



Spatial and seasonal variation of arsenic speciation in Pantanal soda lakes

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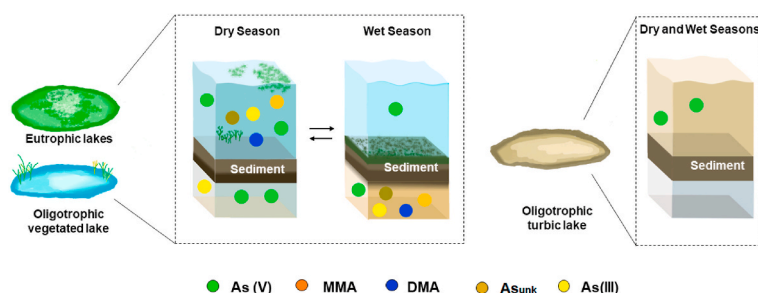
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HIGHLIGHTS

- Arsenic species largely varied in surface and subsurface water of soda lakes.
- Cyanobacteria or macrophytes/algae are involved in As biotransformation.
- Arsenic speciation varies seasonally with lake water level and trophic condition.
- Spatial distribution of As species varies with biogeochemical conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence of high arsenic concentrations (up to $3000 \mu\text{g L}^{-1}$) in water of soda lakes of the Pantanal wetland is a remarkable case of natural arsenic contamination in South America. However, little is known about arsenic speciation in this environment, particularly regarding speciation changes related to lake trophic status and seasonal variations. To fill this gap, arsenic speciation analysis was carried out in surface (SW) and subsurface (SSW) waters sampled in five soda lakes with different eutrophication status, in two dry and one wet season. As(V) was the dominant species in these waters, while As(III), DMA, MMA and likely complex organic species were present in lower amounts. The results allow to conclude that the arsenic speciation in SW and SSW varies seasonally according to the regional wet or dry periods and lake water levels. In eutrophic turbid and in oligotrophic vegetated soda lakes, arsenic speciation was also characterized by spatial differences between edge and center or between the SW and SSW. Cyanobacteria or macrophytes/algae are involved in arsenic biotransformation in soda lakes through its metabolic and detoxification processes. Significant variation in surface water arsenic speciation occurs as a result of seasonal primary production fluctuation or water arsenic concentration changes in the soda lakes, increasing organoarsenics in dry periods, whereas in flood periods, As(V) prevails. Spatial distribution of arsenic species is significantly impacted by biogeochemical conditions at the water/sediment interface in soda lakes.

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1. Introduction

Arsenic (As) is a highly toxic metalloid to a wide range of living organisms, and many studies cite the presence of high concentrations of As in drinking water, a threat that affects several hundred million people on all continents (McGroarty et al., 2017; Shaji et al., 2021). Arsenic pollution of soils, water bodies, and the overall environment has grown to be an important concern (Ravenscroft et al., 2009; Smedley and Kinniburgh, 2002). In the environment, As can be of natural and/or anthropogenic origin and can be found in organic and inorganic forms, with the +3 and +5 oxidation states being the most common. The toxicity, mobility, and fate of As depend on its chemical speciation. In general, inorganic species are considered more toxic than organic forms (Sharma and Sohn, 2009). In reducing aqueous media, arsenite (As(III)), the most toxic species, is expected to predominate, while arsenate (As(V)) is more stable under oxidizing conditions. Organoarsenic species such as monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and complex organoarsenics (e.g., arsenobetaine (AsB) and arsenosugars (AsS)) result from As biotransformation (Goessler and Kuehnel, 2002).

High concentrations of As (up to 3000 $\mu\text{g L}^{-1}$) have been reported in pristine soda lakes in the Pantanal (Brazil) (Richter et al., 2019), the largest wetland in the world (Por, 1995). Although rarely mentioned, it is a remarkable case of natural As contamination in South America (Bundschuh et al., 2020, 2021). The origin of this contamination has been attributed to the evapoconcentration process, in a sodic alkaline geochemical pathway, of the fresh water that regionally floods this wetland (Barbiero et al., 2007; Richter et al., 2019). Several factors are likely to influence As speciation in and around these soda lakes. First, there is high biological activity (Andreote et al., 2014; Azizur Rahman and Hasegawa, 2012; Cotta et al., 2022; Vaz et al., 2015) manifested by seasonal cyanobacterial blooms in green-water lakes and by the presence of vegetation in crystalline-water lakes, while it is very moderate in black-water lakes. Furthermore, due to high pH, dissolved organic matter (DOM) solubility increases, and high contents have been reported with dissolved organic carbon (DOC) values exceeding 700 mg L^{-1} in some cases (Barbiero et al., 2016, 2018; Mariot et al., 2007; Pellegrinetti et al., 2022). Such high concentration of DOM can impact the mobility and bioavailability of As (Aftabtalab et al., 2022; Gao et al., 2016; Guo et al., 2019; Redman et al., 2002). Finally, the low redox conditions in the sediments, down to -400 mV, and the oxygen saturation of the water in some green-water lakes that can exceed the O_2 bubble point (up to 500%), are extremely contrasting conditions that may control As oxidation state (Barbiero et al., 2018). In the face of these environmental conditions, it is impossible to predict the speciation of As in space and time and therefore to assess the potential risk of As concentrations in this specific ecosystem, and more generally in alkaline environments. Despite studies on the occurrence of As in Pantanal soda lakes (Elias et al., 2022; Richter et al., 2019; Viana et al., 2022), knowledge on speciation, and specifically on As species derived from biotransformation processes, remains limited. Furthermore, the impact of seasonal changes within soda lakes on As speciation has never been addressed. The objective of this study is therefore threefold: (i) to investigate the speciation of As in the waters of different types of soda lakes in the Pantanal wetland; (ii) to provide an overview of seasonal and spatial variations in As speciation; and (iii) to identify the factors that control these variations.

