Science of the Total Environment 687 (2019) 917–928

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Dissolved arsenic in the upper Paraguay River basin and Pantanal wetlands

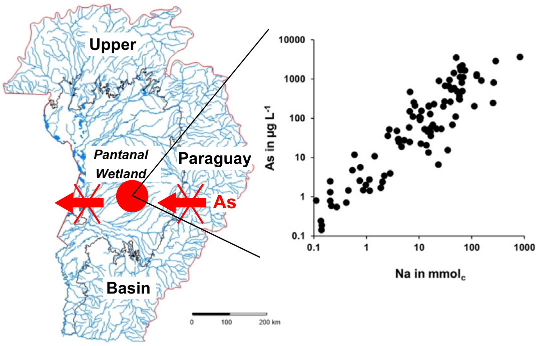
Larissa Richter [a], Amauris Hechavarría Hernández [a], Gustavo S. Pessôa [a], Marco Aurelio Zezzi Arruda [a], Ary T. Rezende-Filho [b], Rafael Bartimann de Almeida [c], Hebert A. Menezes [b], Vincent Valles [d], Laurent Barbiero [a,e,f,g,*], Anne Hélène Fostier [a]

[a] *University of Campinas, Chemistry Institute, Campinas, SP, Brazil*
[b] *Federal University of South Mato Grosso (FAENG), Campo Grande, MS, Brazil*
[c] *Grande Dourados Federal University, UFGD, MS, Brazil*
[d] *Université d'Avignon et des Pays de Vaucluse (UAPV), France*
[e] *Institut de Recherche pour le Développement (IRD), GET, Toulouse, France*
[f] *São Carlos Federal University (UFSCar), Sorocaba, SP, Brazil*
[g] *São Paulo University (CENA-USP), Piracicaba, SP, Brazil*

HIGHLIGHTS

- There is no As-contamination from rivers to the Pantanal floodplain.
- There is no As-contamination from the Pantanal floodplain to the main draining rivers.
- The occurrence of high As-concentration in alkaline waters is a regional process in Nhecolândia sub-region.
- Despite high dissolved As contents, soils and lake sediments in contact with these waters are not As-contaminated.
- Soils and sediments behave as non-reactive matrix.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 January 2019
Received in revised form 7 June 2019
Accepted 9 June 2019
Available online 11 June 2019

ABSTRACT

Although high levels of dissolved arsenic were detected in surface and ground waters of Nhecolândia, a sub-region of the vast Pantanal wetlands in Brazil, the possible sources have not been clearly identified and the potential release from the wetland to the draining rivers has not been investigated. In this study we measured the dissolved As content in all the rivers and small streams that supply the southern Pantanal region, as well as in the two main rivers draining the wetland, i.e., the Cuiaba and Paraguay rivers and tributaries. In addition, Arsenic in surface waters, perched water-table, soils and sediments from 3 experimental sites located in the heart of Nhecolândia were compared. On the one hand, the results show the absence of As contamination in rivers that supply the Pantanal floodplain, as well as a lack of significant release from the floodplain to the main drains. The As contents in the rivers are <2 µg L^{-1}, with variations that depend on the lithology and on the geomorphology at the collection point (uplands or floodplain). On the other hand, they confirm the regional extension of As contamination in Nhecolândia's alkaline waters with some values above 3 mg L^{-1}. Arsenic is mainly in the arsenate form, and increases with the evaporation process estimated from sodium ion concentrations. The pH of soil solution and surface water increases rapidly during evapo-concentration up to values above 9 or 10,

---

* Corresponding author at: University of Campinas, Chemistry Institute, Campinas, SP, Brazil.
E-mail address: laurent.barbiero@get.omp.eu (L. Barbiero).

https://doi.org/10.1016/j.scitotenv.2019.06.147

preventing adsorption processes on oxides and clay minerals and promoting the retention of dissolved arsenic in solution. Solutions from organic soil horizons show higher As contents in relation to Na, attributed to the formation of ternary complex As-(Fe/Al)-OM. In this alkaline pH range, despite high levels of dissolved As, soil horizons and lake sediments in contact with these waters show As values that correspond to uncontaminated environments.

1. Introduction

Arsenic (As) is known to be a serious health risk, a toxic and carcinogenic chemical element. In addition to naturally occurring arsenic, its presence also depends on anthropogenic, mining, industrial or agricultural activities. It is present in the environment under four oxidation states (− 3, 0, + 3, and +5) and different organic and inorganic species. The amounts and relative proportion of oxidation states and chemical species of As in water are the result of a complex reactivity including oxidation/reduction, complexation, adsorption/desorption, precipitation and biological transformations (Bhattacharya et al., 2006; Hasegawa et al., 2010; Redman et al., 2002; Sharma and Sohn, 2009; Welch and Lico, 1998). Average arsenic concentrations of surface water are around 0.1–2 μg L^{-1} in river and lake waters (Gaillardet et al., 2014; Rahman and Hasegawa, 2012), although concentrations may be higher (up to 12 mg L^{-1}) in areas containing natural As sources (WHO, 2008). Guidelines are usually set at the limit of 10 μg L^{-1} for drinking water (Brazil, 2011; EPA, 1991; WHO, 2008) and for the protection of aquatic life in freshwaters (CCME, 2001; CONAMA, 2011; EPA, 1991).

High arsenic contents in surface and groundwater in Latin America have only recently been reported (Bundschuh et al., 2012a). In addition to pollution and contamination related to human activities (mainly mining), high levels of naturally occurring arsenic in water have been detected in Mexico (Armienta and Segovia, 2008; Castro de Esparza, 2010), Nicaragua (Mcclintock et al., 2012), Uruguay (Guérèquiz et al., 2009), Argentina (Bundschuh et al., 2004; Nicolli et al., 2012), Chile (Arriaza et al., 2010). In most of these cases, high contents result from weathering products in the Andean volcanic chain and geothermal surface manifestations (López et al., 2012). Although high arsenic levels have been reported in the Pantanal of Nhecolandia in Brazil, with values approaching 3 mg L^{-1} (Barbiero et al., 2007), this area has not been mentioned in recent research on arsenic occurrence (Bundschuh et al., 2012b).

The Upper Paraguay River Basin (UPRB) can be divided into the plateaus (or uplands) and the enormous Pantanal floodplain, considered the world's largest wetland (Por, 1995). The floodplain is drained by the Paraguay River on its western side and is supplied by about 90 rivers or small watercourses arising from the Brazilian craton that consists of a variety of rocks, i.e. potential sources of arsenic. On the one hand, very few data are available on the chemistry of the rivers that supply the Pantanal, although recent studies have shown that extensive agricultural activities on the highlands are affecting the major ion composition of some rivers down to the floodplain (Rezende Filho et al., 2015, 2012). On the other hand, despite the presence of high arsenic content in the shallow perched water-table and the surface water of Nhecolândia, the most alkaline region of the Pantanal, no study has been directed towards a possible release of arsenic from the wetland towards the main draining rivers. The potential release mainly depends on both, the fate of As during the reduction and trapping mechanisms that favor As stabilization in the wetland (Guénet et al., 2017), and the behavior of arsenic during the re-oxidation process occurring at the wetland-river interface (Pédrot et al., 2015).

In this framework, the objective of this study is double: first, to identify, among the rivers on the uplands, the possible sources for the high arsenic contents observed in the floodplain and to verify if the floodplain is releasing arsenic to the nearby river network, according to the hydrological connectivity between the wetland and the main draining rivers; second, to verify whether arsenic occurrence detected in an alkaline soil system of Nhecolândia is related to local or regional processes and to identify the factors responsible for these high arsenic contents.

2. Regional setting

The Upper Paraguay River Basin: being around 2.8 × 10^6 km^2, the Upper Plata River drainage system is the second largest basin in South America after the Amazonian basin. Its upstream section consists of two basins of similar size, namely the Parana and Paraguay basins. The major difference between these tributaries is the presence of the vast Pantanal floodplain located in the Paraguay headwaters (Fig. 1). The Pantanal (about 0.2 × 10^6 km^2) is a biodiversity hotspot classified as UNESCO Natural World Heritage site, and a priority region for environmental conservation (Olson and Dinerstein, 2002). Unlike the upper Parana basin, whose river chemistry is clearly impacted by the Brazilian megacities, the upper Paraguay basin is still relatively preserved, although some alterations in the water chemical profile have already been detected in downstream areas with extensive cropping (Rezende Filho et al., 2015).

The population density in the UPRB is quite low on the uplands (<4 people km^{-2} in Mato Grosso state and <7 people km^{-2} in South Mato Grosso state, (IBGE, n.d.), and it is low in the Pantanal with <0.5 inhabitant km^{-2}. In addition to extensive livestock ranching, two kinds of crop systems are cultivated on the uplands: sugar cane and a simple system of rotation of cotton, soybeans and corn. The Pantanal is essentially privately owned and the main land use activity is livestock reproduction and extensive ranching.

The climate is classified as tropical humid with short dry season (July to October), i.e. "Aw" type in Köppen classification. Climate patterns are controlled by the seasonal migration of the Intertropical Convergence Zone (ITCZ). The mean annual temperature is about 25 °C, from 21 °C to 32 °C during dry winters and wet summers, respectively. Mean precipitation is about 1100 mm, whereas evapotranspiration is about 1400 mm, resulting in an annual hydrological deficit of about 300 mm. The flood pulse in the floodplain occurs from November in the northern part, to March in the southern part of the Pantanal (Junk and Nunes de Cunha, 2005).

Fig. 1 shows the UPRB geological context, with calcareous formations located in the north (Serra das Araras) and in the south (Serra da Bodoquena), basalts of the Serra Geral formation mainly in the upper part of the Aquidauana and Miranda watersheds, sandstone formations on the eastern part of the basin, and some crystalline rocks interspersed in the eastern, north-western and the narrow southern part of the wetland. The floodplain, covered by quaternary sediments, consists of several sub-regions with their own specificities regarding the date and duration of the flooding (Por, 1995), the transport, deposition, and mineralogy of the sediments (Bergier, 2013) and the water chemical composition (Rezende Filho et al., 2012). It is made up of several alluvial fans (Assine et al., 2015), including one formed by the Taquari River, referred to as one of the largest alluvial fans of the world (Buehler et al., 2011).

