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The Effects of Sediment Classification Pattern on a Water Column Organism, *Ceriodaphnia dubia*

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Abstract

The sediment compartment stands out because it functions as both a temporary sink of pollutants and a potential source of these elements that may become available to the water column.This study aimed to correlate the concentrations of total metals in the crude sediment and in the interstitial water with the ecotoxicity in the water column using an a modified sediment ecotoxicity test with *Ceriodaphnia dubia*. The results indicate that the sediment may contribute to the toxicity in the water column and that such toxicity is possibly not related to the metals present. Based on the chemical analysis of the metals, the Canadian Sediment Quality Guidelines (SQGs) would frame the sediment as non-toxic to benthic organisms, but the SQGs have no reference standards for possible effects on nektonic organisms. Due to the complexity of this compartment, it is fundamental to evaluate the interactions of the different pollutants in the system and possible effects on the nektonic organisms.

Anthropogenic activities generate pollutants, including metals, which can compromise water quality. Contaminants in water bodies can remain in the water column or they can precipitate, becoming part of the sediment, and they can affect the biota in both compartments (Fetters et al. 2016). Sediments are typically complex matrixes composed of organic and inorganic fractions and interstitial water, defined as water occupying the spaces between sediment or soil particles (Alahverdi and Savabieasfahani 2012; US EPA 2000). Changes in pH and the process of mobilization of the sediments, either by natural or anthropic causes, can release these contaminants into the water column, especially those weakly bound to the sediment particles, resulting in peaks of toxicity. As contaminants can persist for long periods in sediments, determining sediment quality patterns for multiple water uses and for aquatic biota protection are of scientific and public interest.

There are three different and non-mutually exclusive ways to assess sediment quality: (i) by the detection and quantification of certain chemical components previously shown to cause toxicity (CCME 1995), hereafter called chemical methods, (ii) by ecotoxicological assays involving the exposure of model organisms, with or without chemical analyses, hereafter called ecotoxicological methods and (iii) bioassays with spiked sediment (formulated or natural) conducted to understand the dynamics of toxicity in association with chemical knowledge (CCME 1995).

The Canadian Sediment Quality Guidelines (SQGs), for instance, have been broadly used; they are based on the bioavailability of metals determined through equilibrium partitioning theory, and they indicate circumstances in which toxicity is unlikely, uncertain or likely to occur. Furthermore, they highlight certain concentrations of individual chemical contaminants, such as the SQGs model TEL (threshold effect level) and PEL (probable effect level). The TEL is the concentration below which adverse biological effects are expected to rarely occur, while the concentration above which adverse effects are expected to occur frequently is defined as the PEL (CCME 2001a). Recent studies demonstrate that both methodologies are valid and present similar results (Nasr et al. 2014; He et al. 2015; McQueen et al. 2016; Zhuang et al. 2016). Although these guidelines also emphasize the importance of evaluating pollutants other than metals, certain organic pollutants, for instance, are usually taken into account only when indirect evidence has previously indicated their potential presence in a target aquatic

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system, i.e., certain pesticides in water bodies located near agricultural areas (CCME 1995).

However, determining the proper body of analyses in situations in which multiple metal contaminants can be present is difficult. Another problem is that protocols based only on the quantification of certain contaminants do not take into account the toxicity resulting from the potential interaction between the toxic components. When sources of pollution are diverse and unpredictable, ecotoxicological analyses can be a potential solution for determining water and sediment quality, but comparative analyses between the metal-based SQGs (CCME 2001a) and ecotoxicological methods are scarce (Anderson et al. 2001; Souza et al. 2016). Here, we analysed the sediments of a subtropical lentic water system and demonstrate that sediment and interstitial water samples classified as non-toxic based on the metal parameters of the SQGs (CCME 2001b) have caused acute and chronic toxicity in *Ceriodaphnia dubia* in the water column. Toxicity analyses of sediments often use organisms that are representative of this component, e.g., *Hyalella* sp., *Chironomus* sp., *Lytechinus* sp. and *Echinometra* sp.

Considering the above, the Itupararanga reservoir was chosen due to the intense agricultural activity that impacts its surroundings, and in which it was investigated the following: 1 – The relationship between the physical and chemical conditions of sediments in the reservoir (with an emphasis on the analysis of metals in the raw sediments and their interstitial waters) with the water ecotoxicity by means of tests with *Ceriodaphnia dubia*, and 2 – Whether the metal values described in the Canadian Sediment Quality Guidelines to classify the toxicity of the sediments can also be used to obtain an ecotoxicological classification for nektonic organisms, considering that these compartments (sediment–water) exhibit dynamic interactions.