2. Material and methods

2.1. Study site and sampling

The Pantanal floodplain is a large wetland located in the heart of the South American continent (Junk and Cunha, 2005), covering an area of about 160,000 km^2 primarily located within central-western Brazil, with portions extending into Bolivia, and Paraguay. Nhecolândia, is a sub-region of the southern Pantanal, being about 24,000 km^2 , and whose

peculiarity is the presence of thousands temporary or permanent, shallow lakes, with a wide range of salinity, from freshwater to saline, sodic alkaline lakes, although they are located a few tens or hundreds of meters from each other in the landscape (Costa et al., 2015; Furian et al., 2013) (Fig. 1).

The alkaline nature ($8.5 < \text{pH} < 11.0$) and high salinity of soda lakes is a consequence of the specific hydrologic regime of each lake, which is controlled by low permeability thresholds in the surrounding soil system. For more details, the reader may refer to the work of Furian et al. (2013). In general, the higher the threshold in elevation, the more lakes evolve into alkaline lakes over the long term. Recent modeling on an alkaline lake located approximately 50 km from our study area suggests that the soil horizons that make up these hydrologic thresholds formed at a rate of approximately 400-650 $\text{kg ha}^{-1} \text{ year}^{-1}$, under current soil-climate conditions, and that continuous functioning of approximately 125 years is required to achieve alkaline water in the lake (Merdy et al., 2022). Among soda lakes, three major types have been distinguished based on water color (green, black, or crystalline) corresponding to distinct and well characterized biogeochemical functioning (Barbiero et al., 2018; Costa et al., 2015; Furian et al., 2013; Martins, 2012). Pellegrinetti et al. (2022) established a typology of shallow lakes in Nhecolândia based on limnological, chemical, and microbiological data. Briefly, the alkaline lakes were divided into 3 groups: (i) turbid eutrophic lakes (ET); (ii) turbid oligotrophic lakes (OT); and (iii) clear oligotrophic lakes with vegetation (CVO). The most extreme conditions (highest pH, alkalinity and electrical conductivity (EC)) are observed in ET lakes, where a strong proliferation of cyanobacteria, responsible for the green coloration, develops. In contrast, although alkaline, CVO lakes have the lowest pH, EC and salinity, and crystalline waters with the development of algae and aquatic macrophytes. The OT lakes have intermediate pH and salinity characteristics between ET and CVO lakes, with turbid waters, blackish in color due to organomineral load, and low primary productivity.

The climate of this region is classified as humid tropical with a short dry season (June to October), i.e., Aw type in the Köppen classification. Approximately 90 rivers and small streams supply the Pantanal (Rezende-Filho et al., 2015; Richter et al., 2019) and the regional hydrological regime is characterized by seasonal flooding depending on rainfall in the surrounding highlands. Thus, flooding can be highly variable in length and intensity (Hamilton et al., 2002; Por, 1995), defining drier and wetter years. The study was conducted in the São Roque farm (19.371850 S, 56.346402 W) in the heart of Nhecolândia, over an area of about 4.3 km^2 (Fig. 1).

2.2. Sampling

A set of 48 water samples were collected from 5 soda lakes (Fig. 1), namely 3 ET lakes (04SR, 05SR, 08SR), 1 OT lake (06SR), and 1 CVO lake (07SR) that were selected for their representativeness of the three types of lakes in the region. The samples were collected in October 2017, September 2018, and September 2019, corresponding to an extremely dry, extremely wet, and intermediate year, respectively, thus encompassing a wide range of regional flood and drought conditions (Pellegrinetti et al., 2022). Surface water (SW) was grab sampled (<30 cm depth) at the edge of each lake in 2017 and 2018, and at the edge and center of the lakes in 2019 (except for 08SR). Due to the extreme drought in 2017, subsurface water (SSW) was only collected in 2018 and 2019 from three auger holes in the beach of each lake (10–50 cm deep) at about 100 m from each other. The water samples were stored in high-density polyethylene (HDPE) bottles, filled, closed without air bubbles, and kept at 4 °C in dark conditions until the samples were processed. Sediments were sampled at the same points as surface water, one sample per lake each year (5 lakes \times 1 sample \times 3 years). One-inch polyethylene tubes were used to collect samples from 0 to 20 cm depth. Sediments were dried and homogenized before analysis and all the results are expressed on a dry weight basis.