Nhecolândia sub-region: Nhecolândia lies in the floodplain on the southern half of the Taquari fan (Fig. 1). It comprises an area of approximately 24,000 km^2, delimited in the north by the Taquari River, in the south by the Negro River, in the west by a portion of the Paraguay River, and in the east by the Maracajú Plateau, which corresponds to

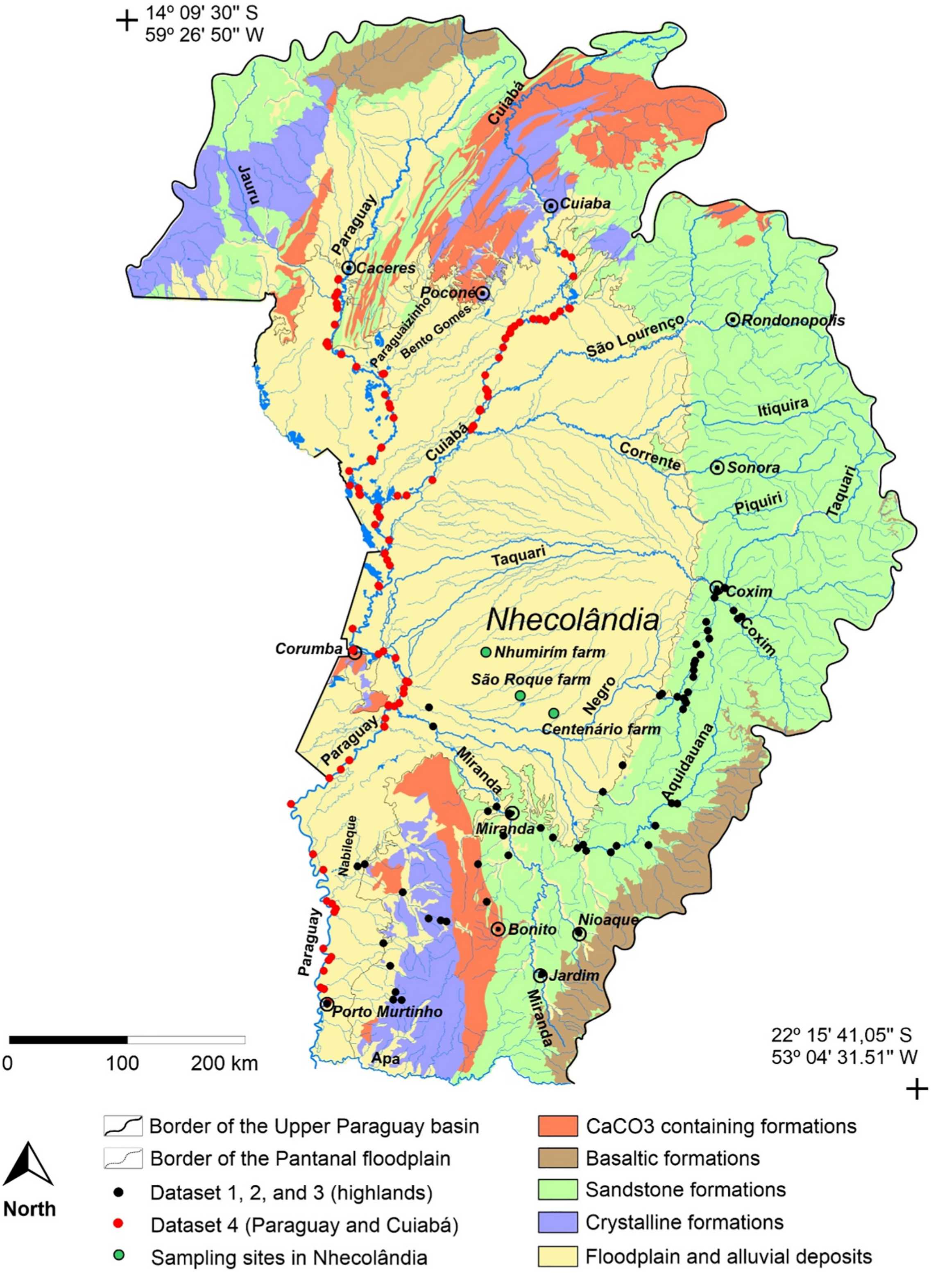


Fig. 1. Map of the Upper Paraguay basin and Pantanal wetland: geological framework and river water sampling and location of the Nhecolândia sub-region and of the 3 studied sites Nhumirím, São Roque and Centenário farms.

the southeastern edge of the Pantanal wetland. Aside from these rivers, the region has a relatively closed drainage with little connection to the major river system, and the water usually flows below the surface within sandy soils and along drainage fields called "vazantes". The peculiarity of this region is the presence of about 15,000 lakes, including about 500 saline-alkaline ones (Furian et al., 2013). While freshwater lakes supply the regional water-table during almost all seasons (Freitas et al., 2019), saline alkaline lakes are disconnected by low permeability soil horizons, and supply the aquifer only fleetingly during strong rainy events (Barbiero et al., 2008; Furian et al., 2013). Previous studies have shown that the alkaline lakes may be classified within 3 different types, depending on their biogeochemical functioning

(Andreote et al., 2018, 2014; Barbiero et al., 2018; Martins, 2012; Vaz et al., 2015), i.e. green, black and crystalline water lakes. Their electrical conductivity ranges usually from 1500 to 15,000 μS cm^{-1}, with exceptional values recorded up to 80,000 μS cm^{-1} at the end of the dry season. In parallel, the pH oscillates from 8.9 to 10.7. High pH and EC result from cumulative evaporation over years of water supplied near the surface from the vazantes and/or freshwater lakes towards the saline lakes (Barbiero et al., 2008; Furian et al., 2013). Soils around alkaline lakes have a standard organization of which a simplified model is shown in Fig. 2 (adapted from Barbiero et al., 2016). It mainly consists of 5 contrasting horizons. Close to the lake, a grey-brown topsoil loamy sand horizon (1) is observed usually with numerous calcareous precipitations. The occurrence of this horizon is limited to the oscillation zone of the lakeshore between the wet and dry seasons. Below, there is a light brown sandy material (2) with <1% clay. Within horizon 2, high water pH conditions favor large dissolved organic carbon contents, which precipitate into blackish volumes at the base of this material and defines horizon (3). Subjacent to this, there is a massive (single grain), greyish loamy sand material (horizon 4) with about 15% clay. The top of this horizon (4) is wavy. Further below lies a loamy sand, olive to light olive-grey colored horizon (5), with 15–20% clay, massive structure (coherent and cemented) and locally extremely firm consistency.

3. Materials and methods

3.1. Sampling and database

3.1.1. Regional UPRB study

For the study at the UPRB scale, we used 4 datasets. Dataset 1, 2 and 3 consists of 56 river samples each, collected in December 2012, March 2013 and May 2013, respectively, i.e. at the beginning, middle and end of the wet season. The collection took place on the uplands, at the south-eastern and southern border of the Pantanal from the cities of Coxím to Porto Murtinho (Fig. 1). Datasets 4 was collected from November 2010 to January 2011 along the main drainage axis of the floodplain, that is, the Paraguay (21 samples) and Cuiaba (nine samples) Rivers, and a few kilometers upstream the confluence with their major tributaries (88 samples). All samples were collected at approximately 0.3-m depth in the middle of the river section. The sampling procedure as well as the major ion chemistry was detailed in Rezende Filho et al. (2015) (Supplementary Material S1 and S2). All samples for trace element determination were filtered (0.45 μm cellulose acetate) in the field and acidified with ultrapure HNO_3.

3.1.2. Local study at Nhecolândia

Water, sediment and soil collection was carried out in two sites of Nhecolândia (São Roque and Centenário farms) and compared with previous results obtained at Nhumirím farm in 2 alkaline lakes and surrounding piezometers (Barbiero et al., 2007). These three sites, located in the central and southern part of Nhecolândia, cover complementary geographical positions intersecting the regional drainage oriented east northeast – west southwest (Fig. 1). At São Roque farm, water samples were collected in extreme dry (September and October 2017) and wet conditions (August and September 2018) in 6 saline lakes (referred to as SR06 with black water, SR01, SR04, SR05, SR08 and SR09 with green water, and SR07 with crystalline water) and three freshwater lakes (BSR03, BSR04, BSR05). Lake sediments were collected in 2017. At the Centenário farm, sampling was carried out in 3 saline lakes (referred as CN01 with green water, CN02 with black water and CN03 with crystalline water), 1 vazante and 1 fresh water lake. Samples

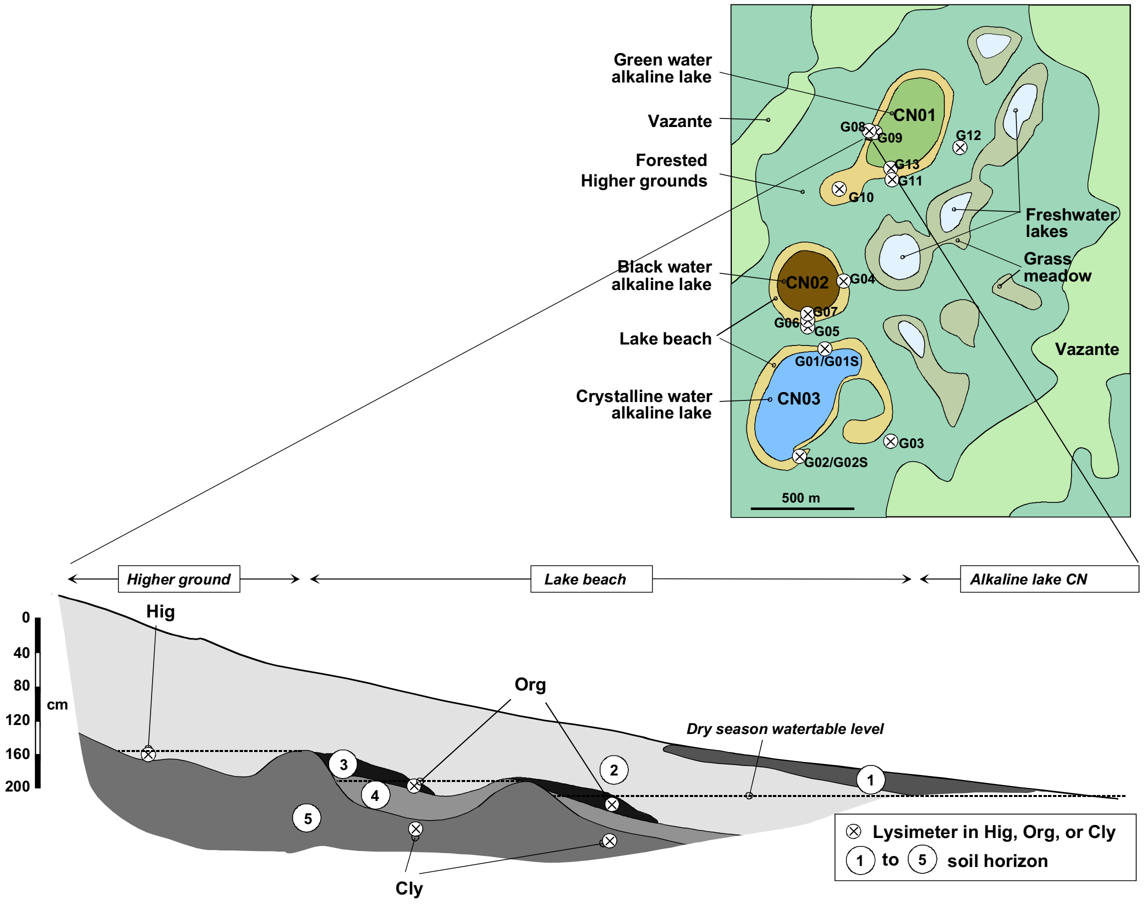


Fig. 2. Centenário study site showing a representative landscape, and a standard soil sequence around saline alkaline lakes; see text for soil horizons description. ⊗ denotes the location of the lysimeters in the perched water table.

were collected during the dry season (September 2015 and 2016, and October 2017) and at the beginning (November 2015) and the end of the wet season (June 2016 and August 2018). Lake sediments (0–20 cm) were sampled in 2016. In addition, water samples were also taken in the perched shallow water-table of the soil systems surrounding the lakes at Centenário site. For this, fifteen water-table samplers (lysimeters) consisting of pierced polyethylene containers (Maître, 1991) were installed in the water-table through auger holes (7 cm in diam.). They are further referred to as (G01S, G02S and G01 to G13). The 120-ml containers were wrapped with a synthetic tissue to prevent clogging by soil particles. Two capillary tubes (1 mm inner diam.), inserted into the container, reach the soil surface. The first one ends at the upper part of the container just below the cap and is used for injecting N_2 gas. The second one, down to the lower part of the container, is used to collect the groundwater sample by depression. After installing the samplers, the holes were filled with the initial material preserving the order of the different layers up to the soil surface. The sampling device prevents contact between the water-table and the atmosphere and thus preserves the redox conditions of the water-table within the sampler. The samples were collected from the lysimeters with a hand-held vacuum pump by gentle pumping while injecting N_2 flow at a maximum pressure of 0.05 atm, in order to avoid turbulences and to prevent drastic changes in redox conditions in the sampler. The samples first reached a closed Erlenmeyer previously filled with N_2 to avoid rapid oxidation. The first drops were driven towards the sensitive part of the potential Pt-probe (ref HI3620D) and the lowest value (usually after ~5 s) was noted. A value of +203 mV was added to the measured potential for its conversion into redox potential Eh, assuming that the temperature was almost constant close to 30 °C. Then the samples were stored into 120 ml acid washed HDPE container filled up and closed without air bubbles. All samples were preserved in a cold and dark place until filtration. Temperature (T), electrical conductivity (EC) and pH were determined in the field in aliquots. Soil horizons in contact with the lysimeters were also collected for arsenic contents determination.

