



Assessing glyphosate concentrations in six reservoirs of Paraíba do Sul and Guandu River Basins in southeast Brazil

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ABSTRACT

Glyphosate is a popular herbicide used worldwide, and several studies consider it to be an environmental hazard affecting human health. The present study aimed to detect glyphosate in six different reservoirs of Paraíba do Sul and Guandu River Basins in Southeast Brazil, used for multiple purposes, including fishery activities and domestic water supply. Ion chromatography was used to analyze the water samples, as it is a fast and environmentally friendly technique to detect glyphosate. Our results revealed that, despite differences related to trophic state, season of the year or distance to urban areas, glyphosate was detected in all reservoirs and in three of them with concentrations above the limit imposed by Brazilian legislation. Among the environmental variables studied, turbidity presented the highest correlation with glyphosate concentrations. The effect of rainfall increasing turbidity in the rivers reinforces the importance of draining waters from surrounding areas that transport glyphosate into the aquatic ecosystems. The detection of the herbicide in the various systems confirms the wide use of this compound in the drainage basins of the studied reservoirs and highlights the importance of water monitoring. Further, the results reveal how urgent and important it is to explore through laboratory experiments the pathways of degradation of this herbicide in tropical and subtropical aquatic environments together with its effects on flora and fauna.

Keywords: herbicide, ion chromatography, tropical reservoir.

Avaliação das concentrações de glifosato em seis reservatórios das bacias dos rios Paraíba do Sul e Guandu, no sudeste do Brasil

RESUMO

O glifosato é um herbicida popularmente usado em todo o mundo, vários estudos estão



considerando-o como um risco ambiental e como afetando a saúde humana. O presente estudo teve como objetivo detectar o glifosato em seis diferentes reservatórios das bacias dos rios Paraíba do Sul e Guandu, no sudeste do Brasil, utilizados para diversos fins, incluindo atividades pesqueiras e abastecimento doméstico. A cromatografia iônica foi a técnica escolhida para analisar glifosato nas amostras de água como uma técnica rápida e ecologicamente amigável. Nossos resultados revelaram que, apesar das diferenças relacionadas ao estado trófico, estação do ano ou distância das áreas urbanas, glifosato foi detectado em todos os reservatórios e em três deles com concentrações acima do limite imposto pela legislação brasileira. Dentre as variáveis ambientais estudadas, a turbidez foi a que apresentou maior correlação com as concentrações de glifosato. O efeito das chuvas aumentando a turbidez nos rios reforça a importância do escoamento da água das áreas circundantes que transportam glifosato para os ecossistemas aquáticos. A detecção do herbicida nos diversos sistemas confirma o amplo uso desse composto nas bacias de drenagem dos reservatórios estudados e destaca a importância do monitoramento da água para este composto. Além disso, os resultados revelam quão urgente e importante é explorar, através de experimentos de laboratório, as vias de degradação desse herbicida em ambientes aquáticos tropicais e subtropicais, juntamente com seus efeitos na flora e fauna.

Palavras-chave: cromatografia iônica, herbicida, reservatório tropical.

1. INTRODUCTION

The increasing availability of inorganic fertilizers and pesticides changed the course of world agriculture. In Brazil, glyphosate is mainly used in the cultivation of rice, coffee, cocoa, corn, sugarcane, soybeans, citrus fruits, bananas, to control aquatic plants, and likewise is applied in urban areas including sidewalks and gardens (Abreu *et al.*, 2008). Other South American countries are also familiar with glyphosate, which is the most commonly used herbicide in Argentina (Lozano *et al.*, 2018). Glyphosate was also widely applied in Colombia to control weeds in coffee plantations (Schrübbbers *et al.*, 2014).

Glyphosate or N-phosphonomethyl glycine is considered a non-selective, systemic and post emergent herbicide. Glyphosate (CAS number 1071-83-6) is a crystalline solid, with a water solubility of 12 g L⁻¹ at 25°C (Okada *et al.*, 2018). The endurance of glyphosate in water is subjected to physical, chemical and microbial characteristics of the environment (Mallat and Barcelo, 1998). Glyphosate can remain active in water ranging between 7 and 100 days depending on environmental conditions such as pH, temperature, suspended matter, cation concentration, aluminum, and iron content and microbial activity (Fouodjouo *et al.*, 2015). Further, temporal variation in environmental glyphosate concentrations can directly depend on the time of application and rain events (Hanke *et al.*, 2010).

When correctly applied, this herbicide inhibits an important enzyme in plants responsible for the production of essential aromatic amino acids. Animals do not produce this enzyme and get the amino acids in question through food. Therefore, this substance was considered non-toxic to many living beings by many regulations and agencies (Moore *et al.*, 2012). Though the accepted dogma was that glyphosate was harmless to humans because our cells do not have the enzyme pathway that glyphosate inhibits, our gut bacteria do have this pathway and we depend on them to supply us with essential amino acids (Samsel and Seneff, 2013).