2.3. Determination of limnological variables

Water pH and electrical conductivity (EC) were measured in the field (pH meter HI 98140, Conductivity meter HI 9835, Hanna Instruments, Brazil). Dissolved organic carbon (DOC) concentration in filtered water samples was determined by a total organic carbon analyzer (TOC-5000 Shimadzu). Total arsenic (TAs) in water was determined by inductively coupled plasma mass spectrometry (ICP-MS, Shimadzu 2030) operating with He gas collision cell and internal standard ^{89}Y . The analytical method and results of TAs in SW samples collected in 2017 and 2018 were previously detailed in Richter et al. (2019). TAs in sediment samples was determined by hydride generation atomic fluorescence spectrometry after acidic digestion as described by Richter et al. (2019). Total phosphorous (TP), total nitrogen (TN) and chlorophyll-a (Chl-a) concentrations were reported by Pellegrinetti et al. (2022) and Cotta et al. (2022) for the same lakes and sampling periods.

2.4. Sample preparation and arsenic speciation analysis

Both SW and SSW samples were centrifugated at $12,500\times g$ for 30 min and filtered through a $0.22\text{-}\mu\text{m}$ membrane (Millipore Millex-GV). As speciation analysis was performed by high-performance liquid chromatography (PS Analytical 10.820 modular interface) hyphenated to hydride generation atomic fluorescence spectrometry (PS Analytical Millennium Excalibur 10.055) (Supplementary Material, Text S1 and Table S1, for details of the methodology and equipment description). The analysis was based on the anion exchange chromatographic method adapted from Ma et al. (2016) for the quantification of As(V), As(III), DMA, MMA and AsB. In order to detect non-hydride generating As species, a treatment using $\text{K}_2\text{S}_2\text{O}_8$ and postcolumn UV oxidation step (HPLC-(UV)-HG-AFS) was applied. Nonanionic As species that did not interact with the column stationary phase were labeled “unknown arsenic” (As_{unk}). This fraction, eluted at the dead time, could include species like arsenobetaine (AsB) and/or arsenocholine (AsCh). Because of the nature of the detection system and the degree of decomposition in the UV reactor, quantification of As_{unk} was not achievable with the AsB calibration curve. In this case, the method only provides qualitative information about the presence of this fraction in the samples. Thus,

arsenite (As(III)), arsenate (As(V)), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and “unknown arsenic” (As_{unk}), could be determined as shown in Supplementary Material, Fig. S1. In these conditions, the limits of detection (LOD) and quantification (LOQ) ($\mu\text{g L}^{-1}$) for each species were 1.7 and 5.2 for AsB, 1.3 and 4.0 for As(III), 0.6 and 1.8 for DMA, 1.4 and 4.4 for MMA, and 0.9 and 2.8 for As(V), respectively. Column recovery was calculated as the ratio (%) between the sum of the concentrations of the eluted species and the TAs concentration. The average recovery of 10 analytical replicates of a standard solution that contained the different species ($20\ \mu\text{g As L}^{-1}$ for each species) ranged from 92% to 107% for all the species. The precision, expressed as the relative standard deviation of the 10 analytical replicates, was 15.5%, 16.6%, 5.8%, 10.0% and 11.8% for AsB, As(III), DMA, MMA and As(V), respectively.

The effects of the UV oxidation step can lead to the peak broadening (Simon et al., 2004) (tailing) of As(III) (Fig. S1) and to an increase in background noise due to the oxidation of samples organic matter, which may decrease As(III) detectability in our samples. Therefore, in order to confirm the “not detected” (ND) results for As(III), an alternative chromatographic method without UV digestion step (HPLC-HG-AFS) based on the method detailed by Richter et al. (2019) was used.

The complete list of reagents can be found in Supplementary Material (Text S2).

2.5. Statistical treatment of data

Spearman test was applied to analyze correlations between variables using an Excel add-in Real Statistics Resource Pack, version Rel 7.10. <http://www.real-statistics.com/>. Redundancy analysis (RDA) was used to correlate the As speciation variables and lake eutrophic factors (Oksanen et al., 2019). The Hellinger transformation was applied to the species dataset; the environmental variables were selected and standardized to reduce collinearity (Legendre and Gallagher, 2001; Legendre and Gillet, 2011). Details of RDA analysis are presented in Supplementary Material (Text S3).

