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Spéciation des métaux traces dans un lac tropical urbain, le lac de Pampulha, Brésil

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RÉSUMÉ

Il est essentiel d'évaluer l'impact du ruissellement des bassins versants urbains sur les milieux récepteurs. Les métaux traces représentent un risque important pour l'environnement et la santé publique. La concentration totale ne reflète pas leur impact environnemental, car leur toxicité dépend de leur spéciation dans le milieu aquatique. Les métaux traces sont principalement étudiés dans les affluents ou dans le sédiment des plans d'eau. Notre objectif est d'étudier la variation saisonnière de leur concentration dans la colonne d'eau et ainsi de contribuer à l'évaluation de l'impact du ruissellement urbain. Cette étude porte sur le suivi saisonnier, durant 10 mois incluant la saison sèche et la saison des pluies, des concentrations en métaux traces dans la colonne d'eau du lac de Pampulha et leur spéciation. Les métaux ont été échantillonnés à deux profondeurs au centre du lac. Trois fractions ont été analysées : total, dissous et inerte. Six métaux ont été étudiés : cadmium, cobalt, cuivre, plomb, nickel et zinc. Les concentrations en cadmium sont sous la limite de détection. Les résultats de spéciation révèlent une biodisponibilité variable de ces métaux, la plus forte étant celle du zinc (~60%). La biodisponibilité du cobalt, fortement dissous, varie selon la profondeur. La biodisponibilité du nickel reste assez stable en surface durant la période étudiée alors que celles du cuivre, du zinc et du plomb sont beaucoup plus variables.

ABSTRACT

Assessing the impact of urban catchment runoff on receiving waters must be addressed. Trace metal contamination represents a significant risk to the environment and public health. But total concentration does not reflect trace metal environmental impact because their toxicity depends especially on the nature of present species. Most studies address the fate of trace metals in lake tributaries or in lake sediments. Our aim was to focus on the seasonal variation of trace metal concentrations in the lake water column in order to improve the assessment of urban runoff impact. This study focuses on the seasonal monitoring, for 10 months including dry and raining seasons, of trace metal concentrations and their speciation in the water column of Lake Pampulha. Trace metals were collected at two depths in the middle of Lake Pampulha. For each collected sample, metal fractions were divided into total, dissolved, and inert metal. Six anthropogenic trace metals were considered: cadmium, cobalt, copper, lead, nickel and zinc. The results showed different behaviour of trace metals in the water column. Cadmium concentration is under the quantification limit. Speciation results indicate a variable metal bioavailability. Zinc is the most bioavailable (~60%). Bioavailability of cobalt which is highly dissolved varies with depth. Nickel bioavailability remains rather constant in the surface layer during the study period and those of copper, zinc and lead are more variable.

KEYWORDS

Tropical urban lake, Trace metal, Speciation, Water column, bioavailability

1 INTRODUCTION

In urban water bodies, trace metals that accumulate in the water column, in the sediment and in the food web, can threaten public health and aquatic organisms. With an increasing development of industrial activities and rapid urbanization, trace metal pollution is a rising public concern. Trace metals enter urban water bodies via several pathways such as atmospheric deposition, industrial and domestic wastewater discharge, agricultural effluents or stormwater runoff (Thévenot *et al.,* 2009, Rule *et al*., 2006). Runoff on traffic areas is a main source of trace metal contamination (Huber *et al.*, 2016). But few studies focused on trace metals in urban lake ecosystems, and most of them regard trace metals in the sediments that are considered as their ultimate destiny. As a result, we have an incomplete image of the fate of trace metals in urban water bodies. The necessity to fill this gap is even more essential for tropical urban lakes.

In addition, total concentration of metals does not reflect their environmental impact because their toxicity depends greatly on the metal species (Akcay *et al*., 2003). Speciation refers to the distribution of different chemical forms of metals in water ecosystems, which is fundamental to estimate their impact on biota.

It is essential to assess the impact of urban catchment runoff on receiving waters. As most studies address the fate of trace metals in lake tributaries or in lake sediments, our aim was to focus on lake water column, in order to complete the description of trace metals in an urban catchment. The main objective of this study was to assess the seasonal evolution of trace metal concentrations and their bioavailability during both dry and raining seasons, in the water column of an urban tropical reservoir, Lake Pampulha, Brazil.