The environmental threat of glyphosate due to its residual presence in crops and food was linked with respiratory problems in men such as pulmonary edema and trouble with breathing. In addition, laboratory experiments have shown that glyphosate can increase the induction of sister chromatid exchange, chromosomal aberrations, lesions in DNA and, in some cases, breaking of genetic material (Roustan *et al.*, 2014). Short-term rodent studies have not shown that glyphosate has high toxicity, but long-term ones related this herbicide with kidney and liver

failure, besides an increased risk of developing cancer (Samsel and Seneff, 2013). Other studies also link glyphosate with autism (Nevison, 2014) and breast cancer (Mesnage *et al.*, 2015).

In general, herbicides can also contribute to food contamination and environmental degradation. Glyphosate can be retained in soils and transported to surface and groundwater. Soil pollution is primarily related to the phenomena of leaching and runoff. Leaching promotes migration of these substances to deeper layers of the soil and can contaminate groundwater; while runoff spreads the herbicide and may favor the contamination of surface water bodies (Borggaard and Gimsing, 2008).

From a broader environmental perspective, the direct application of herbicides in aquatic systems might affect the water quality as well as ecosystem functioning. This type of compound can interfere with species biology and interactions besides decreasing biodiversity, affecting this way the stability and resilience of aquatic environments (Relyea, 2012). The magnitude of those effects can be related to glyphosate's persistence in the environment (Pérez *et al.*, 2011).

Freshwater ecosystems flora and fauna can be affected by glyphosate-based herbicides, as shown by laboratory and outdoor experiments such as those with phytoplankton and periphyton (Pérez *et al.*, 2011; Lozano *et al.*, 2018), invertebrates and vertebrates like fish (Folmar *et al.*, 1979; Cuhra *et al.*, 2013; Geyer *et al.*, 2016) and with larvae and adults of amphibians. Recently, an increase in deviations in ontogenetic development was shown in tropical tadpoles because of chronic exposure to Roundup® (Tuhiran *et al.*, 2020).

In natural lakes and reservoirs, those effects can be serious, since glyphosate can affect the structure of primary producers' communities (Lozano *et al.*, 2018; Hernández-García and Martínez-Jerónimo, 2020) as well as consumers' assemblages (Rico-Martínez *et al.*, 2012; Vajargah *et al.*, 2018), besides being a potential hazard to human health. Evidence like this highlights the threats posed by the presence of glyphosate in multiple-use reservoirs.

In the United States, the maximum concentration of glyphosate allowed by the Environmental Protection Agency is 0.700 mg L⁻¹. In Europe, the Council of the European Union established the value of 0.0010 mg L⁻¹ as the limit for drinking water (European Council, 1998). In Brazil, the National Environmental Council (CONAMA) stipulates the concentration of 0.065 mg L⁻¹ as the limit for waters of Class 1 and 2.

Brazil has a rich network of river basins that supports more than sixty percent of the country's electricity through power generation in hydroelectric reservoirs. Ubiquitous throughout the country, most of those systems frequently have multiple purposes, with the water being used for agriculture, industrial and domestic supply. Brazilian reservoirs have been widely studied in the last decades, especially regarding water quality, biodiversity of aquatic communities, eutrophication and cyanobacteria blooms (Soares *et al.*, 2013). Few studies analyzed glyphosate in Brazilian waters, and the existing ones were in rivers near agricultural and urban areas. Only Pires *et al.* (2020) studied glyphosate concentrations close to soybean-growing fields in the Brazilian Amazon, including a reservoir within the freshwater ecosystem. Still, there is a lack of studies relating to glyphosate in Brazilian reservoirs. This study is therefore a step to close this gap.

Glyphosate detection conventionally is associated with requiring a high cost-analysis and sophisticated methods, such as liquid chromatography coupled with an ultraviolet detector, fluorescence and mass spectrometry (Peruzzo *et al.*, 2008; Catrinck *et al.*, 2014). The determination of glyphosate by ion chromatography (IC) is considered a clean-up procedure, and also a direct, fast and relatively inexpensive method for glyphosate quantification (Zhu *et al.*, 1999; Lambropoulou and Albanis, 2007).

Considering the context above, the objective of the present study was to quantify the concentration of glyphosate in six different reservoirs of Paraíba do Sul and Guandu River Basins, applying the ion chromatography technique. The values found were compared with the ones stipulated by Brazilian legislation. All the reservoirs belong to an energy-generating grid,

are influenced by agriculture and urban drainages, and most of them are used for industrial and domestic water supply, small-scale fishing and aquaculture. Regarding the anthropic influences, it was expected a greater possibility of finding glyphosate in reservoirs under a stronger anthropic influence attested by their respective tropic conditions. We also tried to investigate the possible influence of environmental features and rainfall on glyphosate concentrations in the aquatic environments.