3.2. Analytical methods and data treatment

In the laboratory, triplicates of each water sample were centrifuged (12,500 *g* for 30 min) and filtered through a 0.22-μm membrane (Milipore Millex-GV) before analyses. During centrifugation and filtration very low amount of suspended material was obtained and therefore this fraction was not analyzed. Sediment and soil samples were dried at room temperature and ground (<100 mesh) with a ball mill (Minutem MLW KM1).

3.2.1. Total arsenic

Due to the extension of the study period (2010 to 2018) determination of total As concentration (AsTot) was performed in different laboratories and with different analytical methods. Samples collected from 2010 to 2013 were analyzed by an inductively-coupled plasma mass spectrometer (7500ce ICP-MS, Agilent Technology, USA) at the Géosciences Environnement Toulouse laboratory (France). AsTot was determined together with other trace element concentrations. Indium (In) and Rhenium (Re) were used as internal standards to correct instrumental drift. Accuracy (% of certified concentration) and precision (relative standard deviation of three replicates) were assessed by analyzing the certified reference material (CRM) NRC-NRCC SLRS-4 (Trace elements in natural river water) and reached 104% and 4%. For samples collected from 2015 to 2016, AsTot was determined by ICP-MS (ELAN, Perkin Elmer®) at the Institute of Chemistry from the University of Campinas (UNICAMP, Brazil). Accuracy and precision assessed by analyzing the CRM NIST 1640a *(Trace elements in water)* reached 91% and 1.6%, respectively. AsTot in water samples from 2017 to 2018 were also measured at UNICAMP but by hydride generation atomic fluorescence spectrometer (HG-AFS) (Millennium Excalibur 10.055, PS Analytical). Accuracy (105%) and precision (4.5%) were also assessed by analyzing the CRM NIST 1640a. In all cases, limits of detection (LOD) and quantification (LOQ) were calculated as $LOD = 3\sigma/S$ and $LOQ = 10\sigma/S$ where σ is the standard deviation of blank replicates and S is the angular coefficient of the calibration curve. LOD and LOQ were generally lower than 0.05 and 0.15 $\mu g\ L^{-1}$, respectively. All the samples were analyzed in triplicate and relative standard deviation was typically lower than 5%.

Two decomposition methods were used to determine AsTot in soil and sediment samples. Both methods used microwave radiation to enhance decomposition but different volumes of acids/oxidants and different CRM for methods validation. For 2016 sediment samples, 250 mg of sediment sample were decomposed with 10 mL sub-distilled HNO_3, then analyses were performed by ICP-MS as described for 2015–2016 water samples. LOD and LOQ were 0.02 and 0.08 $\mu g\ L^{-1}$, respectively. Accuracy (96%) and precision (4.3%) were checked by analyzing certified marine sediment NRCC PACS-2. For soil and sediment collected in 2017 and 2018, 200–250 mg of sample was decomposed with 4 mL HNO_3, 2 mL HF, 1 mL HCl and 0.5 mL H_2O_2. Boric acid was added post decomposition to avoid HF excess. Analyses were performed by Hydride Generation Atomic Fluorescence Spectrometer (HG-AFS) (PSAnalytical 10.055 Millenium Excalibur System). LOD and LOQ were always below 0.04 and 0.14 $\mu g\ L^{-1}$, respectively. Accuracy (96% and 103%) and precision (6% and 2%) were checked by analyzing CRM NIST 2702 (Inorganics in Marine Sediment) and CRM BCR 320 (River Sediment), respectively.

3.2.2. As speciation analyses

For water samples collected from 2015 to 2016 (Centenário farm) Speciation analysis was performed by High Performance Liquid Chromatographer (HPLC) coupled to the ICP-MS (ELAN, Perkin Elmer®). Five arsenic species were determined: AsB (Arsenobetaine), MMA (Monomethylarsenate), DMA (Dimethylarsenate) and the ions As (III) (Arsenite, $NaAsO_2$) and As (V) (Arsenate, Na_3AsO_4). Separation was carried out with an anion exchange column (Hamilton PRP-X100 (10 μm, 250 mm × 4.1 mm). The chromatographic method was adapted from Watts et al. (2008), with 4 and 60 $mmol\ L^{-1}$ NH_4NO_3 solutions as mobile phases in a concentration gradient pumping program. The pH of both solutions was adjusted at 8.7, the chromatographic run was 12.5 min, with an injection volume of 150 μL. Daily calibration curves were drawn in the 5–40 $\mu g\ L^{-1}$ linear range for all five species. All standards and reagents used (Merck and Sigma-Aldrich) have high purity for trace metal analyses. LOD and LOQ ($\mu g\ L^{-1}$) were 2.7 and 8.9 for AsB, 4.4 and 14.6 for As(III), 2.4 and 8.1 for DMA, 2.6 and 8.7 for MMA, and 2.8 and 9.0 for As(V).

For samples collected in 2018 on the SR farm, speciation analysis was also performed through HPLC-HG-AFS (Millennium Excalibur 10.055, PS Analytical). The separation of only four As species, As(III), DMA, MMA and As(V) was carried out with an anion exchange column (Hamilton PRP-X100 (10 μm, 250 mm × 4.1 mm). A chromatographic method was adapted from PSAnalytical Application Note APP 160, using Na_2HPO_4 and NaH_2PO_4 20 $mmol\ L^{-1}$ (Sigma-Aldrich reagents with purity ≥99%) as a mobile phase at pH 6.2 in isocratic mode. The chromatographic run was 13 min with an injection volume of 200 μL. LOD and LOQ ($\mu g\ L^{-1}$) for each species were 0.46 and 1.38 for As(III), 0.31and 0.93 for DMA, 1.31 and 3.92 for MMA, and 1.12 and 3.35 for As(V). Some As organic species do not produce a hydride. Therefore, for each sample, a qualitative analysis was performed to confirm the absence of these species. The method was adapted from Ma et al. (2014), including a UV digestion step. The chromatographic separation used the same anion exchange column and a mobile phases, (A): 4 $mmol\ L^{-1}$ $NaHCO_3$ and (B): 4/40 $mmol\ L^{-1}$ $NaHCO_3/NaNO_3$ solutions at pH 9.5. The chromatographic run time was 15 min with the following gradient elution program: 100% A, 3 min; 50% A and 50% B 4 min; 100% B 5 min and 100% A 3 min.

3.2.3. Other chemical analyses

Alkalinity was determined by acid 10^{-1} or 10^{-2} mol L^{-1} HCl titration, other major elements (anions and cations) by ion chromatography, and DOC by combustion (TOC Analyser, Shimadzu).

3.2.4. As relative mobility

The abundance of arsenic in rivers depends both on its abundance in the continental upper crust and its mobility during weathering and transport. The As mobility in the UPRB in relation to Na was estimated using the dissolved As/Na ratio normalized to the As/Na ratio in the upper crust as reference (Li, 2000).

$$E_{As/Na} = (As/Na)_{sample}/(As/Na_j)_{reference} \qquad (1)$$

The results were compared to relative As chemical mobility during weathering and transport processes from the world compilation presented by Gaillardet et al. (2014).

3.2.5. Statistical analysis

For samples collected at Centenário site (70 samples), a covariance analysis (ANCOVA) was conducted in order to test the effect of several parameters, and the location in the soil cover, on dissolved arsenic. The analysis was performed using Xlstat software (AddInSoft) with a 95% reliability threshold. In a first step, the analysis was carried out using quantitative variables representing the evapo-concentration process (sodium and alkalinity (Furian et al., 2013)) and the effect of organic matter (DOC). In a second step, qualitative variables reflecting 4 different origins of the collected sample were added, either from surface (S) waters (lakes and vazantes), or from the lysimeters installed in the soil cover in the organic horizons (Org), in the deep and more clay horizons (Cly) or in the sandy horizons of the higher grounds (Hig) (Fig. 2).

4. Results

4.1. As concentration in the rivers from the UPRB

Descriptive statistics of water samples collected in the highlands (datasets 1, 2 and 3) are shown in Fig. 3 and Supplementary Material S1, in which the sampling points were classified according to the lithology. The lithology does not necessarily refer to the type of rock present at the sampling point, but to the type of rock that has a dominant influence on the river geochemistry (Rezende Filho et al., 2015). The total dissolved arsenic ranged from 0.05 to 1.69 μg L^{-1}, i.e. in a ratio of 34.

On the plateau, the contents were relatively similar for each river during the 3 field campaigns, which suggests good stability of dissolved As values during the rainy season (Fig. 3a and b), and probably throughout the year. It appears that dissolved As mainly depends on the lithology (Fig. 3c). The rivers draining sandstone areas showed the lowest values, generally close to 0.26 μg L^{-1} (ranging from 0.05 to 0.54 μg L^{-1}), except for "Rio do Peixe" with a value close to 1 μg L^{-1} throughout the 3 campaigns (1.15, 0.86 and 1.13 μg L^{-1}, respectively). These contents increased slightly (~0.36 μg L^{-1}) for rivers draining basaltic formations in their upstream part, as it is the case for example for the rivers Taquarussu, Aquidauana, Cachoeirão (Fig. 1). The streams flowing on the calcareous rocks of the Bodoquena region (e.g. rivers Salobra, Betione, Chapena) have higher values, generally ranging between 0.32 and 0.86 μg L^{-1}, with an average concentration of 0.48 μg L^{-1}, whereas in the 5 rivers draining crystalline rocks, the values were between 0.26 and 0.69 μg L^{-1}, with an average concentration of 0.50 μg L^{-1}. The few rivers collected before and after their entry into the Pantanal systematically showed an increase in the order of 20% to 60% of dissolved As values in the floodplain (not shown). When these rivers separate into several channels in the alluvial plain (Negro and Taboco rivers, for example), we observed that the secondary channels, with much lower discharge, showed As contents approximately 20 to 30% higher than the main stream (not shown). Finally, among all the rivers collected in datasets 1, 2 and 3, the Nabileque River, the only one with headwaters in the alluvial plain and not in the surrounding uplands, showed the highest As contents (1.01, 1.69 and 1.37 μg L^{-1} during the 3 campaigns, respectively, Fig. 3c).