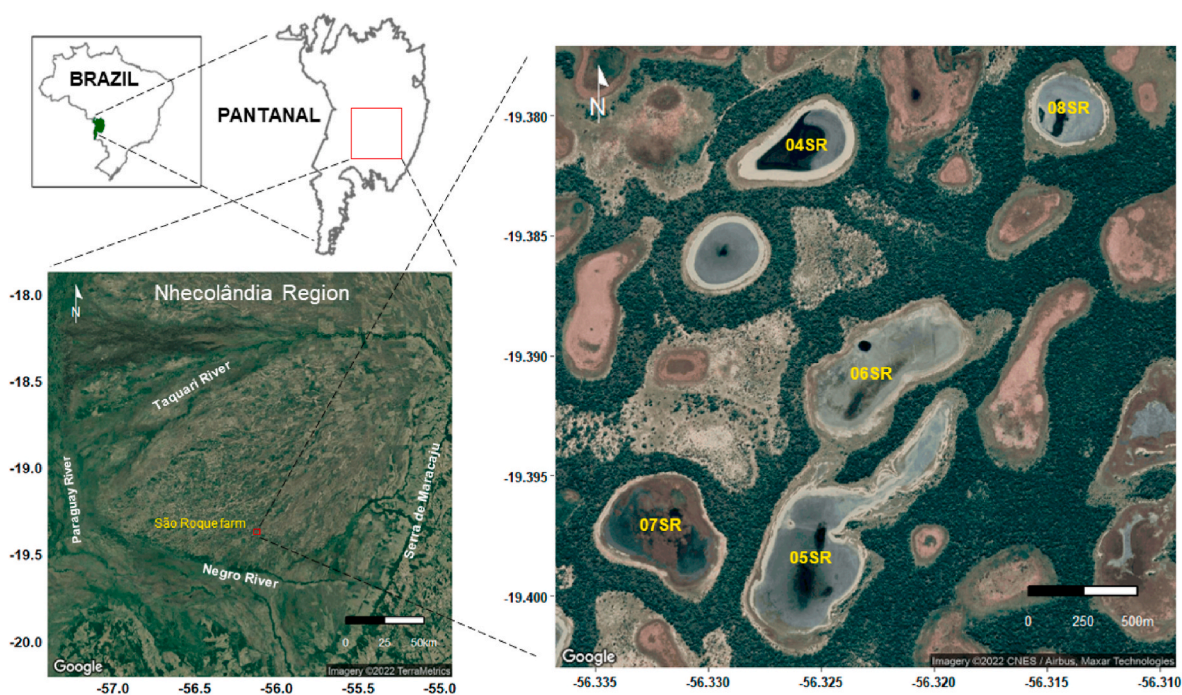


Fig. 1. Locations of saline lakes at the São Roque farm (Nhecolândia, Brazil).

3. Results

3.1. Physicochemical characteristics of soda lakes

Water pH, EC and DOC contents ranged from 8.3 to 10.1, 0.8 to 39.3 mS cm⁻¹ and 3.9–5270 mg L⁻¹, respectively, with the highest values recorded in the driest years 2017 and 2019 (Table 1). These results illustrated the permanent alkaline features of this environment. EC values were always low (0.8–2.0 mS cm⁻¹) in the CVO lake, while the highest values were measured in ET and OT lakes during the driest years (2017 and 2019). TAs concentrations in surface water measured in 2019 ranged from 40 to 262 µg L⁻¹, with the highest values observed in ET lakes in the driest years and the lowest in the CVO lake, consistent with the data previously reported by Richter et al. (2019) for the same lakes sampled in 2017 and 2018. TN, TP and Chl-a concentrations also showed high variability among lakes and years (Supplementary Material, Table S2). Concentrations of TAs and DOC in subsurface waters ranged from 0.6 to 2463 µg L⁻¹ and from 2.9 to 2106 mg L⁻¹, respectively (Supplementary, Table S3). For both parameters, the lowest values were detected in the OT lake, whereas the highest were found in the ET lake (04SR). The sediment TAs concentration in 2019 varied from 4 µg g⁻¹ (ET 04SR) to 12 µg g⁻¹ (CVO) (Table 1).

3.2. Arsenic speciation in lake water samples

As(V) was the main quantified species, averaging 20%–109% of the TAs in SW (Fig. 2 and Table S4) and 18%–96% in SSW samples (Fig. 3 and Table S5). A statistically significant relationship was found between TAs and As(V) concentrations considering all water samples (Spearman, R² = 0.944, P < 0.05). As(III) was detected in SW, only at the lake center of ET and CVO lakes (Fig. 4), and in SSW of CVO and ET(05SR) lakes (Fig. 3), with concentrations ranging from 4.8 µg L⁻¹ to 64.5 µg L⁻¹. The methylarsenicals (DMA + MMA) accounted for 1.9%–45.4%. These species and the As_{unk} fraction were identified in the SW and SSW samples, but their simultaneous occurrence was only observed in the ET lakes.

Column recoveries for samples analyzed ranged from 21% to 110%.

3.3. Temporal variations and distribution of arsenic speciation

Arsenic speciation varied depending on the lake water level. There were organoarsenics species (i.e. DMA, MMA or As_{unk} fraction) in SW in the dry years 2017 and 2019, whereas in high water conditions, only As(V) and low quantities of DMA were observed (Fig. 2). In contrast, organoarsenicals were detected in SSW only in the high-water conditions in 2018. In this compartment, in 2019, only the inorganic forms As(III) and As(V) were measured (Fig. 3). We noted speciation differences between the edge and the center of ET and CVO lakes (Fig. 4), specifically for As(III) which content was consistently higher in the center of both lakes, accounting from 20.4% to 27.4% of TAs, respectively. In the OT lake, no As(III) was identified, either at the edge or at the center.

3.4. As speciation and soda lake eutrophication

The relative contribution of limnological parameters to As speciation in lakes is expressed by the redundancy analysis (RDA, Fig. 5). The first two axes contributed to 77.3% and 6.74% of the total variation, respectively. The environmental variables explain 84.0% of the variation in As speciation across the soda lakes. Organoarsenic species were positively correlated with Chl-a, TN, TP, DOC and TAs. In contrast, As(V) showed a negative correlation with these parameters. Soda lakes were clustered based on their trophic status reflecting a seasonal distribution.

Table 1
Characteristics of soda lakes surface water and total arsenic content in sediment determined in the three sampling campaigns.