2 MATERIALS AND METHODS

2.1 Study area

Lake Pampulha is located in the city of Belo Horizonte, the capital of state Minas Gerais, south-east of Brazil (Figure 1). The population of Belo Horizonte metropolitan region reaches 5.8 millions inhabitants (IBGE 2014). The climate is of tropical highland type, with a yearly rainfall of 1600 mm of which 90% mainly occurs during the raining season from October and March. The reservoir has an area of approximately 1.9 km^2, a volume of about 10 million m^3. Its maximum depth is 16 m and the average depth is 5 m. The Pampulha catchment has an area of 98 km^2. Lake Pampulha is fed by 8 streams; two of them, Ressaca and Sarandi contribute to 70% of the inflow into the lake (Friese *et al.,* 2010). Lake Pampulha is an important tourist spot, the area around the lake is used for recreational and sportive activities and it contributes to reduce flood risk in the neighborhood (Silva *et al*., 2014). Lake silting and frequent episodes of phytoplankton blooms are the main environmental problems of this water body (Figueredo and Giani, 2001).

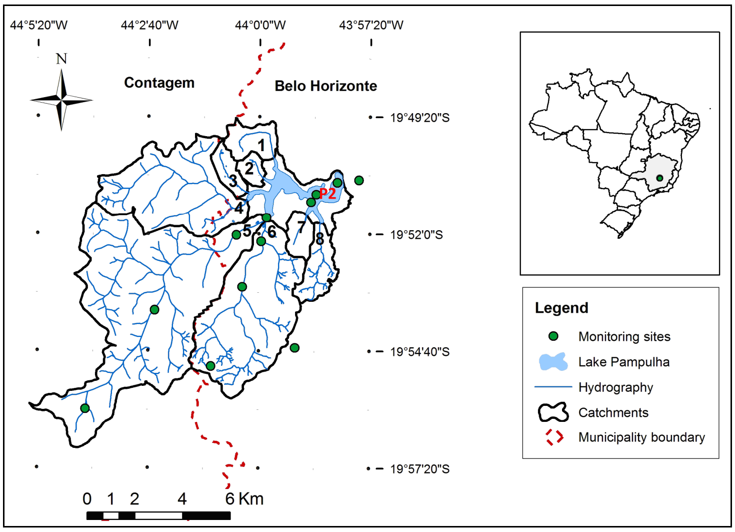

Figure 1 Location of monitoring point P2 at Lake Pampulha (Belo Horizonte, Brazil) (from Silva et al. 2015)

2.2 Lake monitoring

Monthly field campaigns (n=13) were conducted on Lake Pampulha at point P2 (Figure 1) from August 2012 to June 2013, period including the dry and the raining seasons. Water samples were collected at 0,5 m and 7,0 m depth in the water column. All the water samples were collected with low-density polyethylene material, pre-cleaned in 5% (v/v) in detergent (Extran), rinsed many times with ultrapure water and pre-cleaned again in an acid bath of 10% (v/v) nitric acid (Vetec 65% metal ultrapure) during at least 24h to avoid metal contamination.

2.3 Trace metal analysis

In this study, we use an operational definition of speciation based on the separation of the labile metal fraction by resin Chelex 100 (Davison and Zhang, 1994).This method is increasingly used for metal speciation in freshwaters (*e.g.* Chaminda *et al.,* 2008, Varrault *et al.,* 2012, Lemaire *et al*., 2014).

In the lake samples, the total metal concentration was divided into particulate and dissolved fractions, and the dissolved fraction subdivided into inert and labile fractions. Total metal corresponds to the unfiltered sample. Particulate and dissolved metal concentrations are separated using cellulose acetate membrane filter (0.45µm).