Materials and Methods

The Itupararanga reservoir is located at the head of the Sorocaba river, in the southeastern region of Brazil. This reservoir receives water from the Sorocabaçu and Sorocamirim rivers, which come together to form the Sorocaba river (Smith and Petrere, Jr. 2008), located between the parallels 23°34′49″ and 23°40′12″S and meridians 47°13′11″ and 47°24′34″W. Although it is located within an Area of Environmental Preservation, the main types of land use and occupation are characterized by intense agricultural activity, with 393 km^2 occupied by vegetable crops such as cabbage, lettuce, potatoes and tomatoes, and 35 km^2 is occupied by farms, which are also used for agriculture and leisure (Sardinha et al. 2010; Conceição et al. 2011). Six collection points were defined along the dam in order to characterize the Itupararanga system horizontally. The collections

occurred in September (2013) and in March (2014). These points are susceptible to point and diffuse pollution of agricultural origin, which may lead to nutrients entering the bodies of water, as shown in Fig. 1.

The sediment samples for the physical and chemical analyses were obtained with a Petersen-type dredger, with three replicates per point, which were immediately homogenized and conditioned in plastic containers with a capacity of 1 L. A portion of the samples remained in the refrigerator, and the other samples remained at room temperature for drying and subsequent analyses.

Physical and chemical analyzes of sediment samples as organic matter by incineration were performed according to Trindade (1980); granulometry, screening and desimeter, second ISO 13320 (2009), total phosphorus through spectrophotometry according to EPA 6010C (2007) and total organic nitrogen by KJEDHAL (APHA 2005).

For the quantification of extractable metal in crude sediments, 0.1 mol L^{-1} hydrochloric acid extraction was used (a smooth extraction and without heating), adapted Luoma and Bryan (1981) with the purpose of evaluating the biological availability of metals in the sediments. This methodological procedure consisted of weighing 1 g of dry sediment, transferring it to an Erlenmeyer flask and adding 25 mL of 0.1 mol L^{-1} hydrochloric acid. This mixture was transferred to a shaker table at 200 rpm for 2 h. Subsequently, the suspension was filtered through a 0.45 μm cellulose nitrate membrane and diluted in a 100 mL volumetric flask.
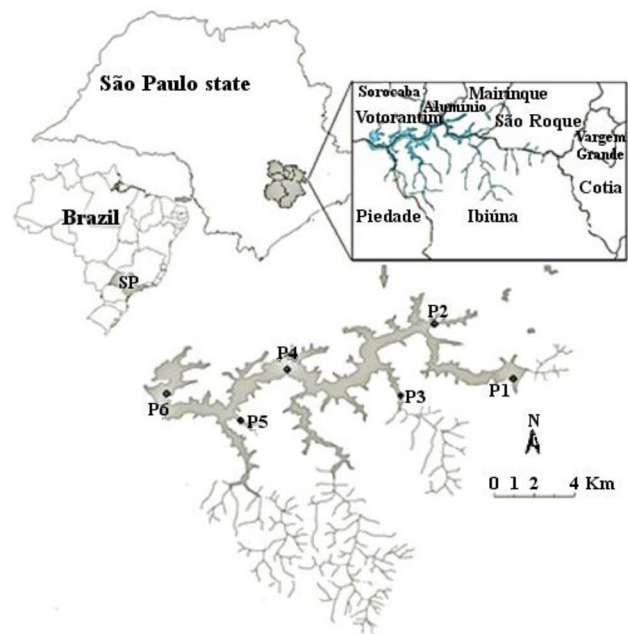

Fig. 1 Localization of Itupararanga reservoir (São Paulo state – Brazil), and sampling points (P1, P2, P3, P4, P5 and P6). Reproduced with permission from Lira et al. (2017)

Readings were performed by atomic emission spectroscopy using inductively coupled plasma optical emission spectrometry (ICP-OES 720 series), and the results were expressed as mg kg^{-1} of dry sediment. For the total interstitial metals, the sediment samples were centrifuged at 2500 rpm to a volume of 100 mL. Subsequently, they were preserved with concentrated nitric acid and submitted to a digestion process. The determination of metals was conducted using a methodology adapted from US EPA method 3005A (1992), which describes the digestion of water samples and quantification using optical emission spectroscopy. Thus, 100 mL of the filtered contents from each of the sampled points was maintained at temperatures of up to 100°C on a heating plate, and 15 mL of concentrated nitric acid was added. After reduction of the digested contents, each sample was voluted in a 25 mL flask and subsequently submitted to the determination of metal concentrations by atomic emission spectroscopy using inductively coupled plasma optical emission spectrometry (ICP-OES 720 series).