Regarding the Cuiaba and Paraguay rivers (dataset 4), which are the two main draining rivers of the floodplain, there was a trend of increasing As levels towards downstream (Fig. 4). Arsenic values in the Cuiaba River (Fig. 4a) gradually increased from 0.25 μg L^{-1} just downstream the city of Cuiaba to 0.65 μg L^{-1} at its confluence with the Paraguay River. The first increase to a value of about 0.35 μg L^{-1} occurred after the mixing with the waters of "Baia do Agapito" (1.02 μg L^{-1}) and the confluence with River Urutubinha (0.37 to 0.49 μg L^{-1}). The second increase (0.40 μg L^{-1}) occurred after the contribution of the Muquem River (0.64 μg L^{-1}). The confluence with São Lourenço River (0.73 and 1.04 μg L^{-1}) and its secondary channels (0.93 to 1.8 μg L^{-1}) caused an increase in As content up to 0.52 μg L^{-1}, then a final contribution of the Piquiri River (0.76 μg L^{-1}) stabilized the value at about 0.65 μg L^{-1} down to the Cuiaba-Paraguay confluence. Throughout the upper stretch of the Paraguay (from Caceres to "Baia do Tamengo" close to the city of Corumba) (Fig. 4b), As water contents were rather stable ranging from 0.21 to 0.32 μg L^{-1}. This stability can be attributed to two characteristics: on the one hand the high Paraguay River flow compared to that of its tributaries (from field estimate, no quantitative data are available), and on the other hand the moderate As levels in the tributaries that ranged from 0.17 to 0.56 μg L^{-1} (0.35 ± 0.12 μg L^{-1}), with the only exceptions of two tributaries ("Boca inferior da Baia Branca" and "Boca do Tuiuiu") in which the As concentrations were 0.70 and 0.80 μg L^{-1}, respectively. Downriver from Corumba city, As concentration in the Paraguay water kept increasing gradually, first up to 0.43 μg L^{-1} after the confluence with Taquari (0.48 to 0.58 μg L^{-1}) and Negro Rivers (0.91 μg L^{-1}), then 0.50, 0.60, and 0.65

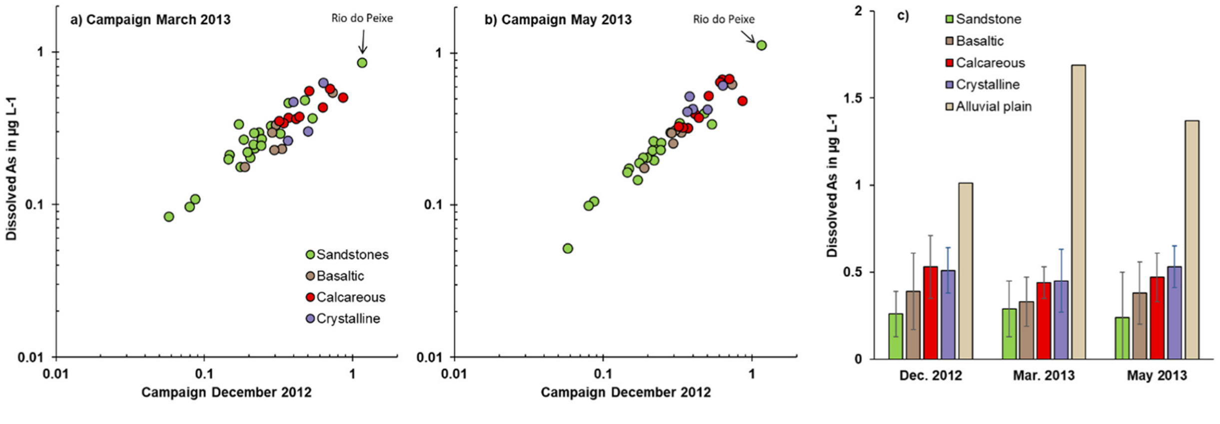


Fig. 3. Total dissolved As contents (a and b), mean value and standard deviation (c) in rivers on the highlands and alluvial plain (Nabileque River) during 3 campaigns in 2012–2013.

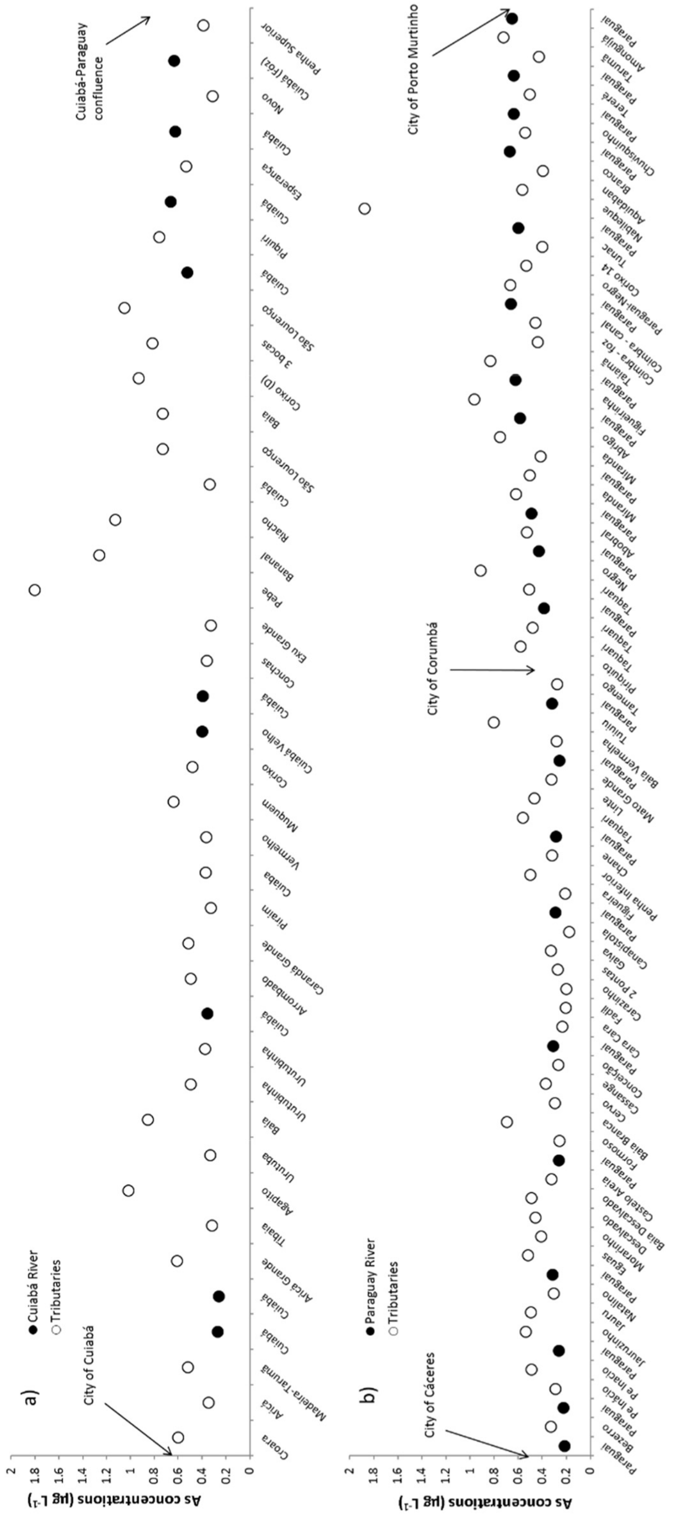


Fig. 4. Upstream-downstream As concentration throughout the (a) Cuiaba and tributaries, and (b) Paraguay and tributaries. Note the gradual increase in As concentration throughout both, Cuiaba and Paraguay rivers.

µg L^{-1} after receiving the water from the Abobral (0.53 µg L^{-1}), Miranda (0.41 to 0.62 µg L^{-1}), and Nabileque (1.88 µg L^{-1}) Rivers, respectively.

The histogram drawn in Fig. 5 shows the distribution of the log-normal transformation for As mobility in relation to Na ($E_{As/Na}$) in the UPRB. On the highlands (Fig. 5a), Log($E_{As/Na}$) had a bimodal distribution with a first mode focused on 0.2 ($E_{As/Na}$~2) and most of these samples matched with rivers flowing from crystalline bedrock in the southern part of the basin (e.g. rivers Naitaca, Terere, Branco) where dissolved Na is higher than in the rest of the sampling (Rezende Filho et al., 2012). The second mode focused on the value 1.1 ($E_{As/Na}$~13) and corresponded to the rivers coming from the sandstone formations mainly on the eastern part of the basin. For these rivers with very low mineral charge, both the dissolved As and Na contents are close to the limit of detection, which confers a high uncertainty on the calculation of $E_{As/Na}$ value. A bimodal distribution was also observed for the samples collected in the floodplain (Fig. 5b, dataset 4) with a strong mode centered on 0.6 ($E_{As/Na}$~4), which corresponds to the general trend in As mobility, and a second one of 1.2 ($E_{As/Na}$~20), which corresponded to some rivers at effluence of the wetland (São Lourenço and Piquiri Rivers and secondary channels) just before their confluence with the Cuiaba River.

4.2. Arsenic concentrations in the Nhecolândia region

4.2.1. Concentration ranges in waters

Arsenic concentration in vazante at the end of the dry period and in a freshwater lake at the end of the wet season were 3.47 and <0.04 µg L^{-1}, respectively (Table 1).

Table 1**:** As concentrations in sediment (µg g^{-1}) and water (µg L^{-1}) of green, black and crystalline alkaline lakes and freshwater environments at Centenario (CN) and São Roque (SR) farms, compared with values from Nhumirim (NH) farm (Barbiero et al., 2007).

By contrast, dissolved arsenic contents in alkaline lakes were much higher, ranging from 28.8 to 2916 µg L^{-1} (Table 1), and fluctuate depending of the season and year of collection. This effect is particularly clear when comparing the concentrations in samples collected from the same lakes at the CN site in October 2017 (atypical dry season with very low water level and high concentrations) and in August 2018 (atypical dry season with high water level and low concentrations). The lowest concentrations were always found in the crystalline water lakes (CN03 and SR07), whereas the highest ones were observed in the green and black water lakes. The As concentrations reported for the two lakes of the Nhumirím Farm, collected during a particularly dry episode, were of the same order of magnitude (Table 1). In water-table, samples collected from lysimeters at the CN site, arsenic concentrations ranged from 0.8 to 3581.5 µg L^{-1} (Table 2). Low values were observed in deep samples collected on higher grounds (G03, G05 and G12), whereas the highest concentrations were found in samples collected within organic horizons (G01S, G02S and G13) around the alkaline lakes. In comparison, dissolved As in groundwater around the lakes on the Nhumirím farm (collected from piezometers) ranged from 0.14 to 266 µg L^{-1}.

Table 2**:** As concentrations (µg L^{-1}) in shallow water-table samples collected from lysimeters at Centenário farm around the three alkaline lakes (type of environment G, B and C) and As contents in the soil horizon (µg g^{-1}) at the contact with the lysimeter.