Lake Sample ^(a)	pH			DOC (mg L ⁻¹)			EC (mS cm ⁻¹)			Water TAs (µg L ⁻¹)			Sediment TAs (µg g ⁻¹)						
	2017	2018	2019	2017	2018	2019	2017	2018	2019	2017 ^(c)	2018 ^(c)	2019 ^(b)	2017 ^(c)	2018 ^(c)	2019 ^(b)				
ET lakes	04SR	10.0	8.8	9.9	9.9	9.9	66	164	164	16.3	2.4	4.7	4.5	104	262	235	3	2	4
	08SR	10.1	8.4	9.8	9.8	9.8	38	200	200	39.3	1.4	4.4	–	1722	148	–	8	6	–
	05SR	9.9	9.3	9.7	9.8	9.8	4103	31	120	21.8	1.1	5.0	5.0	822	102	102	6	3	5
OT lake	06SR	9.7	8.5	9.1	9.1	9.1	306	3.9	26	18.0	1.2	2.4	2.3	1324	125	121	12	16	12
CVO lake	07SR	8.6	8.3	8.7	8.6	8.6	76	18	100	1.8	0.8	1.0	2.0	53	40	40	20	8	7

^a Sample identification as reported in previous published studies on the same lakes (e.g. Viana et al., 2022).

^b Collected at the center of the lake (when not mentioned, samples were collected at the lake's edge).

^c Data from Richter et al. (2019).

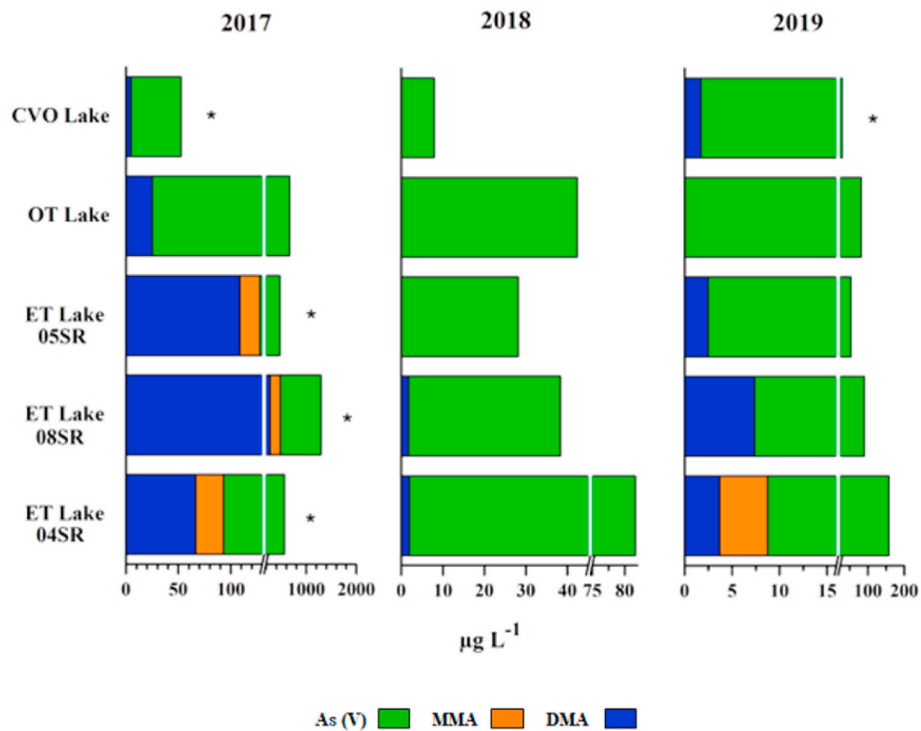


Fig. 2. Arsenic speciation in surface waters of soda lakes, samples collected at lakes edge. * Indicate sample in which the As_{unk} fraction was detected.

