17	–	–	–	–	–	–
Bragado	BR	25/11/15	48	Lake	4.03	9.30	1.31	–	–	–	–	–	–
Indio Muerto	IM	2/12/15	48	Lake	4.77	19.42	2.51	–	–	–	–	–	–
Monte	MT	2/12/15	48	Lake	6.49	11.47	1.27	–	–	–	–	–	–
Sevigne	SE	15/9/15	49	Lake	0.81	3.68	1.15	1.50	–	–	–	–	–
Kakel Huincul	KH	15/9/15	49	Lake	16.41	29.22	2.03	–	–	–	–	–	–
Samboy	SY	15/9/15	49	Lake	3.83	11.31	1.63	–	0.13	–	–	–	–
Salada Grande	SG	15/9/15	49	Lake	46.67	74.45	3.07	–	0.12	–	–	–	–
Los Horcones	HR	15/9/15	49	Lake	3.30	16.81	2.61	–	–	10.73	–	–	–
Mar Chiquita (MDQ)	MA2	15/9/15	50	Lagoon	45.32	69.08	2.89	–	–	–	–	–	–
De los Padres	LP	16/9/15	50	Lake	2.99	10.32	1.68	–	–	–	–	0.07	–
La Brava	BV	16/9/15	50	Lake	4.23	12.15	1.67	–	–	–	0.77	–	16.04
Embalse Paso de las Piedras	PI	28/9/15	51	Reservoir	29.41	58.86	3.06	<QL	–	9.91	–	–	–
Sauce Grande	SU	29/9/15	51	Lake	22.54	31.76	1.89	–	–	5.10	–	–	–
La Tigra	Tl	29/9/15	51	Lake	3.75	9.62	1.40	–	–	–	–	–	–
La Lujan	LU	29/9/15	51	Flooded lake	1.36	4.74	1.15	–	–	20.34	–	–	32.89
La Juanita	LJ	30/9/15	51	Lake[d]	0.74	5.34	1.75	1.61	–	–	–	–	–
San Pablo	SP	30/9/15	51	Lake	2.45	10.33	1.86	–	–	11.43	–	–	–
Salada de Tedin Uriburu	ST	30/9/15	51	Lake	2.36	11.49	2.11	2.16	–	12.16	–	–	–
El Chifle	EC	30/9/15	51	Lake	1.49	5.12	1.18	–	–	–	–	–	–
La Barrancosa	LB	30/9/15	51	Lake	2.26	7.50	1.41	–	–	–	–	–	–
Chasicó	CS	28/9/15	61	Lake	55.76	47.20	1.78	4.52	–	10.28	–	00.6	–
Cuero de Zorro	ZO	1/12/15	96	Lake	11.04	18.00	1.53	–	–	7.30	–	–	–
Los Quilmes	QU	1/12/15	96	Lake	12.88	18.76	1.47	–	–	–	–	–	–
Hinojo Grande	HG	1/12/15	96	Lake	48.63	44.49	1.80	–	–	–	–	–	–
Pehuajó	PE	2/12/15	96	Lake	9.72	25.25	2.28	–	–	–	–	–	–
Flamencos Sur	FS	28/9/15	98	Lake	7.27	19.10	2.00	1.64	0.04	10.92	–	–	–
Flamencos Norte	FN	28/9/15	98	Lake	18.90	30.22	1.96	–	–	12.35	–	–	–
Cochicó	CO	27/10/15	98	Lake	49.43	45.41	1.82	–	–	4.65	–	–	–
Del Monte	MO	27/10/15	98	Lake	153.51	76.14	1.73	1.25	–	–	–	–	–
Del Venado	VE	27/10/15	98	Lake	76.62	71.18	2.29	–	–	–	–	–	–
Epecuén	EP	27/10/15	98	Lake	157.81	111.02	2.49	–	–	–	–	–	–
Los Patos	PA	28/10/15	98	Lake	1.22	4.77	1.22	–	–	–	–	–	–
La Cortada	CT	28/10/15	98	Lake[d]	0.20	1.91	1.21	–	–	–	–	–	28.25
Puán	PU	28/10/15	98	Lake	7.10	11.50	1.22	–	–	–	–	–	–
Alsina	AL	28/10/15	98	Lake	78.49	93.07	2.96	–	–	–	–	–	–

[a] According to Subsecretaria de Recursos Hídricos de la Nación Argentina. For references see Table 2.
[b] Calculated using QGIS.
[c] Calculated according to Quirós (2004).
[d] Semi-permanent lake, <LQ = Below quantification limit.