2. MATERIALS AND METHODS

2.1. Chemicals and materials

For decontamination of all the materials applied in this study, we used a solution of hydrochloric acid 18% (m/v) (prepared from the dilution of concentrated acid) and 2% (v/v) solution of Extran[®] MA02. Glyphosate 45521 - PESTANAL[®] Sigma Aldrich[®] standard and Milli-Q water (Direct-Q3[®] UV, Millipore, resistivity 18.2 mΩ cm⁻¹ at 25°C) were used to prepare the solutions of the calibration curve. The water samples were filtered with a membrane GV (durapore) in PVDF of 0.22 μm pore and 25 mm of diameter from Millipore[®].

2.2. Study Area

The water samples were collected in six distinct reservoirs belonging to Paraíba do Sul River Basin (Tocos, Santana, Vigário and Santa Branca) and the Guandu River Basin (Ribeirão das Lajes and Ponte Coberta) (Figure 1).

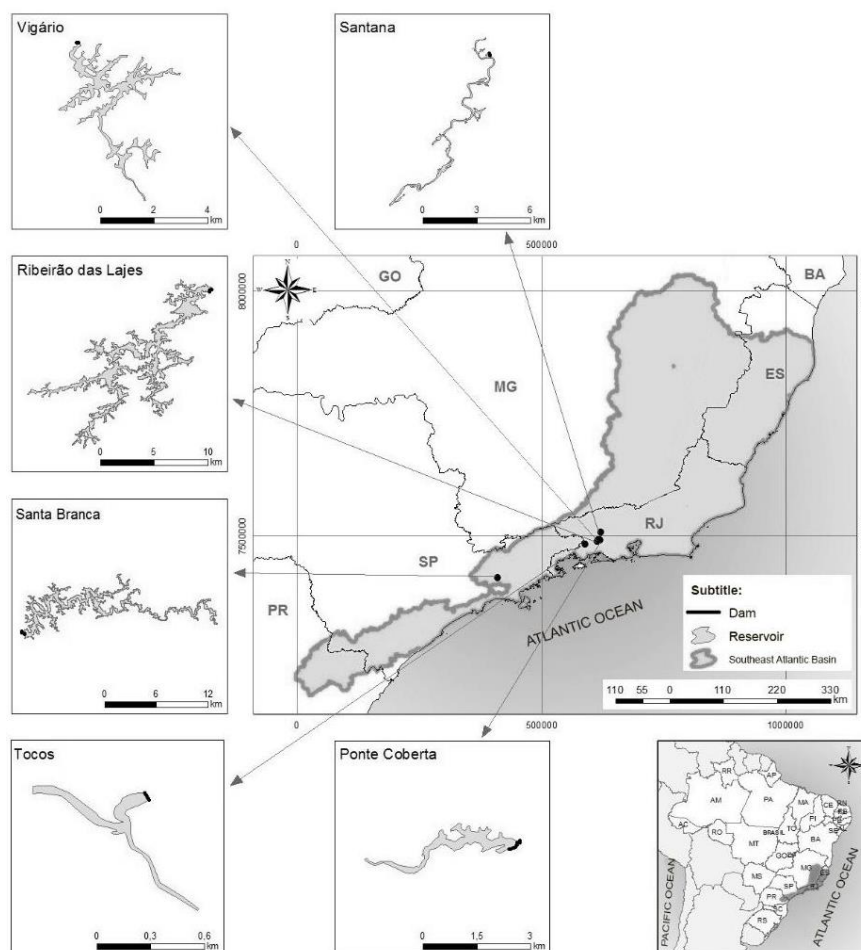


Figure 1. Location of the reservoirs: Santana, Vigário, Ribeirão das Lajes, Santa Branca, Tocos and Ponte Coberta, included in the present study.

The climate of the region is sub-humid, considered as Aw in Köppen's system composed of a rainy summer (from January to March) and dry winter (from July to September). The reservoir of Santa Branca is in the main axis of Paraíba do Sul River; the others form a complex of reservoirs, which comprises a hydroelectric generating system and are the main water supply system for the city of Rio de Janeiro. These reservoirs have different characteristics related to morphometric features, anthropogenic impacts and trophic conditions (Klippel *et al.*, 2020). In accordance with Resolution 357 related to water quality (CONAMA, 2005), Ribeirão das Lajes and Santa Branca are considered Class 1 (better quality, they can be used for water supply after simple chlorination) and oligo-mesotrophic, while all the others are Class 2 (they need conventional treatment for domestic supply) and considered mesotrophic to eutrophic. The number of sampling points was according to the size of the reservoir, one sampling point in the smallest (Tocos) and five in the largest (Ribeirão das Lajes Reservoir).

The geographic coordinates of each point are in Table 1. Ribeirão das Lajes Reservoir was sampled monthly from January 2013 to April 2014 (except December). All the other reservoirs were sampled in January 2013, July 2013 and January 2014. January is the rainy season while in July starts the dry season.

Table 1. Geographic coordinates of the sampling points.