4.2.2. As and major elements

The concentration diagrams based on Na contents (São Roque, Centenário and Nhumirím farms) are presented in Fig. 6. A similar increase in alkalinity was observed for the three sites, and the values were in agreement with the Alk-Na relationship established by Furian et al. (2013) from a regional sampling (147 samples). Although the plots were scattered, dissolved arsenic concentrations increased in proportion to Na at the Nhumirím and São Roque sites. At the Centenário site, a similar trend was observed for surface waters (S), deep waters of the higher grounds (Hig), and waters collected in the clay (Cly) horizons. Nevertheless, samples taken from organic horizons (Org) slightly departed from this trend, showing values about 5 to 10 times higher compared to Na.

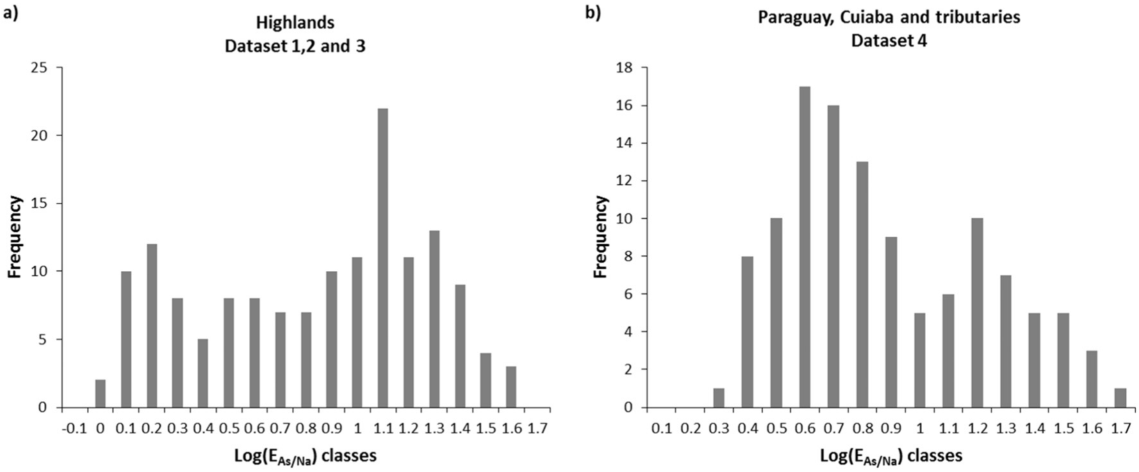


Fig. 5. Frequency distribution of log($E_{As/Na}$) a) on the highlands and b) in the floodplain of the UPRB.

Table 1
Total Arsenic concentrations in sediment (μg g^{-1}) and water (μg L^{-1}) of green, black, and crystalline alkaline lakes and freshwater environments at Centenario (CN) and São Roque (SR) farms, compared with values from Nhumirim (NH) farm (Barbiero et al., 2007).

Lake type	Sample code	09/2015	11/2015	09/2016		09/2017	10/2017		08/2018	09/2018	Barbiero et al., 2007
		Water	Water	Water	Sediment[a]	Water	Water	Sediment[b]	Water	Water	
Green	CN01	174.12	473.40	215.66	10.2 ± 4.7		923.65	–	67.83	–	–
	SR01	–	–	–	–	765.93	2916.24	14.2 ± 2.0	–	67.71	
	SR04	–	–	–	–	474.30	929.88	3.8 ± 0.8	–	102.86	–
	SR05	–	–	–	–	224.40	821.49	5.1 ± 0.6	–	25.66	–
	SR08	–	–	–	–	–	1721.69	5.7 ± 0.8	–	35.31	–
	SR09	–	–	–	–	–	1209.67	5.3 ± 1.1	–	–	–
	NH1	–	–	–	–	–	–	–	–	–	619
	NH2	–	–	–	–	–	–	–	–	–	3680
Black	CN02	129.28	214.40	157.30	1.7 ± 1.8	–	575.33	–	56.74	–	–
	SR06	–	–	–	–	383.15	1323.54	11.4 ± 1.3	–	39.47	–
Crystalline	CN03	28.83	36.27	37.00	17.0 ± 4.4	42.25	134.16	–	31.11	–	–
	SR07	–	–	–	–	–	53.17	18.2 ± 1.8	–	9.24	–
Freshwater	CN	–	3.47[c]	–	–	–	–	–	<0.04[d]	–	–
Freshwater	BSR03	–	–	–	–	0.90	–	0.16 ± 0.01	–	–	–
	BSR04	–	–	–	–	0.44	–	0.38 ± 0.04	–	<0.04	–
	BSR05	–	–	–	–	0.56	–	–	–	–	–

a: mean ± standard deviation of two sampling points; b: mean ± standard deviation of three sampling points; c: vazante; d: freshwater lake.

The results of the ANCOVA are presented in Table 3. The results show a clear relationship between total dissolved arsenic and alkalinity, sodium and DOC (Step 1). By including the origin of the water samples according to the pedological system (step 2), it appears that the parameters DOC and the origin of an organic horizon (Org) have significant influence on the total As contents.

4.2.3. Arsenic speciation in alkaline lakes and perched shallow water-table around the alkaline lakes

The samples collected from the lysimeters and surface waters on the CN site are plotted in the Pourbaix diagram in Fig. 7, showing that for the main part of the samples, As(V) may be expected. Only a few samples from deep down and more clayey horizons could show a predominance

Table 2
As concentrations (μg L^{-1}) in perched water-table samples collected from lysimeters at Centenário farm around the three alkaline lakes (type of environment G, B and C) and As contents in the soil horizon (μg g^{-1}) at the contact with the lysimeter.

Type of environment	Lysim.	Horizon	09/2015	11/2015	06/2016	09/2016	10/2017	08/2018	Soil
Green (G)	G08	Cly	–	69.3	35.9	22.6	–	19.6	1.3
	G09	Cly	–	231.1	201.0	210.8	–	137.6	–
	G10	Cly	–	–	259.4	152.0	310.8	70.5	4.1
	G11	Cly	348.1	502.2	313.4	377.5	307.1	208.2	7.4
	G12	Hig	–	–	4.0	1.7	–	0.8	1.1
	G13	Org	2505.1	1138.5	590.5	2265.7	–	2255.1	–
Black (B)	G04	Cly	–	815.6	545.5	494.5	–	313.3	2.9
	G05	Hig	–	11.9	5.7	2.8	–	3.4	0.4
	G06	Cly	–	52.8	25.2	48.2	28.5	23.7	1.2
	G07	Cly	–	271.1	61.0	92.2	76.7	42.7	2.7
Crystalline (C)	G01	Cly	29.6	58.8	29.8	27.7	79.4	84.9	4.7
	G01S	Org	1144.1	1444.4	680.7	951.1	1060.0	–	1.0
	G02	Cly	157.5	104.6	110.3	111.4	–	231	1.3
	G02S	Org	2083.1	3581.5	917.5	670.0	–	1746.9	0.9
	G03	Hig	–	4.8	2.1	2.4	–	1.5	0.6

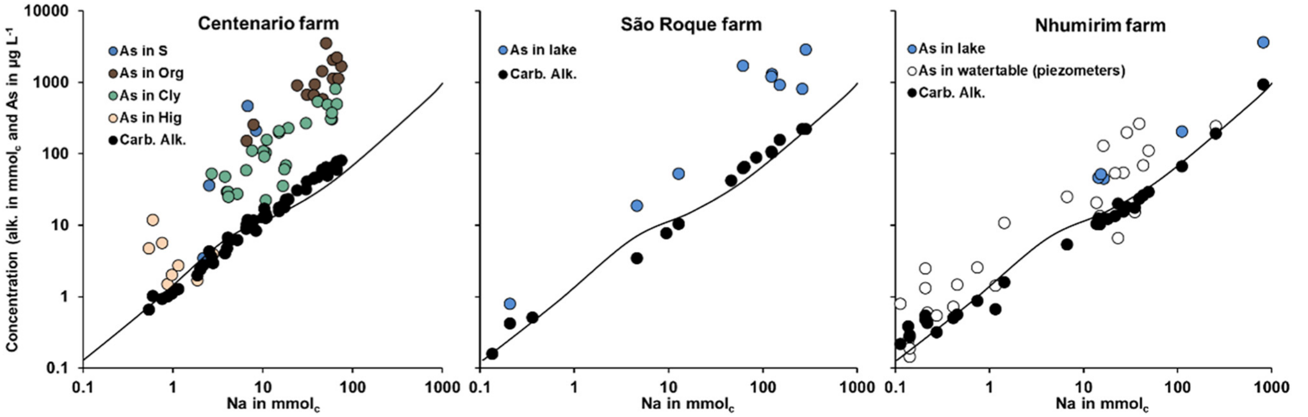


Fig. 6. Arsenic and carbonate alkalinity in concentration diagrams based on Na contents (Centenário, São Roque and Nhumirím farms). The solid line denotes the regional Alk-Na relationship established by Furian et al. (2013) from 147 samples of surface water.

of As(III). Analytical results from water sampled at CN (Fig. 8) and SR sites (not shown) confirmed that As(V) was the main species detected in the waters from both shallow perched water-table and alkaline lakes, accounting for >95% of the total As concentration. Although MMA and DMA appeared in some chromatograms, their concentrations were below the limit of quantification, with the exception of SR04 and SR08 samples collected in September 2018, for which DMA concentrations were 1.43 and 1.47 µg L^{-1}, respectively. As(III) was not detected.

4.2.4. As in lake sediments and soil horizons

Arsenic contents in soil horizons at the contact with the lysimeters were low, ranging from values below the limit of quantitation (0.23 µg g^{-1}) up to 7.4 µg g^{-1} (Mean = 2.2 µg g^{-1} and SD = 1.65 µg g^{-1}). Values were slightly higher in lake sediments, ranging from 1.7 to 8.2 µg g^{-1}. The highest values were observed in sediments from crystalline water alkaline lakes (CN01 and SR07) (Table 1).

5. Discussion

The uplands and floodplain data indicate standard levels (0.1–1.7 µg L^{-1}) of dissolved arsenic in UPRB rivers, i.e. in the range of non-As-contaminated rivers. The waters draining the uplands show a dissolved As variability depending on the type of rock that controls the chemistry of the major ions on each watershed (Rezende Filho et al., 2015, 2012). These variations are in agreement with the As contents in rocks, reported in the literature, with the following order: Sandstone (0.5–1 mg kg^{-1}) < basalts and granites (~0.7 mg kg^{-1}) < limestone (1.0–1.5 mg kg^{-1}) (Matschullat, 2000). It confirms that dissolved As in rivers supplying the floodplain is mainly controlled by the lithology of the uplands. Although a slightly higher arsenic relative mobility was observed with respect to Na in UPRB (~5) (Fig. 5) than the world average (close to 2, Gaillardet et al., 2014), these data clearly show that the waters that supply the floodplain are not contaminated with As. A gradual upstream-downstream increase in dissolved As concentrations was observed in the Cuiaba and Paraguay waters suggesting that arsenic concentrations may be explained by the simple hydrological mixing with the tributaries that usually have higher As concentration and lower flow than the main rivers (Fig. 4b). This is the opposite of what was reported for trace-elements in other hydro-systems such as in the Mississippi basin (Shiller, 1997; Shim et al., 2016) or Amazon basin (Seyler and Boaventura, 2003) where a decrease of trace-element concentration downstream was observed and attributed to a dilution effect from the upstream source. Notwithstanding this trend of a slight increase in dissolved arsenic, the values recorded in dataset 4 indicate a lack of high dissolved arsenic transfer from the floodplain to the Cuiaba and Paraguay rivers. Some rivers at the exit of the wetland have arsenic levels significantly ($p < 0.05$) higher than the dataset mean value, as well as higher mobilities ($E_{As/Na}$ ~ 20). This is particularly the case of

Table 3
Results of the ANCOVA carried out with quantitative (step 1) and taking into account the origin of the samples (step 2).