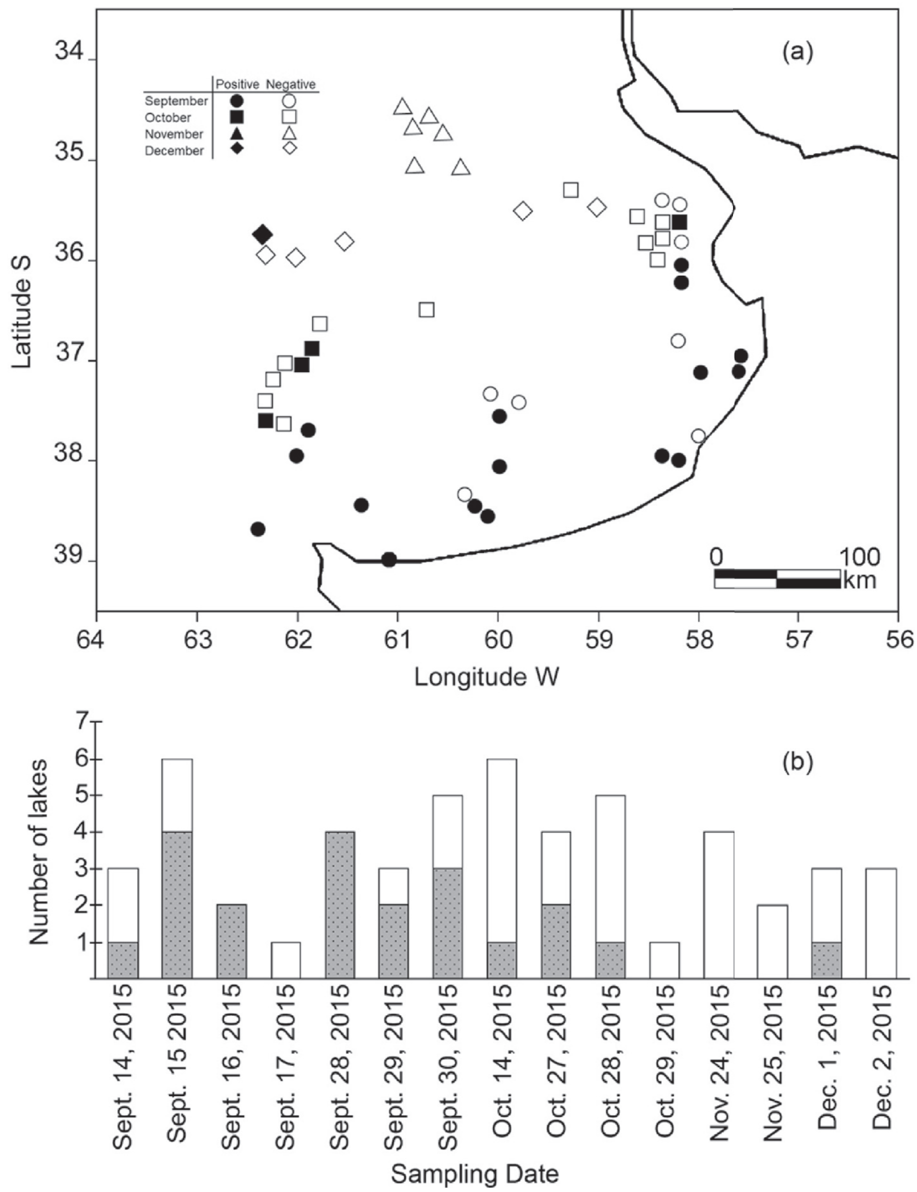

Fig. 3. The occurrence of glyphosate and AMPA in shallow Pampean lakes. a) According to lake location. Symbol placement indicate approximate lake locations (close-by lakes are slightly offset to avoid overlapping). Solid symbols are used to indicate lakes in which the herbicide was detected in at least one compartment (water, SMP, or sediment); symbol shapes indicate the month of sampling (see inset legend). b) According to sampling date. The number of lakes on each date in which glyphosate residues were detected (grayed bars) or not-detected (open bars).

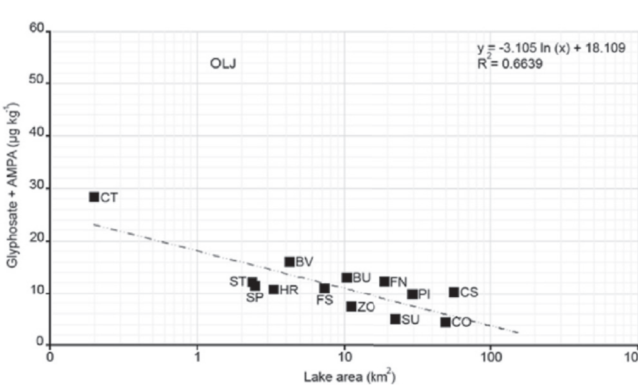

Fig. 4. Concentration of the herbicide (glyphosate + AMPA) present in the sediment fraction vs lake area. Only lakes in which the herbicide was detected in sediments are included. LJ (circle), probable outlier, was not included in the linear regression analysis. Lake ID's as in Table 3.

negative correlations with lake area and perimeter (Rho = −0.7407, P_{value} = 0.0024; P_{value} = −0.7011, Rho = 0.0052; respectively) (Fig. 4). No relationships between glyphosate + AMPA found in SPM and water samples and lake morphometry were found.