The dissolved inert fraction is obtained by passing the filtrated sample on chelating disk (EMPORE™ Chelex 100"). The chelating disks are constituted by polymers (polystyrene divinylbenzene) carrying chelating sites (imino-diacetic), which allow them to retain the labile fraction containing the free metals. The inert fraction crosses through the disk and can afterward be analyzed. Dissolved labile metals retained by the chelating disk were estimated as the difference between total dissolved and dissolved inert concentrations (Bracmort, 2010, Varrault *et al,* 2012). Dissolved labile fractions are considered as metal species that can have a high affinity for inorganic or organic complexes and therefore are potentially bioavailable (Zhang and Davison, 2000).

Trace metal concentrations were determined using inductively coupled plasma mass spectrometry (ICP-MS). Total metal concentrations were analyzed in 50 mL of unfiltered water acidified with ultrapure HNO_3 65% and HCl 30% using a graphite digestion block (DigiPrep of SCP SCIENCE) programmed to reach 95 ºC for 150 min. After digestion, samples were refilled with Milli-Q ultrapure water to 50 mL and then filtered through 0.45 µm Teflon filter. A blank with Milli-Q ultrapure water was systematically done for each mineralization cycle to estimate eventual contamination. Mineralized samples were analyzed using ICP-MS. Dissolved concentrations and dissolved inert concentrations were analyzed in 20 mL of filtered water acidified with 500 µL ultrapure HNO_3 65% (pH<2) and conserved in temperature 4ºC until being analyzed by ICP-MS.

Each sample was analyzed in triplicate. Total uncertainty, the sum of analytic uncertainty and operational uncertainty, varies from 8%-12% of mean value. The limit of quantification in ICP-MS varies from 0.01 µg/L for cadmium, cobalt, copper, nickel, lead, and 0.05 µg/L for zinc.

3 RESULTS

3.1 Trace metals in the lake water column

In most samples, Cd concentrations were under quantification limit, so they will not be presented here. The concentrations of total and dissolved metals, Co, Ni, Cu, Zn and Pb, under the surface (0.5 m) and at the bottom of the water column (7 m) are presented in Table 1.

Table 1 Mean concentration of total and dissolved metals at 0.5 and 7m depth, n = 13

Depth	*Co Total* µg/L	*Co Diss.* µg/L	*Ni Total* µg/L	*Ni Diss.* µg/L	*Cu Total* µg/L	*Cu Diss.* µg/L	*Zn Total* µg/L	*Zn Diss.* µg/L	*Pb Total* µg/L	*Pb Diss.* µg/L
Surface	0.65 ± 0.20	0.45 ± 0.12	1.58 ± 0.42	0.94 ± 0.26	2.53 ± 1.05	0.90 ± 0.38	10.48 ± 4.25	4.54 ± 1.44	0.29 ± 0.15	0.06 ± 0.04
Bottom	0.88 ± 0.32	0.64 ± 0.22	1.49 ± 0.35	0.91 ± 0.22	1.69 ± 0.61	0.54 ± 0.38	11.44 ± 6.17	4.05 ± 2.83	0.77 ± 0.78	0.14 ± 0.21

For assessing the distribution of particulate and dissolved metals, we calculated the ratio between dissolved and total fractions (Table 2). This distribution is very variable among the metals. Dissolved fraction varies between 21% for Pb and 72% for Co. Ni is also highly dissolved, around 60%. For Cu and Zn, the dissolved and particulate fractions at the surface are nearly equal, between 40 and 50%. The distribution between dissolved and particulate fractions is rather similar at surface and bottom of the water column for Co and Pb. The standard deviation of these ratios varies from 8% to 28% for the

5 trace metals. The distribution between the particulate and dissolved fractions of Ni and Co is rather constant over the study period while the distribution of Cu and Zn is much variable.