Standardized coefficients (Astot):								
Step 1					Step 2			
Source	Value	Stand. error	t	Pr > |t|	Value	Stand. error	t	Pr > |t|
Alk	1.497	0.571	2.622	**0.011**	0.276	0.739	0.373	0.710
Na	−1.672	0.428	−3.906	**0.000**	−0.774	0.547	−1.417	0.162
CE	0.573	0.496	1.156	0.252	0.783	0.525	1.492	0.141
DOC	0.384	0.132	2.903	**0.005**	0.306	0.138	2.213	**0.031**
Hor. Cly					0.001	0.087	0.011	0.991
Hor. Hig					−0.009	0.116	−0.079	0.937
Hor. Org					−0.011	0.079	−0.139	0.890
S					0.314	0.141	2.230	**0.029**

Most significative probability are in bold.

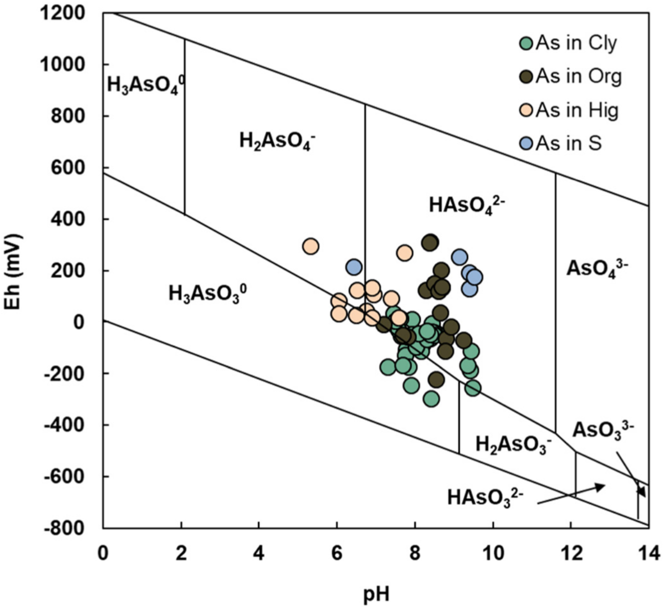


Fig. 7. Arsenic Pourbaix diagram showing the As speciation expected for the watertable samples collected in surface water (S) and soil horizons (Hig, Cly or Org) at Centenário farm (see Table 1 for the corresponding total As concentrations). Both, pH and Eh were measured in the field, under N_2 flux.

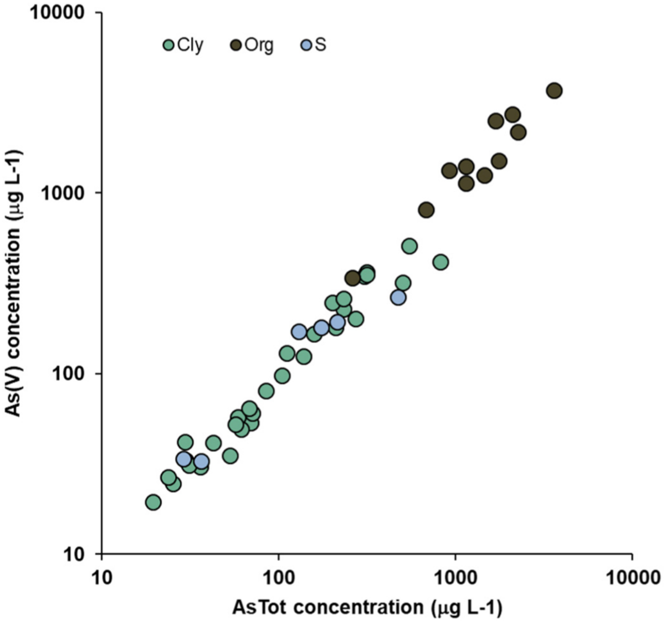


Fig. 8. Concentration of As(V) vs Total As in water samples from Centenário farm: S (surface water), Cly (water from clay horizons), Org (water from organic horizons). In water samples from the higher grounds (Hig), As(V) contents were below the limit of quantification.

the São Lourenço and Piquiri rivers and their secondary channels just upstream of their confluence with the Cuiabá River. A previous study conducted on the same dataset showed that the major ion chemistry of these rivers is impacted by extensive agricultural activities on the uplands (Rezende Filho et al., 2015), particularly by an increase in sulfate and ammonium contents together with a slight increase in alkalinity. Such alteration of the chemical profile was detected at the entry of these rivers in the Pantanal. It has been attributed to the fertilization practices together with field liming on the uplands, and it is detectable until the confluence with the river Cuiabá. Therefore, slightly higher dissolved As levels at the confluence of these rivers with the Cuiaba may also be a consequence of these activities. Unfortunately, we do not have the dissolved As content of these waters as they enter the floodplain, which does not allow further discussion. The highest As concentrations (1.36 ± 0.34 µg L^{-1}) were found in the Nabileque river, the only one that has its source in the alluvial plain. In this environment, during the high water levels, anaerobic conditions favor the reductive dissolution of wetland-soil Fe-oxihydroxides and associated elements, such as arsenic and organic matter (Guénet et al., 2017). Such a process could be responsible for the slightly higher As concentration observed in the Nabileque river.

On the other hand, the results are much more contrasting in the Nhecolândia floodplain. At all three studied sites, elevated As levels are noted, indicating that its occurrence is a consequence of processes that operate on a regional scale. In addition, the similar behavior of arsenic with respect to sodium confirms that the same processes are at work in these three sites. Huge As variations are observed over short distances, i.e. a few hundred meters that separate the vazantes and freshwater lakes from the alkaline lakes, as well as the few tens of meters that separate the higher grounds at the top of the beaches from the border of the alkaline lakes. The results of the speciation carried out at Centenário site show that As mainly occurs as arsenate (Fig. 8). The As contents variability must be related to the hydrological and hydrochemical functioning of this system of lakes. The vazantes are the water supplying areas (Furian et al., 2013). In the short term, they mainly receive water from the seasonal rains, but over the long term, they are also supplied by the overflows of the Taquari River. Therefore, this river arising from sandstone area imposes its chemical characteristics, in particular the low arsenic contents (Table 1) and a positive calcite residual alkalinity ($RA_{calcite}$) (Oliveira Junior et al., 2019; Rezende Filho et al., 2012). During the wet season, while freshwater lakes are generally supplied by overflow during the flood pulse, alkaline saline lakes receive a reduced amount of freshwater through subsurface flows from the vazantes. During the dry season, waters concentrate under the effect of evaporation, not only in the alkaline lakes but also in the perched water-table and of surrounding beaches. In the geochemical context of positive $RA_{calcite}$ (Barbiero et al., 2002), alkalinity increases with increasing evapo-concentration while calcium levels remain very low due to calcite precipitation. The solution pH increases, mainly controlled by carbonate species. Close to alkaline lakeshores, the solutions are more concentrated due to higher evaporation by wicking in the sandy material (Barbiero et al., 2016). Magnesium silicates precipitate (in horizon 1, see Fig. 2), controlling dissolved Mg at a low level, while alkalinity keep increasing (Furquim et al., 2008). Finally, the mineralization of dissolved organic matter a few tens of meters from the lake shore releases iron and aluminum allowing the synthesis of Fe-micas (in horizons 4 and 5, Barbiero et al., 2016; Furquim et al., 2010). This succession of saline precipitations (calcite, Mg-silicate, Fe-micas) is standard in alkaline environments (Barbiero et al., 2004).

Dissolved As is usually controlled by adsorption processes that can take place in three main different adsorbents, namely metallic (Al, Fe and Mn) oxides and hydroxides, clay minerals and organic matter. However, in this alkaline geochemical framework, three factors favor the maintenance of arsenic in solution. First, from the beginning of the evapo-concentration, arsenic concentrates together with other dissolved species such as carbonates and secondarily fluorides (Barbiero et al., 2008), and to a lesser extent chlorides and sulfates. Competitive adsorption between As and those ions prevents As fixation onto any adsorbent (Goldberg, 2002). Second, increasing dissolved As contents occur simultaneously with increasing pH (Fig. 9) and therefore a decrease in its adsorption affinities. Indeed, arsenate adsorption on oxides and clays is highest at low pH and strongly decreases with increasing pH, namely, above pH 9 for Al oxide, pH 7 for Fe oxide or hydroxide, illite and kaolinite (Cornu et al., 1999; Goldberg, 2002).

Third, high Fe and Al concentrations (Barbiero et al., 2016) likely favor the formation of ternary complexes As-Fe/Al-humic acids. As can be seen in Table 2, the solutions sampled in organic horizons (G01S, G02S, G13) have the highest As concentrations, suggesting that some of the As does not migrate in free dissolved form, but likely complexes with aquatic humic substances (AHS). AHS represent one of the main

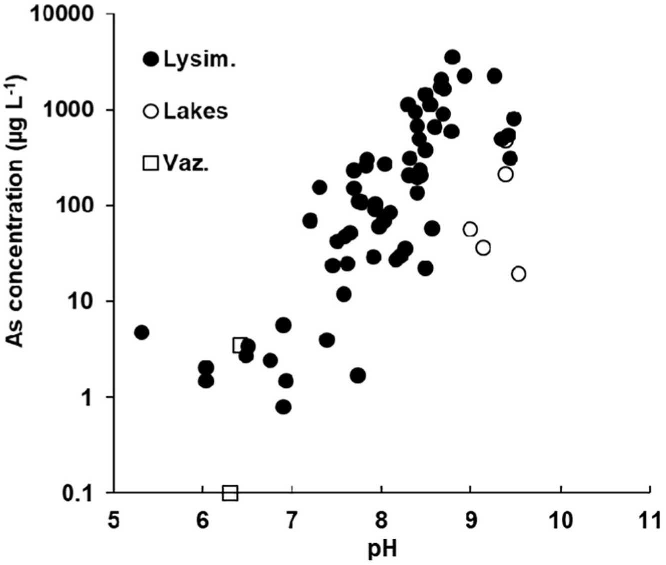


Fig. 9. Dissolved As concentration vs pH in lysimeters, lakes and vazante at Centenário farm.