4. Discussion

The agricultural production in Argentina is fundamentally based on a technological package that combines NTF practices and glyphosate-based herbicides for the production of GR crops. Glyphosate-based herbicides are the most frequently used herbicides in the country, where 180–200 million liters are applied annually (Aparicio et al., 2013). However, strong regional differences in agricultural practices are remarkable: while glyphosate is widely used in Buenos Aires Province, where over 70% of the arable land is committed to NTF practices (CASAFE, 2012; Pac, 2015), its agricultural use is limited to very specific areas of Patagonia, being virtually negligible for the most part of this region. The lakes included in this study can be considered as a representative sample of shallow Pampean and Patagonian lakes. In other words, their limnological characteristics (nutrient and chlorophyll concentrations, conductivity, and water transparency) were well within the ranges of values reported for Pampean (Diovisalvi et al., 2015) and Patagonian environments (Zagarese et al., 2017). Our results confirmed the absence of glyphosate and AMPA residues from all Patagonian sites, suggesting that the use of glyphosate (either agricultural or non-agricultural) around our sampling sites was minimal or non-existent. On the other hand, herbicide residues were detected in 40% of Pampean lakes, suggesting that glyphosate and AMPA are habitual contaminants of Buenos Aires Province standing waters. Herbicide detection frequencies (30.8% and 13.5% of lakes for glyphosate and AMPA, respectively) were comparable to those reported by Battaglin et al. (2014) for a set of lakes, reservoirs and ponds in the USA (33.7 and 29.7%, for glyphosate and AMPA, respectively).

Owing to the lack of information on the presence of glyphosate and AMPA residues in shallow Pampean lakes, comparisons are restricted to reported values for other aquatic environments. The ranges of concentrations of glyphosate (water: 0–4.52 $\mu g\, l^{-1}$, SPM: 0–0.13 $\mu g\, l^{-1}$, sediment: 0–20.34 $\mu g\, kg^{-1}$) and AMPA (water: 0–0.90 $\mu g\, l^{-1}$, SPM: 0–0.07 $\mu g\, l^{-1}$, sediment: 0–32.89 $\mu g\, kg^{-1}$) in the study lakes were comparable to (or lower than) those reported for streams and rivers in Argentina. In their study of the Paraná river and its main tributaries, Ronco et al. (2016) reported that glyphosate occurred in 15% ($n = 23$) of the water samples, and found a maximum concentration of 1.2 $\mu g\, l^{-1}$. Bonansea et al. (2017) surveyed the Suquía river from Córdoba Province and reported that 35% of samples contained glyphosate residues, with maximum concentration of 125 $\mu g\, l^{-1}$and 1882.3 $\mu g\, kg^{-1}$ in water and sediment, respectively. Aparicio et al. (2013) studied 44 streams from South Eastern Buenos Aires. They reported the occurrence of glyphosate in 67% of SPM samples (maximum concentration: 562 $\mu g\, kg^{-1}$) and that of AMPA in 20% of SPM samples (maximum concentration: 210 $\mu g\, kg^{-1}$). Finally, Peruzzo et al. (2008) reported higher maximum concentrations of glyphosate (water: 2000 $\mu g\, l^{-1}$, sediment: 3000 $\mu g\, kg^{-1}$) in samples from a wetland formed by a first-order stream, after flowing through a soybean field in northern Buenos Aires Province.

Considering that AMPA is the main degradation product of glyphosate, the percentage of AMPA to the total herbicide concentration (%AMPA) has been proposed to provide clues on the fate and transport of the herbicide (Coupe et al., 2012). According to Coupe et al. (2012), low %AMPA values indicate that little degradation of glyphosate has occurred, either because of a low degradation rate, and/or because the sample could have been collected soon after the application of the herbicide. Reciprocally, high % AMPA indicate that most glyphosate have been degraded at the time of sample collection. Remarkably, within the set of 52 shallow Pampean lakes included in the present study, glyphosate and AMPA were seldom detected together, the two exceptions being lakes La Luján and Chasicó. Such a seemingly mutually exclusive occurrence pattern has not been anticipated. The detection frequency of Glyphosate was higher (30,8% of lakes) than that of AMPA (13,5% of lakes).