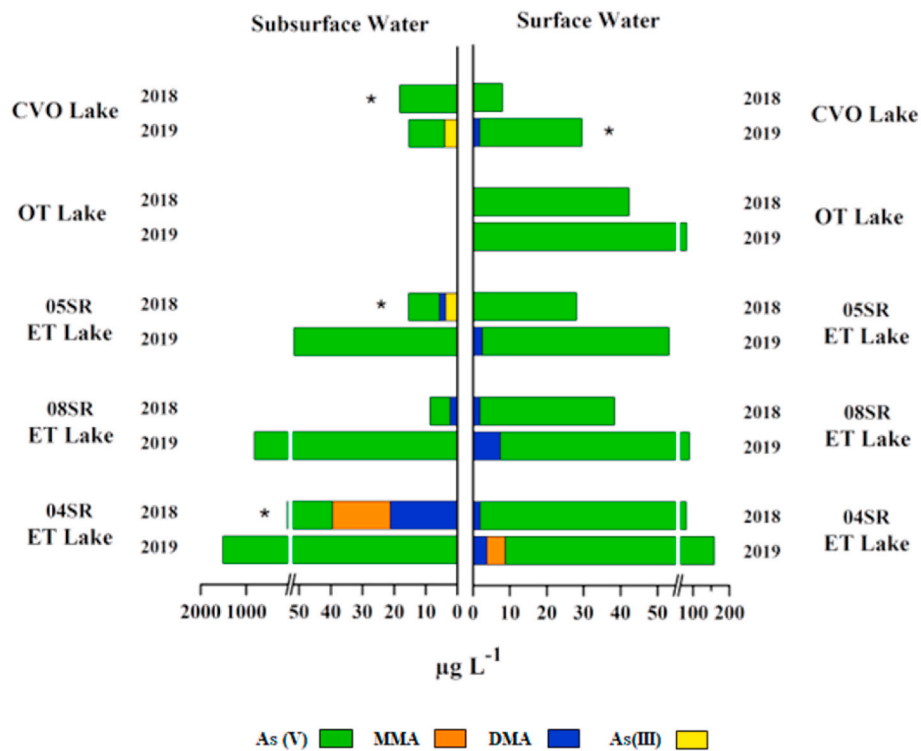


Fig. 3. Distribution of As species between subsurface and surface waters (collected at lakes edge) in 2018 and 2019. For SSW, the As species concentrations correspond to the mean of three samples collected at the beach of each lake. As species in SSW were not detected at OT lake. * Indicates sample in which the As_{unk} fraction was identified.

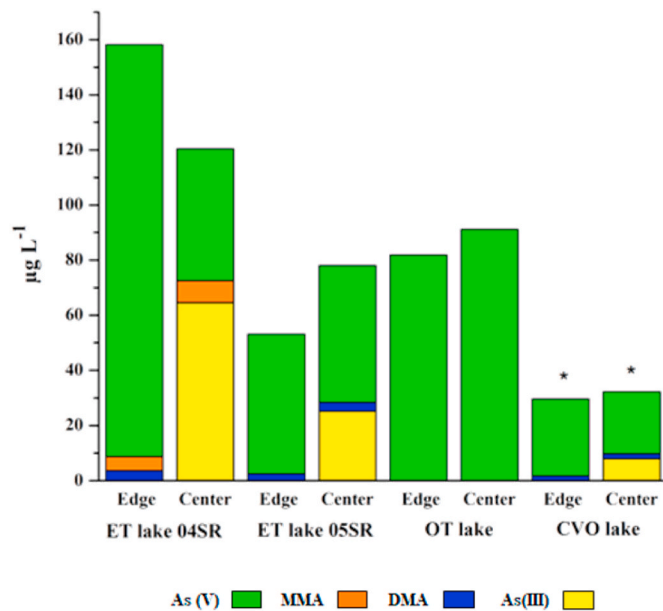


Fig. 4. Distribution of arsenic speciation between edge and center of soda lakes in 2019. * Indicates samples in which the As_{unk} fraction was detected.

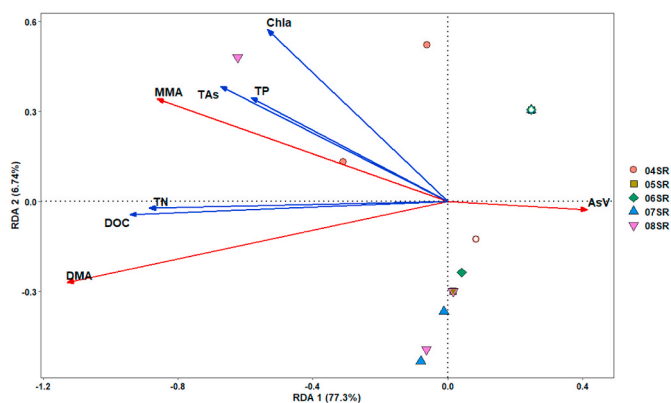


Fig. 5. Redundancy analysis (RDA) depicting the distribution of As speciation (As(V), MMA and DMA) in relation to the lake's eutrophication parameters. Red arrows represent As species, blue arrows represent lake's parameters. The empty symbols represent the lakes during the flood period. Data from surface water samples collected at the lake's edge.

4. Discussion

4.1. Seasonal dynamics and functioning

The seasonal biogeochemical variations (Table 1) described here are representative of Pantanal alkaline lakes and support previously reported evidence (Barbiero et al., 2002, 2007, 2008, 2016; Merdy et al., 2022). Cotta et al. (2022) and Pellegrinetti et al. (2022) described changes in lake trophic status as a function of regional flooding and/or local rainfall, and permanent differences in trophic conditions. Annually, ET lakes exhibit green water caused by cyanobacterial bloom(s) (Andreote et al., 2018; Cotta et al., 2022; Vaz et al., 2015), which never occurs in CVO and OT lakes that maintain crystalline waters with macrophyte and algae (mainly *Characeas*) development, or black with low biological activity, respectively (Martins, 2012). Thus, despite seasonal fluctuations in limnological parameters, the lakes maintain their biogeochemical functioning. Similar variations were observed in dissolved As concentrations with consistently higher TAs values in ET lakes, intermediate in OT lakes, and lower in CVO lakes (Richter et al.,

2019).