parts of the organic matter (Mariot et al., 2007) and act as complexing agents increasing As mobility (Sharma et al., 2011; Warwick et al., 2005). As(V) is present in anionic forms ($H_2AsO_4^-$ and $HAsO_4^{2-}$, Fig. 7), which results in repulsion forces between As and negatively charged AHS at high pH. However, the presence of dissolved Fe and Al, as mentioned in Barbiero et al. (2016), leads to the formation of ternary complexes (As-Fe/Al-AHS) (Oliveira et al., 2016). This behavior could be at the origin of the results of the ANCOVA, emphasizing that the evaporation, but also the DOC content and the origin of the samples coming from the organic horizons have a significant influence on dissolved As (Table 3) (Ghosh et al., 2015; Mariot et al., 2007). In summary, the solid phase does not act as a factor controlling dissolved As, which appears to be mainly regulated by the evapo-concentration process. Such a behavior of As in alkaline and/or evaporative environment have already been mentioned by Bhattacharya et al. (2006) and Welch and Lico (1998). Changes in the concentration of As first results from its conservative behavior during seasonal evaporation and dilution as shown by the increase in proportion to Na (slope close to 1, Fig. 6). For water samples arising from organic horizons and with high DOC contents, an additional fraction of arsenic is maintained in the solution likely through the formation of ternary As-metals-AHS complexes. Then dissolved As increase in a factor of 5 to 10 compared to sodium. This behavior of arsenic in this alkaline environment is also demonstrated by the low levels of arsenic measured in soils. Despite high levels of As in the solutions, soils in contact, including organic horizons, have low As levels (Table 2), in the range of non-As-contaminated soils (Matschullat, 2000). The same is observed for lake sediments. By way of comparison with the work of Caumette et al. (2011), although dissolved As contents in Canadian lakes were much lower (250 ± 100 $\mu g\ L^{-1}$) than in alkaline lakes of Nhecolândia (up to 3 $mg\ L^{-1}$), these authors reported As values in sediments ranging from 34 $\mu g\ g^{-1}$ in an uncontaminated freshwater lake to 698 $\mu g\ g^{-1}$ in a highly contaminated lake. Nevertheless, in these lakes, the pH ranging from 7.6 to 7.9 is more favorable to As adsorption on particulate matter, as mentioned above. The values reported in Table 1 for alkaline lakes in the Pantanal are much lower, in the range of uncontaminated soils and sediments. These low As concentrations in soils and sediments confirm that an alkaline environment favors the maintenance of arsenic in solution and that the solid phase acts as a non-reactive matrix. Arsenic accumulates in alkaline lake waters and surrounding water-table from year to year as do sodium ions (Fig. 6).

6. Conclusion

The behavior of arsenic in alkaline environments is little documented and still poorly understood. A previous study reported high levels of dissolved arsenic in the waters of the Pantanal, the largest wetland on the planet, and more specifically in the vast sub region "Nhecolândia". On the one hand, our data collected at the level of the UPRB show that the rivers that supply the alluvial plain of the Pantanal have low As contents. All concentrations are below 2 $\mu g\ L^{-1}$, that is to say in the range for non arsenic-contaminated river waters. The relative mobility of arsenic in relation to sodium is slightly higher than the global average, but remains moderate. In addition to the absence of noticeable As source on the plateaus upstream of the alluvial plain, the data show a lack of significant As release from the alluvial plain towards the main draining rivers, namely the Cuiaba and Paraguay rivers. On the other hand, the study confirms the high dissolved As levels in the alkaline waters of Nhecolândia. The relations between As and the major ions are similar in the 3 sites studied, which confirms that As responds to the same control processes throughout the region. The chemical speciation indicates that it mainly occurs in the form of As(V). In surface water, the proportions are substantially the same in the 3 sites and increase with the sodium amount, itself resulting from long-term cumulative evaporation over many years. In the soil solution, the As levels in the surface aquifer depend on the type of saturated soil horizon, the organic horizons having As/Na ratio 5 to 10 times higher, compared to the trend in the rest of the samples. Future studies should therefore focus on details of arsenic dynamics within the alkaline lake and associated soil system.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.06.147.

Acknowledgments

This research was supported by grants from the Consulate of France in São Paulo, and São Paulo and Campinas Universities and the Sao Paulo Research Foundation (FAPESP) (n°2017/23301-7) to L. Barbiero, by the National Center for Scientific and Technological Development (CNPq) to A.T. Rezende-Filho (n°248550/2012-8) and A. Hechavarría Hernández (n°142323/2017-9), by the South Mato Grosso Foundation for the Development of Education, Science and Technology (FUNDECT) to R. B. de Almeida, by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brazil (CAPES - Finance Code 001) to L. Richter.

This research was funded by FAPESP (n°2011/12770-0, n°2013/09192-0, n°2016/14227-5), the Brazilian Research National Center (CNPq, n°405898/2012-6) and French National Institute of Science of the Universe (INSU-CNRS, Ec2co).

References

Andreote, A.P.D., Vaz, M.G.M.V., Genuário, D.B., Barbiero, L., Rezende-Filho, A.T., Fiore, M.F., 2014. Nonheterocytous cyanobacteria from Brazilian saline-alkaline lakes. J. Phycol. 50, 675–684. https://doi.org/10.1111/jpy.12192.

Andreote, A.P.D., Dini-Andreote, F., Rigonato, J., Machineski, G.S., Souza, B.C.E., Barbiero, L., Rezende-Filho, A.T., Fiore, M.F., 2018. Contrasting the genetic patterns of microbial communities in Soda Lakes with and without cyanobacterial bloom. Front. Microbiol. 9, 244. https://doi.org/10.3389/fmicb.2018.00244.

Armienta, M.A., Segovia, N., 2008. Arsenic and fluoride in the groundwater of Mexico. Environ. Geochem. Health 30, 345–353. https://doi.org/10.1007/s10653-008-9167-8.

Arriaza, B., Amarasiriwardena, D., Cornejo, L., Standen, V., Byrne, S., Bartkus, L., Bandak, B., 2010. Exploring chronic arsenic poisoning in pre-Columbian Chilean mummies. J. Archaeol. Sci. 37, 1274–1278. https://doi.org/10.1016/j.jas.2009.12.030.

Assine, M.L., Merino, E.R., Pupim, F.N., Macedo, H.A., Santos, M.G., 2015. The quaternary alluvial systems tract of the Pantanal Basin, Brazil. Brazilian J. Geol. 45, 475–489. https://doi.org/10.1590/2317-4889201520150014.

Barbiero, L., Queiroz Neto, J.P., Ciornei, G., Sakamoto, A.Y., Capellari, B., Fernandes, E., Valles, V., 2002. Geochemistry of water and ground water in the Nhecolandia, Pantanal of Mato Grosso, Brazil: variability and associated processes. Wetlands 22, 528–540. https://doi.org/10.1672/0277-5212(2002)022[0528:gowagw]2.0.co;2.

Barbiero, L., Valles, V., Cheverry, C., 2004. Reply to J.W. van Hoorn "Some observations with respect to sodicity hazard of irrigation waters". Agric. Water Manag. 68, 177–184. https://doi.org/10.1016/j.agwat.2004.03.011.

Barbiero, L., Furquím, S.C., Valles, V., Furian, S., Sakamoto, A., Filho, A.R., Fort, M., 2007. Natural arsenic in groundwater and alkaline lakes at the upper Paraguay basin, Pantanal, Brazil. Trace Met. other Contam. Environ. 9, 101–126. https://doi.org/10.1016/S1875-1121(06)09004-3.

Barbiero, L., Rezende Filho, A.T., Furquim, S.A.C., Furian, S., Sakamoto, A.Y., Valles, V., Graham, R.C., Fort, M., Ferreira, R.P.D., Neto, J.P.Q., 2008. Soil morphological control on saline and freshwater lake hydrogeochemistry in the Pantanal of Nhecolândia, Brazil. Geoderma 148, 91–106. https://doi.org/10.1016/j.geoderma.2008.09.010.

Barbiero, L., Berger, G., Rezende Filho, A.T., Meunier, J., Martins-silva, E.R., Furian, S., 2016. Organic control of dioctahedral and trioctahedral clay formation in an alkaline soil system in the Pantanal wetland of Nhecolândia, Brazil. PLoS One, 1–23 https://doi.org/10.1371/journal.pone.0159972.

Barbiero, L., Siqueira Neto, M., Braz, R.R., Carmo, J.B. do, Rezende Filho, A.T., Mazzi, E., Fernandes, F.A., Damatto, S.R., Camargo, P.B. de, 2018. Biogeochemical diversity, O2-supersaturation and hot moments of GHG emissions from shallow alkaline lakes in the Pantanal of Nhecolândia, Brazil. Sci. Total Environ. 619–620, 1420–1430. https://doi.org/10.1016/j.scitotenv.2017.11.197.

Bergier, I., 2013. Effects of highland land-use over lowlands of the Brazilian Pantanal. Sci. Total Environ. 463–464, 1060–1066. https://doi.org/10.1016/j.scitotenv.2013.06.036.

Bhattacharya, P., Claesson, M., Bundschuh, J., Sracek, O., Fagerberg, J., Jacks, G., Martin, R.A., Storniolo, A.D.R., Thir, J.M., 2006. Distribution and mobility of arsenic in the Río Dulce alluvial aquifers in Santiago del Estero Province, Argentina. Sci. Total Environ. 358, 97–120. https://doi.org/10.1016/j.scitotenv.2005.04.048.

Brazil, 2011. Portária No 2914/2011 [WWW Document]. URL. http://bvsms.saude.gov.br/bvs/saudelegis/gm/2011/prt2914_12_12_2011.html.

Buehler, H.A., Weissmann, G.S., Scuderi, L.A., Hartley, A.J., 2011. Spatial and temporal evolution of an avulsion on the Taquari River distributive fluvial system from satellite image analysis. J. Sediment. Res. 81, 630–640.

Bundschuh, J., Farias, B., Martin, R., Storniolo, A., Bhattacharya, P., Cortes, J., Bonorino, G., Albouy, R., 2004. Groundwater arsenic in the Chaco-Pampean plain, Argentina: case study from Robles county, Santiago del Estero Province. Appl. Geochem. 19, 231–243. https://doi.org/10.1016/j.apgeochem.2003.09.009.

Bundschuh, J., Litter, M.I., Bhattacharya, P., 2012a. Science of the Total Environment Arsenic in Latin America, an unrevealed continent: occurrence, health effects and mitigation. Sci. Total Environ. 429, 1. https://doi.org/10.1016/j.scitotenv.2012.04.047.

Bundschuh, J., Litter, M.I., Parvez, F., Román-ross, G., Nicolli, H.B., Jean, J., Liu, C., López, D., Armienta, M.A., Guilherme, L.R.G., Gomez, A., Cornejo, L., Cumbal, L., Toujaguez, R., Rica, C., 2012b. Science of the Total Environment One century of arsenic exposure in Latin America: a review of history and occurrence from 14 countries. Sci. Total Environ. 429, 2–35. https://doi.org/10.1016/j.scitotenv.2011.06.024.

Castro de Esparza, M.L., 2010. Mejoramiento de la calidad del agua de pozos en zonas rurales de Puno, Perú. In: Litter, M.I., Sancha, A.M., Ingallinella, A.M. (Eds.), Tecnologías Económicas Para El Abatimiento de Arsénico En Aguas, pp. 243–256 Buenos Aires, Argentina.

Caumette, G., Koch, I., Estrada, E., Reimer, K.J., 2011. Arsenic speciation in plankton organisms from contaminated lakes: transformations at the base of the freshwater food chain. Environ. Sci. Technol. 45, 9917–9923. https://doi.org/10.1021/es2025092.