Reservoir	Surface area (km ²)	Retention time (days)	Sample Point	Latitude South	Longitude West
Ribeirão das Lajes	30.7	300.1	L1	22°47'18"	44°01'48"
			L2	22°49'44"	43°59'45"
			L3	22°46'19"	43°57'54"
			L4	22°42'33"	43°54'51"
			L5	22°42'09"	43°52'58"
Ponte Coberta	1.09	1.1	PC1	22°41'32"	43°51'24"
			PC2	22°41'12"	43°49'41"
Santa Branca	27.23	62.6	SB1	23°21'07"	45°46'01"
			SB2	23°18'36"	45°45'59"
			SB3	23°19'55"	45°47'54"
			SB4	23°22'26"	45°52'09"
Santana	5.23	1	S1	22°31'30"	43°49'20"
			S2	22°34'36"	43°50'18"
			S3	22°36'29"	43°52'06"
Tocos	0.36	<1	T1	22°47'07"	44°04'39"
Vigário	3.33	2	V1	22°38'09"	43°53'49"
			V2	22°39'23"	43°53'17"
			V3	22°40'13"	43°52'51"

2.3. Samples Analysis

Water samples for glyphosate analysis were taken at the sub-surface of each point. Environmental variables were measured at the same time *in situ* with a multi-probe 6920 Yellow Spring Instrument. The variables measured were: water temperature, pH, electrical conductivity, total suspended solids, dissolved oxygen, turbidity, and chlorophyll-*a*. Water transparency was evaluated using a Secchi disk. All the rainfall data as well as the reservoir water levels were obtained from meteorological and hydrological stations of the Light Energy

Company located near the reservoirs. The ion chromatography technique was used to determine the presence of pesticide in water. This technique dispenses with the use of cartridges, reagents and solvents that can potentially contribute to environmental degradation and waste generation. The calibration curve was constructed from nine aqueous solutions of glyphosate standard, with concentrations ranging from 0.01 mg L⁻¹ to 1.0 mg L⁻¹. Six replicates were analyzed for each concentration.

The filtered samples, with a membrane GV (durapore) in PVDF of 0.22 µm pore Millipore®, were analyzed on an ion chromatograph ICS-2100 (Dionex Inc.) equipped with AS-19A and AG-19A columns, self-regenerating suppressor ASRS-Ultra II, with a sample loop of 500 µL and flow rate of 0.3 mL min⁻¹. KOH was the eluent, from 0-10 minutes its concentration was 10 mM and from 10-23 it was 60 mM, the retention time was 20.5 minutes. Each analyzed sample had six replicates and all of them were tested.

2.4. Statistical Analysis

Normality of data was assessed with a Shapiro-Wilk test. Due to non-normality, the Kruskal-Wallis test on ranks was performed to detect significant differences ($p < 0.05$) in glyphosate concentrations among reservoirs. In order to explore the relationship between glyphosate concentrations and environmental variables, we calculated Spearman rank correlation coefficients in the software Statistic Version 7.0. For statistical analysis, only results where glyphosate was detected above the quantification limit (QL) were used. In the specific case of pluviometry, monthly values were taken into consideration as well as rainfall values that occurred three days before the sampling day and also in the previous week.

3. RESULTS AND DISCUSSION

3.1. Detection and quantification of glyphosate

The analytical method of ion chromatography has the advantage of allowing the quantification of glyphosate in water through direct injection, without the need for preconcentration or derivatization, steps that involve sample manipulation render the analysis expensive and time-consuming. In the chromatograms, the peak retention time corresponding to glyphosate was of 20.5 min (Figure 2A). The calibration curve obtained for the standard solutions was adjusted using a linear regression equation, relating the results to the concentration of the analyte (Figure 2B). The correlation coefficient found was 0.99121.

The detection limit (DL) and the quantification limit (QL) were 2.8x10⁻⁴ mg L⁻¹ and 8.5x10⁻⁴ mg L⁻¹, respectively. They were calculated according to Equations 1 and 2:

$$DL = 3.3 \times s/S \quad (1)$$

$$QL = 10 \times s/S \quad (2)$$

Where s is the standard deviation of the blank sample and S is the slope of the regression line equation. The recovery was calculated according to Ribani *et al.* (2004) using known values of glyphosate added in an exempted matrix. The recovery mean values were between 59% and 103%. These numbers are within the acceptable range established in the literature; the US-FDA recommends the recovery trend to be between 50% - 150%, while the European Union Commission says 40% - 160% (Imoto and Freitas, 2008). The precision of the value obtained in this study was 13.98%, and it was determined by the relative standard deviation (RSD). This parameter represents the dispersion of the results, and in case of experiments with trace elements, it is accepted a RSD of up to 20% (Ribani *et al.*, 2004).