4.2. Trophic status and arsenic speciation in lakes

A wide variety of As species was observed in the studied lakes when compared to the most common species in fresh water (Cullen and Reimer, 1989) and those reported in alkaline lakes (Héry et al., 2020; Hollibaugh et al., 2005). Chemical speciation in environmental samples is always challenging due to the possibility of species interconversion during sampling, sample storage and sample preparation (Viana et al., 2022). For this reason, a maximum of precautions has been taken during these steps to limit this risk (cf. section 2.2 and 2.4). The very different biogeochemical functioning of the lakes suggests that many chemical and biological factors contribute to the observed diversity of As species. The most significant variations in As speciation observed between sampling periods were for organoarsenics (DMA, MMA or As_{unk}). Richter et al. (2019) reported predominance of As(V) in the waters of alkaline lakes of the Pantanal, attributing it mainly to the thermodynamic stability of this species in natural waters. Our results are consistent with this work, but to a lesser extent, as, overall, As(V) accounts for only 59% of AsT in our study compared to 95% in the study by Richter et al. (2019). Seasonal biotransformation processes, dependent on trophic conditions, may explain this difference. For ET and CVO lakes, biological activity, namely cyanobacteria and macrophytes/algae, respectively (Costa et al., 2016; Pellegrinetti et al., 2022), can promote the appearance of distinct As species such as DMA, MMA, As(III) (Miyashita et al., 2016; Pell et al., 2013; Rahman and Hassler, 2014; Yin et al., 2011). Metabolic pathways in various living organisms produce DMA, MMA, or complex species (e.g., arsenosugars) by transformation of As(V) to As(III), followed by methylation (Hasegawa et al., 2019; Hellweger et al., 2003; Lorente-Mirandes et al., 2010; Mamun et al., 2019; Pell et al., 2013; Wang et al., 2002). This is a well-documented mechanism in a variety of aquatic environments (Lloyd and Oremland, 2006; Miyashita et al., 2016; Papry et al., 2019; Yin et al., 2011).

Total nitrogen (TN), total phosphorus (TP), and chlorophyll (Chl-a) are commonly used to assess eutrophication in aquatic systems. Several factors attest to the influence of biological activity on arsenic speciation in alkaline lakes of the Pantanal. (1) The presence of organic species accompanies the occurrence of cyanobacterial bloom indicated by the increase of Chl-a in ET lakes, mainly during the hypereutrophication observed in the extreme dry year 2017 (Figs. 2 and 5). This supports the role of cyanobacterial blooms, and more generally lake eutrophication degree, on As speciation in the Pantanal, as described in other aquatic environments (Azizur Rahman and Hasegawa, 2012; Yan et al., 2016). Conversely, during wet periods and flooding in the Pantanal, the decline in trophic conditions and disappearance of blooms is accompanied by low As species diversity in all surface waters (Figs. 2 and 5). (2) Costa (2020) detected As bioaccumulation by phytoplankton in Pantanal soda lakes, implying the mediation of biotransformation processes (Hasegawa et al., 2019), but unpublished results from our research group suggest that the capacity of the planktonic community to bioaccumulate As depends on limnological characteristics and season. (3) The interaction between biological activity and As is consistent with the detection of only As(V) and DMA in OT lakes where black, turbid waters (100–350 NTU, Barbiero et al., 2018; Martins, 2012 and Pellegrinetti et al., 2022), rich in colloidal material restrict light penetration. In these conditions, cyanobacterial blooms are prevented (Andreote et al., 2018) and the development of all photosynthetic organisms is limited, decreasing the possibilities of As biotransformation, thus confirming their role in As speciation within the other types of alkaline lakes. (4) Finally, for the CVO lake, the trophic status is consistently low (Table 1 and S2) and the biotransformation of As during macrophyte/algae development suggests that variations in As speciation should be attributed to uptake and efflux of metabolized As by macrophytes/algae related to variation in TAs concentration in the water (Table 1). Mamun et al. (2019) reported that increasing the concentration of As(V) in solution increases the excretion

of metabolized As as a detoxification mechanism for macroalgae. In this lake, the green algae *Chara* sp. is particularly abundant, as already observed in this region (Bueno et al., 2009), and the ability of this Chlorophyceae to bioaccumulate inorganic As was previously reported (Amirnia et al., 2019; Fereshteh et al., 2007; Taleei et al., 2019). Similarly, plants can take up As in its inorganic forms primarily through a concentration gradient between the As source (soil or water) and the plant (Abbas et al., 2018).

In summary, variation in lake trophic status is associated with changes in As speciation in ET and OT lakes, whereas in the CVO lake, independent of trophic conditions, variation in As speciation is associated with changes in water total arsenic concentration.

The low recovery (<60%) observed in some samples suggests the presence of As associated with molecules too large to elute from the column during anion chromatography (García-Salgado et al., 2012). Previous work suggests that this could be due to the presence of complex As species such as water-soluble As bound to proteins, extracellular polymeric substances (EPS), and/or As-organic matter complexes (Al-Sid-Cheikh et al., 2015; Naveed et al., 2020). Byproducts derived from the biological activity of cyanobacteria and macrophytes/algae interact with As in lakes, forming complex molecules. Barbiero et al. (2016) showed that high content of labile OM, consisting of macromolecules complexed with metals such as Fe and Al, control the formation of the soil system that surrounds alkaline lakes in the Pantanal favoring first the synthesis of Mg-smectites at the lake shoreline, and then Fe-illites a few tens of meters further out. It is reasonable to speculate that such macromolecules can also fix arsenic, illustrating the complexity of As speciation in this environment. However, this point should be confirmed by a specific study. We point out that unpublished results from our research group suggest that poorly labile organo-arsenic complexes, mediated by dissolved metals such as Fe or Al, may act as limiting factors for the availability of As to the biological community of lakes.