CCME, 2001. Canadian Water Quality Guidelines for the Protection of Aquatic Life.

CONAMA, 2011. Resolução 357/2005. [WWW Document]. URL. http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=459.

Cornu, S., Saada, A., Breeze, D., Gauthier, S., Baranger, P., 1999. Influence de composés organiques sur l'adsorption de l'arsenic par les kaolinites. C. R. Acad. Sci. Paris 328, 649–654.

EPA, 1991. Arsenic, Inorganic; CASRN 7440-38-2.

Freitas, J.G., Furquim, S.A.C., Aravena, R., Cardoso, E.L., 2019. Interaction between lakes' surface water and groundwater in the Pantanal wetland, Brazil. Environ. Earth Sci. 78, 139. https://doi.org/10.1007/s12665-019-8140-4.

Furian, S., Martins, E.R.C., Parizotto, T.M., Rezende-Filho, A.T., Victoria, R.L., Barbiero, L., 2013. Chemical diversity and spatial variability in myriad lakes in Nhecolândia in the Pantanal wetlands of Brazil. Limnol. Oceanogr. 58, 2249–2261. https://doi.org/10.4319/lo.2013.58.6.2249.

Furquim, S.A.C., Graham, R.C., Barbiero, L., de Queiroz Neto, J.P., Vallès, V., 2008. Mineralogy and genesis of smectites in an alkaline-saline environment of Pantanal wetland, Brazil. Clay Clay Miner. 56, 579–595. https://doi.org/10.1346/CCMN.2008.0560511.

Furquim, S.A.C., Barbiero, L., Graham, R.C., Neto, Queiroz, de, J.P., Ferreira, R.P.D., Furian, S., 2010. Neoformation of micas in soils surrounding an alkaline-saline lake of Pantanal wetland, Brazil. Geoderma 158, 331–342. https://doi.org/10.1016/j.geoderma.2010.05.015.

Gaillardet, J., Viers, J., Dupré, B., 2014. 7.7 - trace elements in river waters, in: Holland, H.D., Turekian, K.K.B.T.-T. on G. (Second E. (Eds.), . Elsevier, Oxford, pp. 195–235. doi:https://doi.org/10.1016/B978-0-08-095975-7.00507-6.

Ghosh, D., Routh, J., Bhadury, P., 2015. Characterization and microbial utilization of dissolved lipid organic fraction in arsenic impacted aquifers (India). J. Hydrol. 527, 221–233. https://doi.org/10.1016/j.jhydrol.2015.04.051.

Goldberg, S., 2002. Competitive adsorption of arsenate and arsenite on oxides and clay minerals. Soil Sci. Soc. Am. J. 66, 413–421.

Guénet, H., Davranche, M., Vantelon, D., Bouhnik-Le-Coz, M., Jardé, E., Dorcet, V., Demangeat, E., Jestin, J., 2017. Highlighting the wide variability in arsenic speciation in wetlands: a new insight into the control of the behavior of arsenic. Geochim. Cosmochim. Acta 203, 284–302. https://doi.org/10.1016/j.gca.2017.01.013.

Guérèquiz, R., Mañay, N., Goso-Aguilar, C., Fernández-Turiel, J.L., García-Valles, M., 2009. Environmental risk assessment of arsenic in the Raigón aquifer. Uruguay Biol. 7, C0130.

Hasegawa, H., Rahman, M.A., Kitahara, K., Itaya, Y., Maki, T., Ueda, K., 2010. Seasonal changes of arsenic speciation in lake waters in relation to eutrophication. Sci. Total Environ. 408, 1684–1690. https://doi.org/10.1016/j.scitotenv.2009.11.062.

IBGE, n.d. Censo 2010 [WWW Document].

Junk, W.J., Nunes de Cunha, C., 2005. Pantanal: a large south American wetland at a crossroads. Ecol. Eng. 24, 391–401. https://doi.org/10.1016/j.ecoleng.2004.11.012.

Li, Y.H., 2000. A Compendium of Geochemistry: From Solar Nebula to the Human Brain. Princeton University Press, Princeton and Oxford.

López, D.L., Bundschuh, J., Birkle, P., Aurora, M., Cumbal, L., Sracek, O., Cornejo, L., Ormachea, M., 2012. Science of the Total Environment Arsenic in volcanic geothermal fluids of Latin America. Sci. Total Environ. 429, 57–75. https://doi.org/10.1016/j.scitotenv.2011.08.043.

Ma, J., Sengupta, M.K., Yuan, D., Dasgupta, P.K., 2014. Speciation and detection of arsenic in aqueous samples: a review of recent progress in non-atomic spectrometric methods. Anal. Chim. Acta 831, 1–23. https://doi.org/10.1016/j.aca.2014.04.029.

Maître, V., 1991. Protocole d'extraction, de conservation et de filtration des eaux libres du sol. Sci. du sol 29, 71–76.

Mariot, M., Dudal, Y., Furian, S., Sakamoto, A., Vallès, V., Fort, M., Barbiero, L., 2007. Dissolved organic matter fluorescence as a water-flow tracer in the tropical wetland of Pantanal of Nhecolândia, Brazil. Sci. Total Environ. 388, 184–193. https://doi.org/10.1016/j.scitotenv.2007.08.003.

Martins, E.C.R., 2012. Tipologia de lagoas salinas no Pantanal da Nhecolândia (MS). University of São Paulo https://doi.org/10.11606/T.8.2012.tde-14012013-172446.

Matschullat, J., 2000. Arsenic in the geosphere — a review. Sci. Total Environ. 249, 297–312. https://doi.org/10.1016/S0048-9697(99)00524-0.

Mcclintock, T.R., Chen, Y., Bundschuh, J., Oliver, J.T., Navoni, J., Olmos, V., Villaamil, E., Ahsan, H., Parvez, F., 2012. Science of the Total Environment Arsenic exposure in Latin America: biomarkers, risk assessments and related health effects. Sci. Total Environ. 429, 76–91. https://doi.org/10.1016/j.scitotenv.2011.08.051.

Nicolli, H.B., Bundschuh, J., Blanco, C., Tujchneider, O.C., Panarello, H.O., Dapeña, C., Rusansky, J.E., 2012. Science of the Total Environment Arsenic and associated trace-elements in groundwater from the Chaco-Pampean plain, Argentina: results from 100 years of research. Sci. Total Environ. 429, 36–56. https://doi.org/10.1016/j.scitotenv.2012.04.048.

Oliveira Junior, J.C., Furquim, S.A.C., Nascimento, A.F., Beirigo, R.M., Barbiero, L., Valles, V., Couto, E.G., Vidal-Torrado, P., 2019. Salt-affected soils on elevated landforms of an alluvial megafan, northern Pantanal, Brazil. Catena 172, 819–830. https://doi.org/10.1016/j.catena.2018.09.041.

Oliveira, L.K., Melo, C. de A., Fraceto, L.F., Friese, K., Rosa, A.H., 2016. Interaction of arsenic species with tropical river aquatic humic substances enriched with aluminum and iron. Environ. Sci. Pollut. Res. 23, 6205–6216. https://doi.org/10.1007/s11356-015-5816-5.

Olson, D.M., Dinerstein, E., 2002. The global 200: priority ecoregions for global conservation. Ann. Mo. Bot. Gard. 89, 199–224. https://doi.org/10.2307/3298564.

Pédrot, M., Dia, A., Davranche, M., Martin, S., Al-Sid-Cheikh, M., Gruau, G., 2015. Unravelling the fate of arsenic during re-oxidation of reduced wetland waters: experimental constraints and environmental consequences. Compt. Rendus Geosci. 347, 304–314. https://doi.org/10.1016/j.crte.2015.03.002.

Por, F.D., 1995. The Pantanal of Mato Grosso (Brazil): Worlds Largest Wetland. Kluwer Academic Publishers, Dordrecht.

Rahman, M.A., Hasegawa, H., 2012. Arsenic in freshwater systems: influence of eutrophication on occurrence, distribution, speciation, and bioaccumulation. Appl. Geochem. 27, 304–314. https://doi.org/10.1016/j.apgeochem.2011.09.020.

Redman, A.D., Macalady, D.L., Ahmann, D., 2002. Natural organic matter affects arsenic speciation and sorption onto hematite. Environ. Sci. Technol. 36, 2889–2896.

Rezende Filho, A.T., Furian, S., Victoria, R.L., Mascré, C., Valles, V., Barbiero, L., 2012. Hydrochemical variability at the upper Paraguay basin and pantanal wetland. Hydrol. Earth Syst. Sci. 16, 2723–2737. https://doi.org/10.5194/hess-16-2723-2012.

Rezende Filho, A., Valles, V., Furian, S., Oliveira, C.M.S.C., Ouardi, J., Barbiero, L., 2015. Impacts of lithological and anthropogenic factors affecting water chemistry in the upper Paraguay River basin. J. Environ. Qual. 44, 1832–1842. https://doi.org/10.2134/jeq2015.01.0019.

Seyler, P.T., Boaventura, G.R., 2003. Distribution and partition of trace metals in the Amazon basin. Hydrol. Process. 17, 1345–1361. https://doi.org/10.1002/hyp.1288.

Sharma, V.K., Sohn, M., 2009. Aquatic arsenic: toxicity, speciation, transformations, and remediation. Environ. Int. 35, 743–759. https://doi.org/10.1016/j.envint.2009.01.005.

Sharma, P., Rolle, M., Kocar, B., Fendorf, S., Kappler, A., 2011. Influence of natural organic matter on As transport and retention. Environ. Sci. Technol. 45, 546–553. https://doi.org/10.1021/es1026008.

Shiller, A.M., 1997. Dissolved trace elements in the Mississippi River: seasonal, interannual, and decadal variability. Geochim. Cosmochim. Acta 61, 4321–4330. https://doi.org/10.1016/S0016-7037(97)00245-7.

Shim, M.J., Cai, Y., Guo, L., Shiller, A.M., 2016. Floodplain effects on the transport of dissolved and colloidal trace elements in the East Pearl River, Mississippi. Hydrol. Process. 31, 1086–1099. https://doi.org/10.1002/hyp.11093.

Vaz, M.G.M.V., Genuario, D.B., Andreote, A.P.D., Malone, C.F.S., Sant'Anna, C.L., Barbiero, L., Fiore, M.F., 2015. Pantanalinema gen. nov. and Alkalinema gen. nov.: novel pseudanabaenacean genera (cyanobacteria) isolated from saline-alkaline lakes. Int. J. Syst. Evol. Microbiol. 65, 298–308. https://doi.org/10.1099/ijs.0.070110-0.

Warwick, P., Inam, E., Evans, N., 2005. Arsenics interaction with humic acid. Environ. Chem. 2, 119–124.

Watts, M.J., Button, M., Brewer, T.S., Jenkin, G.R.T., Harrington, C.F., 2008. Quantitative arsenic speciation in two species of earthworms from a former mine site. J. Environ. Monit. 10, 753–759. https://doi.org/10.1039/B800567B.

Welch, A.H., Lico, M.S., 1998. Factors controlling As and U in shallow ground water, southern Carson Desert, Nevada. Appl. Geochem. 13, 521–539. https://doi.org/10.1016/S0883-2927(97)00083-8.

WHO, 2008. Guidelines for Drinking-Water Quality. WHO Press, Geneva.