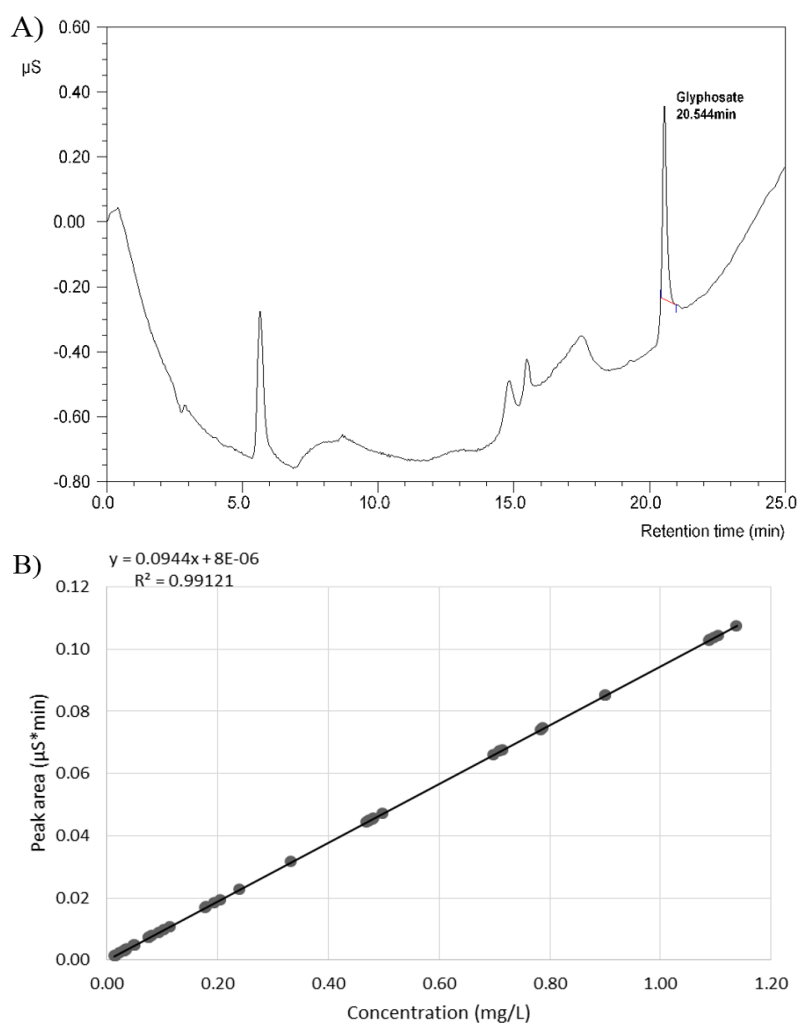


Figure 2. A. Chromatogram of aqueous standard solution (1.033 mg L^{-1}); B. Analytical curve of different standard concentrations.

3.2. Glyphosate in the six reservoirs

In the present study, glyphosate was detected in all six reservoirs, regardless of their trophic state or closeness to anthropic areas. According to the Kruskal-Wallis test, there were no differences in glyphosate concentrations among reservoirs ($H=7.9486$ (15, $N=47$), $p=0.1591$).

The herbicide was found above the quantification limit in 43% of all analyzed water samples. The percentage of positive results were different among the reservoirs. Glyphosate was detected in 100% of the water samples from the following reservoirs: Tocos, Vigário and Ponte Coberta. In Ribeirão das Lajes Reservoir, 32% of the samples showed the presence of glyphosate, while in Santa Branca that number was equal to 50% of the samples. The lowest percentage was found in Santana Reservoir, with 11% of the samples contaminated with the herbicide.

Systematic assessments of glyphosate presence in lakes and rivers in South America are scarce, despite the widespread use of this herbicide. In the present study, the percentage of 43% of samples in which glyphosate was detected was similar to the results of a survey of glyphosate in Pampean lakes (40%) (Berman *et al.*, 2018), in which the samples were analyzed by high performance liquid chromatography and mass spectrometry (HPLC-MS) after derivatization with 9-fluorenylmethoxycarbonyl chloride. However, these results were higher than other glyphosate studies, such in surface waters of agricultural basins in Argentina, where the maximum percentage of surface water samples containing glyphosate reached 35% (Aparicio

et al., 2013).

Our results were also higher when compared with the first survey of glyphosate on a basin-wide scale in the main tributaries of the Paraná River Basin in Brazil. In this case, 30% of the water samples reported the presence of the herbicide (Ronco *et al.*, 2016). These authors related the positive results to intensive agriculture activities.

Considering all analyzed samples, the concentrations of glyphosate varied from 0.0003 mg L⁻¹ to 0.1684 mg L⁻¹, and in three samples the concentration exceeded the maximum allowed by Brazilian legislation (CONAMA 357) (Figure 3). The higher values were found in both Class 1 (Ribeirão das Lajes and Santa Branca) and Class 2 (Vigário) oligo-mesotrophic reservoirs (Klipell *et al.*, 2020).