The presence of As(III) in the surface water of ET and CVO lakes can be attributed to the either biological reduction of As(V) (Smedley and Kinniburgh, 2002), or the redox conditions present in these lakes. As both types of lakes present high primary productivity (cyanobacteria in ET and macrophytes/algae in CVO) more reducing conditions, that favor As(III), can be expected resulting from OM degradation. For the ET lake, the hyperoxygenation identified by Barbiero et al. (2018) concerns only a few decimeters where light penetrates, i.e., the whole water column at the edge of the lake, but only the top of the water column in the center. Thus, As(III) is likely to remain within the water column in the center of the lake. These results are in agreement with those reported by Elias et al. (2022), who measured As(III) concentration in the water column by using the diffusive gradient in thin film (DGT). Due to the variation in depth between the edge and the center, these lakes are not expected to be a homogeneous environment and it is likely that redox conditions vary both spatially and temporally (Barbiero et al., 2018).

4.3. Arsenic species in subsurface water

In 2019, in ET lakes, TAs was up to 10 times higher in SSW than in SW, and As(V) was the only quantified species (Fig. 3). The same trend was reported by Viana et al. (2022) who studied the As speciation at the sediment/water interface on the beach lakes by using DGT. For the ET lake 04SR, the authors showed that the high As(V) concentration gradient in the sediment porewater results from the flow of water and solutes during the dry period due to the wicking effect and strong evaporation on the beach. Accordingly, in the wet year 2018, the trend was a decrease in TAs in SSW. In CVO, OT and some ET, an opposite flux of fresh water (i.e. from the beach to the lake as suggested by Martins (2012)) may explain more diluted porewater (Viana et al., 2022). In this alkaline geochemical environment, sediments behave as a nonreactive matrix, and the solid phase does not interfere (or only slightly) with As transfers (Richter et al., 2019; Viana et al., 2022). The low TAs content

in sediments (Table 1) when compared to those of contaminated sites confirm this hypothesis. Still in 2019, organic species were only quantified in the SW of ET and CVO lakes. As discussed above, organic species in the water column should originate from biological activity (phytoplankton in ET and macrophytes/algae in CVO). Our hypothesis is that in a typical dry season as in 2019, the evapoconcentration process that results in the increase of As concentration and other elements (Barbiero et al., 2008) in the SSW, also results in biogeochemical conditions that favor the mineralization of As organic species into the sediments; e.g., oxic conditions were detected in SW of all lakes during the dry period, Pellegrinetti et al. (2022). Biodegradation of organoarsenics is known to occur in aerobic aqueous environments and in soils, providing CO₂ and As(V) by oxidative processes (Craig, 2003; Hirmer and Emons, 2004).

In 2018, TAs and organic As contents in SW were lower than in the dry period likely due to the lower biological activity (DOC and Chl-a decreased in the wet period, Pellegrinetti et al. (2022)) and to a dilution effect. Conversely, more species were present in the SSW of ET and CVO lakes compared to 2019 (Fig. 3). During the wet periods, the low primary productivity results in lower dissolved oxygen content than during the dry one, and anoxic conditions have even been observed in 05SR and 08SR (Pellegrinetti et al., 2022). Furthermore, during this period, the level of the lakes' water was very high, covering the higher part of the beach that is normally covered by vegetation (Supplementary Material, Fig. S2). The degradation of this biomass should result in O₂ depletion. More reducing conditions, mainly at the water/sediment interface, and high availability of organic carbon due to biomass decomposition, would therefore be created that limit the mineralization of the organoarsenic species in SSW (Gao and Burau, 1997; Huang et al., 2007).

5. Conclusions

This study provides new information on the diversity of arsenic species in soda lakes of the Pantanal wetland in Brazil. The dominant species identified was As(V), which coexisted with lower concentrations of As(III), DMA, and MMA, as well as other organic species (As_{unk}). Our results shed light on the temporal and spatial variations of arsenic speciation in relation to the eutrophication and biological activity observed in soda lakes. The study supports the hypothesis that cyanobacteria in eutrophic turbid (ET) lakes and macrophytes/algae in oligotrophic vegetated (CVO) lakes control the biotransformation of arsenic and favor the presence of organoarsenicals in surface water during dry periods. In contrast, As(V) prevails in flooding periods. The speciation of arsenic in the oligotrophic turbid lake (OT) could be influenced by other factors that require further study. The distribution of As species in soda lakes varies significantly between surface waters and subsurface waters, as well as spatially within the same lake. Seasonal changes in biogeochemical conditions at the water/sediment interface have a significant impact on the spatial distribution of arsenic speciation in soda lakes. However, as these statements were based on a limited number of studied lakes (N = 5), we recommend that they be confirmed by further studies. We also suggest that future research focus on the dynamics of As(III) and the occurrence of As bound to large complex molecules and their identity. This knowledge will be valuable in addressing the challenges of global arsenic pollution and anticipating the fate of As species likely to change under climatic constraints affecting the biogeochemical functioning of these lakes.

Author contribution

Amauris Hechavarría-Hernández: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Writing – review & editing. José Lucas Martins Viana: Writing – review & editing. Laurent Barbiero: Conceptualization, Investigation, Writing – review & editing. Ary Tavarez Rezende-Filho: Investigation. Celia Montes: Project administration. Adolpho Jose Melfi: Project administration. Anne

Helene Fostier: Conceptualization, Project administration, Writing – original draft, Writing – review & editing, Supervision.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2023.138672>.

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