The sampling of Pampean lakes was performed from September 14th to December 2nd, 2015. Due to the large geographic extension of Buenos Aires Province, lakes located close to each other were visited almost at the same time, while the time gap between sampling dates was in the order of weeks for lakes that are located further apart from each other. With these caveats in mind, it is suggestive that positive herbicide detections were predominantly observed during September and October, with only one occurrence detected during late November and early December. Therefore, we suspect that the timing of sampling may have affected the probability of positive detections. The relationship between the frequency of positive detections and the time of the year in Buenos Aires has been specifically investigated in streams. Aparicio et al. (2013) assessed the occurrence of the herbicide in water samples from 44 streams that run across farmed fields managed with the herbicide. They reported that occurrence of glyphosate and AMPA decreased from April (35% and 33%) to September (4% and 0%). In their study, however the occurrence of the herbicide in sediment samples remained high during the whole study (66% and 89% for glyphosate and AMPA, respectively).

A priori, we would have expected to find some association between herbicide detection and descriptors of the main human activities in the vicinity of lakes, either at small (our defined 5 km buffer zone around each lake) or large geographical scale (watersheds). Indeed, we observed a spatial structure for the land use/ land cover classes, related to the precipitation gradient. However, we did not find differences between watersheds, main agricultural activities in the area, or differences in land cover/land use surrounding each lake. In fact, lack of positive herbicide detections in lakes from the upper Salado River watershed was unexpected. That area is one of the most productive agricultural zones of Buenos Aires Province. Although the reason for this remains unknown, we suspect that it may be related to the aforementioned differences in the time of sampling. However, at a smaller scale (both geographically, i.e., lakes with substantial overlap of their buffer zones; and temporally, i.e., lakes sampled on the same day) we found large differences in herbicide concentrations between nearby lakes that were sampled almost at the same time. Collectively, our results suggest that the likelihood of detecting the presence of the herbicide in different compartments varies widely from lake to lake, and likely also over time.

For the set of lakes in which the herbicide was detected in sediment samples, we found a significant negative relationship between herbicide concentration in sediment samples and lake area. Similarly, Coupe et al. (2012) found the median concentration of glyphosate and AMPA was several orders of magnitude higher in lakes belonging to small basins than in those within larger basins. They discussed the possibility that the travel time of the herbicide from its sources to the lakes increased with the size of the watershed, therefore large watershed could provide more time and opportunities for the degradation of the herbicide in soils or streams, before reaching the lakes. In addition, larger lakes tend to have a lower perimeter-to-area ratio, which could result in higher dilution rates in large lakes than in small ones. Glyphosate may reach aquatic systems either by accidental or wind driven drift of the herbicide spray, or by surface runoff of suspended particulate matter (Bowmer, 1982; Feng and Thompson, 1990; Goldsborough and Brown, 1988; U.S. Environmental Protection Agency, 1993). In addition, in Argentina it has been observed that another way that glyphosate may reach water bodies is by direct human action, washing the tanks of the fumigation machines in streams and shallow water bodies near cultivation fields (Vera et al., 2010). Thus, aquatic communities are potentially exposed to glyphosate formulations via several different pathways (Geyer et al., 2016). None of the observed concentrations of glyphosate exceeded the maximum acceptable value (280 $\mu g\, l^{-1}$), according to the Argentine legislation, and are also within the recommended levels for Australia (1000 $\mu g\, l^{-1}$), Canada (280 $\mu g\, l^{-1}$), Japan (4000 $\mu g\, l^{-1}$) and the USA (700 $\mu g\, l^{-1}$)(Hamilton et al., 2003); however, they were higher than the more stringent level established by the European Community (0.1 $\mu g\, l^{-1}$) (Dolan et al., 2013). The presence of glyphosate in the reservoir Paso de las Piedras and other recreational water bodies should warn us about the possibility of human exposure to this chemical, by direct contact or ingestion.

5. Conclusions

The different pieces of information collected in this study can be assembled together to produce a preliminary picture of the occurrence of the herbicide in shallow Pampean lakes: i) the herbicide predominantly occurred as glyphosate or its degradation product, AMPA, but simultaneous detection of both chemicals was infrequent; ii) similarly, the herbicide was more frequently detected in only one fraction, more often in sediments; iii) there were no obvious differences in herbicide detection between watersheds, or between lakes surrounded by contrasting landscapes; iv) there were large differences in herbicide concentrations between nearby lakes that were sampled almost at the same time; and v) the frequency of positive determinations was high in September–October, but virtually nil on November–December. Collectively, all these pieces of information suggest that the process of herbicide transport and degradation are highly dynamic and complex. Regional scale processes are likely to dictate the timing of herbicide pulses, due to increased rates of application and water runoff due associated with rain events. However, local process (i.e., individual farmers' choices on crops and herbicide application timing, washing of fumigating machinery) would probably play important roles. Therefore, glyphosate contribution to lake pollution remains highly unpredictable (Neumann et al., 2002).

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.02.103.

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