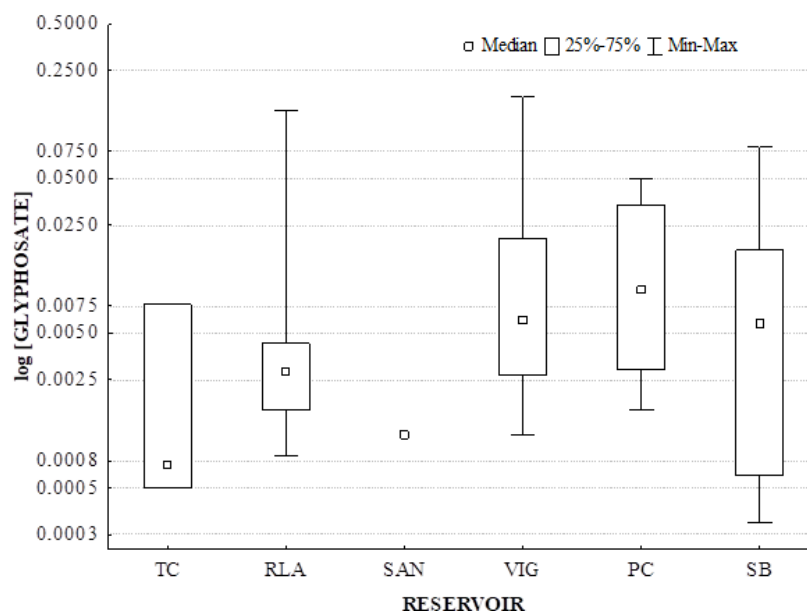


Figure 3. Log of Glyphosate concentration (mg L⁻¹) in the six reservoirs during the period of the study. RLA=Ribeirão das Lajes, TC=Tocos, PC=Ponte Coberta, SB=Santa Branca, SAN= Santana and VIG = Vigário.

Once again, the results found in the present study (between 0.0003 mg L⁻¹ and 0.1684 mg L⁻¹) were higher when compared with the other two mentioned researches in aquatic ecosystems in South America. The shallow lakes in Argentina showed glyphosate concentration values of up to 0.00452 mg L⁻¹ (Berman *et al.*, 2018), while Paraná River and tributaries presented values between 0-0.0012 mg L⁻¹ (Ronco *et al.*, 2016). However, areas under agricultural influence showed higher results than ours, such as in a wetland of a stream receiving flowing from a soybean field near Buenos Aires where glyphosate ranged from 0.1 to 0.7 mg L⁻¹ (Peruzzo *et al.*, 2008).

3.3. Trophic conditions and glyphosate

Regarding the anthropic influences on the reservoirs, we noticed that at some sampling sites glyphosate was always found above the quantification limit, independently of the trophic conditions. This happened in the eutrophic Vigário Reservoir (V3), and in the oligo-mesotrophic Santa Branca (SB2) and Ribeirão das Lajes (L1) Reservoirs. Vigário Reservoir presented a concentration 2.6 times higher (0.1684 mg L⁻¹) than the ones determined by law, Santa Branca, 1.24 times (0.0804 mg L⁻¹), and Ribeirão das Lajes, 2.1 times higher (0.01366 mg L⁻¹). The wide use of glyphosate in several crops and in other agricultural activities, such as weed control in pastures along the Paraíba do Sul and Guandu River Basins, can explain the

frequent presence of this herbicide in the studied systems. Except for Ribeirão das Lajes Reservoir, all the other reservoirs are under the influence of former coffee farm areas that were transformed into pasture or Eucalyptus plantation during the last century.

Within the eutrophic reservoirs (Vigário, Santana and Ponte Coberta), only Santana Reservoir showed dissimilar results (Figure 3) with a comparatively lower concentration of glyphosate.

Although receiving anthropically impacted waters from the Paraíba do Sul River, Santana Reservoir differs from the others, since it presents intense colonization by aquatic macrophytes (Pitelli *et al.*, 2008). This condition suggests a possible reduction in glyphosate levels in water by aquatic macrophytes as reported in other studies (Brogan and Relyea, 2013; Moore *et al.*, 2017). Still, further experimental studies to check and confirm such correlation are needed.

Even though Ribeirão das Lajes Reservoir is considered oligo-mesotrophic, has the surrounding area covered by remains of the Atlantic Forest, and possesses the best water quality among the reservoirs studied, still glyphosate was found in it. The detection of this herbicide at point L1 reflects the degradation of this reservoir area, which is influenced by drainage from pastures and upstream waters impacted by different types of crops and chicken farms. Therefore, we suggest that glyphosate enters the reservoir from runoff and leaching of upstream areas or from direct contamination by the use of this herbicide to control weeds in a nearby pasture.

In this way, our results for Ribeirão das Lajes Reservoir confirmed the main tributary as an important source of glyphosate into the lake and the relevance of the surrounding rainforest to prevent any input of the herbicide from land into other parts of the reservoir. Even with a high concentration of glyphosate at L1, the other sampling points seemed not to be affected by this herbicide, showing very low concentrations of glyphosate.