Table 2 Mean ratio of dissolved to total metals at 0.5 and 7m depth, n = 13

Mean ratio Dissolved/Total	Co (%)	Ni (%)	Cu (%)	Zn (%)	%Pb
Surface (0.5m)	69.8 ± 11.4	58.1 ± 8.0	40.7 ± 23.8	49.1 ± 22.9	22.4 ± 13.3
Bottom (7m)	72.3 ± 10.0	60.0 ± 9.6	32.4 ± 28.6	36.2 ± 18.6	21.5 ± 16.4

For estimating the fraction of metal that is potentially bioavailable, we calculated the ratios between labile and dissolved fractions of the 5 metals (Table 3). The standard deviation of these ratios varies from 7% to 34%, indicating a low to medium seasonal variability of the metal bioavailability. Bioavailability is variable between metals but also between the surface and the bottom of the water column. At the surface, it varies between 9% and 26% and at the bottom of the water column, between 7% and 34%. Cobalt is the less labile in the surface layer. The lowest ratio of Co labile fraction (16%) was measured during a period of phytoplankton bloom, when the concentration of chlorophyll a was particularly high (220 µg/L). This result suggests that biological activity in the lake can have an impact on the bioavailability of Cobalt but additional data are required to confirm this hypothesis.

Table 3 Mean ratio of labile to dissolved metals at 0.5m and 7m depth

Mean ratio Labile/Dissolved	Co (%)	Ni (%)	Cu (%)	Zn (%)	Pb (%)
Surface (0.5m)	30.9 ± 15.4	51.8 ± 8.7	37.9 ± 19.4	61.2 ± 15.4	39.3 ± 25.6
Bottom (7m)	71.6 ± 6.9	53.0 ± 20.7	36.3 ± 28.0	68.1 ± 22.9	55.9 ± 34.1

3.2 Comparison with water standards

Water standards regarding trace metals in freshwaters in Brazil (resolution CONAMA 357, 17/03/2005) and in Europe (Water Framework Directive 2008/105/CE, EU WFD) are presented respectively in Table 4 and
Table *5.* There are two main differences between CONAMA resolution and the European Union Water Framework Directive. Firstly, CONAMA states a classification framework to water bodies according to their intentional use. The decision on which water quality class is assigned to a particular water body is influenced by a participatory process organized by the concerned river basin committee where stakeholders (representatives of water users, the civil society and the government) have seat. Water Framework Directive aims at the good chemical and ecological status at Community level and national level depending on each substance. Secondly, CONAMA resolution sets the thresholds based on metal total fraction (in mg/L), except for Cu, while in the WFD the limits for good chemical status are based on the metal dissolved fraction (in µg/L). WFD also considers a maximum acceptable concentration (MAC) and an annual average (AA). Depending on the legislative context, trace metal concentrations in Lake Pampulha could exceed the limit of these water standards. Considering the CONAMA resolution, high cyanobacteria biomass and low dissolved oxygen concentration in Lake Pampulha would lead to classifying it in class 3 for freshwaters, meaning that this water can be used for drinking water after advanced water treatment, for irrigation of trees, but not of greenery; no primary neither secondary contact with water is allowed in this class. According to CONAMA resolution, all trace metal values measured in Lake Pampulha are also under the limits for class 3 water-bodies. Considering European WFD, only dissolved copper exceeded the maximum acceptable value in one sample among the 26 collected samples and no dissolved metal exceeded the annual average concentration.

Table 4 Maximum concentrations according to CONAMA resolution 357 for freshwater class 3

	Co total	Cu dissolved	Cd total	Ni total	Pb total	Zn total
Maximum concentration (mg/L)	0.2	0.013	0.01	0.025	0.033	5

Table 5 Water standards for surface water in Europe (MAC:Maximum concentration, AA :Annual average)

	Co dissolved	Cu dissolved	Cd dissolved	Ni dissolved	Pb dissolved	Zn dissolved
MAC (µg/L)	-	1.4	1.5	34	14	-
AA (µg/L)	-	1.4	0.25	4	1.2	7.8

4 CONCLUSIONS

In this study we assessed the seasonal evolution of trace metal concentrations in the water column of an urban tropical lake, Lake Pampulha, Brazil. The 10-month study period included the dry and the raining seasons. Field measurements of three forms of metals were performed: total, dissolved and inert concentrations. As this speciation gives information on potential bioavailability of metals in the water column, an estimate of their potential toxicity is provided. Nickel bioavailability at surface remains rather constant during the study period and those of copper, zinc and lead are more variable. Comparison with Brazilian and European water quality standards indicates that, during our study period, the central area of Lake Pampulha, where the samples were collected, cannot be considered as contaminated by trace metals.

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