Since this reservoir is used for domestic supply through simple chlorination, the study of herbicides in its waters is highly important in terms of public health, especially if we consider that the Report of the International Agency for Research on Cancer (IARC, 2015) has classified this herbicide as belonging to the Group 2A, which means, as an agent probably carcinogenic to humans.

Glyphosate was detected at all sampling points in the Santa Branca, the other reservoir considered as oligo-mesotrophic. Although its waters are used for domestic supply, this reservoir suffers anthropic influences related to the *Pinus* plantation, industrial and mining activities in its marginal area. Sampling Point 2, which presents a high glyphosate content, is located near the entrance of the Capivari River, which has intensive agricultural activities in its basin that can introduce the herbicide to the reservoir. Yet, it is important to highlight that other sources of the herbicide cannot be discarded, because aside from agriculture, inputs from maintenance of roadsides and effluents of wastewater treatment plants can also be an important source of such substance (Hanke *et al.*, 2010).

The detection of glyphosate throughout the year in the reservoirs of Ribeirão das Lajes and Santa Branca in both rainy and dry seasons, as well as in all other reservoirs, reflected the constant use of the herbicide in the drainage basins of these water bodies. Local processes, such as application by farmers to control undesirable weeds, would likely play important roles in the highly dynamic and complex processes of herbicide transport and degradation (Berman *et al.*, 2018).

3.4. Relationship of rainfall and environmental factors with glyphosate concentrations in the six reservoirs

The pluviosity in reservoirs was as expected, with higher rainfall in the summer (January) and lower in the winter (July) samplings (Figure 4). However, rainfall was higher in the rainy season of 2013 than in 2014.

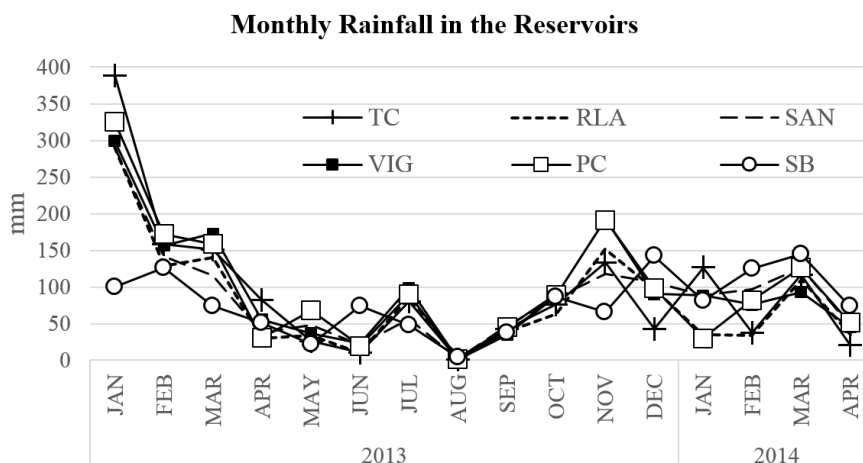


Figure 4. Monthly rainfall (mm) in the six reservoirs during the period of the study. RLA=Ribeirão das Lajes, TC=Tocos, PC=Ponte Coberta, SB=Santa Branca, SAN= Santana and VIG = Vigário.

The results of the correlation analysis between rainfall data and glyphosate concentrations in water showed no significant interrelation when considering monthly rainfall ($Rho = 0.029$; $P_{value} < 0.05$). However, when considering the rainfall in the days before the sampling, the results were different. There was a higher correlation between rainfall in the three days before the sampling ($Rho = 0.056$; $P_{value} < 0.05$) and glyphosate concentration, and a significant correlation between rainfall in the seven days before the sampling and glyphosate ($Rho = 0.155$; $P_{value} < 0.05$).

The influence of rains on glyphosate dispersion has been discussed by several authors, most of them in the temperate region. In tropical Brazil, where rainfall governs most of the dynamics of the aquatic systems, the pathways of glyphosate from soils to water is scarcely documented (Correia *et al.*, 2020; Pires *et al.*, 2020). Even so, the existence of mechanisms of dilution of the surface material with adsorbed glyphosate by runoff cannot be discarded. Rainfall has been linked with the decrease in glyphosate concentrations in the soil. These lowering levels can be explained by the high solubility of glyphosate in water and by the existence of adsorption sites, which have already been linked with glyphosate in soils causing the carriage of the non-adsorbed glyphosate to streams (Peruzzo *et al.*, 2008). Furthermore, surface runoff with the movement of soil particles can carry glyphosate adsorbed and end up in streams where glyphosate can be desorbed, biodegraded and accumulated in sediments (Aparicio *et al.*, 2013). A significant increase in glyphosate concentrations in water due to rainfall is explained by the carrying of glyphosate present in soil through mechanisms of dilution of surface material by runoff (Peruzzo *et al.*, 2008).

In relation to the environmental variables (Table 2), the reservoirs were characterized by water temperature average ranging from 21.9 to 25.8 °C, waters around neutrality (pH average from 6.96 to 7.35), lower turbidity in the less impacted Tocos, Ribeirão das Lajes and Santa Branca reservoirs (from 4.35 to 8.59 NTU) and higher in the others (from 18.89 to 27.55 NTU). Total dissolved solids (TDS) and electrical conductivity were lower ($< 20 \text{ mg L}^{-1}$, and $< 30 \text{ } \mu\text{S cm}^{-1}$, respectively) in the less impacted and higher in the others (average between, respectively, 36.89 and 38.50 mg L^{-1} and 80.63 and 84.38 $\text{ } \mu\text{S cm}^{-1}$). Average water transparency was higher in Ribeirão das Lajes and Santa Branca Reservoirs (respectively, 2.07 and 2.31 m). Chlorophyll-*a* average concentrations were considered low in all reservoirs ($< 2.5 \text{ } \mu\text{g L}^{-1}$). We found a significant positive correlation between glyphosate and water turbidity ($Rho = 0.366$; $N=47$; $P < 0.05$) and a negative between glyphosate and water transparency ($Rho = -0.375$). On the other hand, as expected, turbidity was negatively correlated with water transparency ($Rho = -0.88$) and positively with total dissolved solids ($Rho = 0.31$), and with monthly rainfall ($Rho = 0.33$).

Table 2. Average and standard deviation (SD) of environmental variables in the studied reservoirs.

Variable		Temp ¹ (°C)	DO ² (mg L ⁻¹)	pH	Turb ³ (NTU)	TDS ⁴ (mg L ⁻¹)	SD ⁵ (m)	EC ⁶ (µS cm ⁻¹)	Chl- <i>a</i> ⁷ (µg L ⁻¹)
Tocos (N=3)	average	21.9	7.86	7.00	8.59	11.00	1.20	26.63	0.57
	SD	4.2	1.68	1.04	6.20	0.00	0.35	2.82	0.40
Ribeirão das Lajes (N=80)	average	24.6	7.00	7.12	6.59	13.61	2.07	28.60	2.43
	SD	3.7	1.32	0.56	10.07	4.22	1.10	4.75	2.15
Santana (N=10)	average	25.1	4.99	7.37	26.03	36.89	0.80	81.21	2.31
	SD	3.3	2.06	0.71	17.66	4.34	0.36	8.22	1.01
Vigário (N=10)	average	24.8	5.80	7.35	27.55	37.11	0.65	84.38	1.94
	SD	3.1	0.92	0.39	22.75	5.16	0.30	13.75	1.58
Ponte Coberta (N=6)	average	25.6	7.31	7.29	18.89	38.50	0.91	80.63	1.90
	SD	3.6	1.03	0.18	14.88	9.09	0.44	14.21	1.40
Santa Branca (N=12)	average	25.8	6.24	6.96	4.35	18.33	2.31	36.08	1.30
	SD	4.2	1.15	1.21	4.49	4.83	0.84	5.27	0.62

¹temperature, ²dissolved oxygen, ³turbidity, ⁴total dissolved solids, ⁵transparency, ⁶electrical conductivity, ⁷chlorophyll-*a*. N= number of samples.

Ponte Coberta and Tocos reservoirs presented higher glyphosate concentrations during the rainy period, when turbidity was also higher. The plausible explanation for this is that during the rainy period the soil runoff is more intense, dragging soil and consequently glyphosate into the water, increasing in this way the concentration of the herbicide in both reservoirs during this season.

Despite a low correlation between daily rainfall and glyphosate, the positive correlation between glyphosate and turbidity suggests an indirect relation between rainfall and the herbicide. This variable is one of the most monitored along the river basins, since several uses of the water depend on its value. The increase in turbidity in tropical rivers during rainfall, associated with the draining of the surroundings areas' soil into the aquatic systems is well recognized (Branco *et al.*, 2019), making it possible to associate this draining with the carriage of glyphosate into the water.

4. CONCLUSIONS

The ion chromatography used in this study allowed the quantification of glyphosate in the water of reservoirs, with the advantage of eliminating any prior treatment, resulting in time gain and low waste generation.

We expected a greater possibility of finding the presence of glyphosate in reservoirs under greater anthropic influence and trophic conditions, but our results showed that regardless the size of the reservoir or its anthropic influences and trophic condition, the presence of glyphosate was detected. The constant presence of glyphosate in water is evidence of the frequent use of this herbicide throughout the reservoirs' river basins and corroborates how human activities can influence and impact aquatic ecosystems. This fact highlights the need for continuous monitoring to obtain a more accurate view of the emission sources and their control, since environmental standards levels for glyphosate in water have been exceeded.

Due to the ubiquity of glyphosate use in countries of South America, such as Argentina and Brazil, the need for laboratory experiments to explore the pathways of degradation of this herbicide in tropical and subtropical aquatic environments and its effects on resident flora and fauna are preeminent and unpostponable. This is especially true in cases like those reported here, where the water stored in reservoirs is not only used for generating electricity but also for providing water supply to households, fishing activities and farming.

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