Tests of the toxicity of the sediment samples were performed with the test organism *Ceriodaphnia dubia*, which is representative of the water column, by adapting a methodology from the US EPA (2000) for *H. azteca*, exposing it to 5 g of sediment in 30 mL of reconstituted water for 8 days both being renewed every 48 h, following the recommendations of US EPA Method 1002 (2002). The formulated sediment was used as a control, a mixture of clay and different granulometries of sand (US EPA 2000). Test organisms with 6- to 24-h lifecycles (neonates) were used at the beginning of the experiment, and individuals were 8 days old at the end, as adults. The end points analysed were survival and reproduction (number of neonates). The data were analysed statistically by means of the assessment of the significance of the mortality using Fisher's exact test, and reproduction in the toxicity tests was analysed using the Kruskal–Wallis test conducted in the BioEstat 5.0 software (Ayres et al. 2007). A principal component analysis (PCA) was carried out to explain the variation in the chemical and physical variables among sampling sites using the PAST software 2.17 (Hammer et al. 2001). Correlations between metals (in crude sediments and interstitial) and survival and reproduction parameters of *C. dubia* were analysed using multiple linear regressions in the software BioStat 5.0 (Ayres et al. 2007).

Results and Discussion

Concentrations of metals in crude sediments (CMs) were found in the following descending order: Mn > Zn > Cu > Pb > Co > Cr > Ni > As > Cd. The potentially toxic metals Cu and Pb were the metals that stood out. Interstitial metals (IMs) were found in the following decreasing order: Mn > Pb > Cr > Cu > Zn > As > Ni > Co > Cd. The concentrations of IMs are usually low (Leonard et al. 1996; Kay et al. 2008; De Jonge et al. 2009), as seen in Table 1.

In both years, the concentrations of CMs were below the level at which adverse effects to the biota are likely (PEL) (Table 1), but the use of only this empirical model of the SQGs may not reflect the true potential of sediment toxicity (He et al. 2015). Since the IMs Cu and Ni were above the LC50 (48-h) values for *C. dubia* at almost all points, considering a pH range of 7–8.5 (Table 2). Similarly Cr (P3, P4 and P5) and Zn (P1, P3, P5) to a pH of 7.8–8.5. Among the potentially toxic IMs, chromium was the most abundant, followed by Cu, Ni and Co (Table 1). The environmental agency responsible for monitoring the reservoir also reported the constant presence of Cr in the sediment and acute toxicity to *Vibrio fischeri* bacteria in interstitial water extracted from the samples obtained in the years of 2013 and 2014 (Cetesb 2015). Evidence indicates that these pollutants in both the sediment and interstitial water can cause toxicity to the biota.

When assessing the behaviour of trace metals and the potential role of sediment resuspensions in the contamination of the water column, Superville et al. (2015) realized that during spring and summer, when bacterial activity is more important, the daily reduction of Fe(III) in the surface sediments promotes the weaker adsorption of Pb and Zn, and the concentrations are higher as a consequence. Which would justify the greater amounts of these metals in the study in question, considering that the same results occurred during those seasons.

In 2013 complete mortality was observed in P2 and P3, but in the remaining samples there were no significant effects on survival or reproduction (Fig. 2). There was no significant mortality in 2014, only point P2 had significantly reduced reproduction, as shown in Fig. 2. It should be noted that the results of mortality in points P2 and P3 in 2013, were probably due to the pH, since the average pH in the toxicity tests were 5.74 ± 0.21 and 5.31 ± 0.19, respectively. These are also the points at which the highest concentrations of potentially toxic CMs, Cu, Co, Cr and As at point P2 and Cu, Pb and Co at point P3, were also detected. Schubauer-Berigan et al. (1993) when testing the acute toxicity of metals to *C. dubia* at three pH values (6.3, 7.3, and 8.3) noted that toxicity of Cd, Ni, and Zn was greatest at pH 8.3 and least at pH 6.3 and conversely, the toxicity of Cu and Pb was greatest at pH 6.3 and least at pH 8.3.

The same point P2 (2014) also differed significantly in comparison to points P4 and P6; the pH at P2 was 7.16 ± 1.43. Points P1, P2 and P5 were points where the reproduction of *C. dubia* was lower in relation to the control and the OM levels were also higher. Although P4 contains practically all metals in quantities that are much higher than those of the other points, with emphasis on Cr, Cu and Ni at concentrations higher than LC50 (48-h) for *C. dubia*, there

Table 1 Results of the analysis of metals in the crude sediment and interstitial water of the samples collected in the Itupararanga reservoir

	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Crude sediment (mg kg⁻¹)									
2013									
P1	<LQ	<LQ	0.17	0.07	0.31	9.03	0.05	<LQ	0.26
P2	0.19	<LQ	0.65	0.35	1.56	65.46	0.30	<LQ	12.07
P3	<LQ	<LQ	0.35	0.21	1.50	11.75	0.17	0.89	1.38
P4	<LQ	<LQ	0.14	0.05	0.39	63.82	0.07	<LQ	4.36
P5	<LQ	<LQ	<LQ	0.18	0.84	149.80	0.04	<LQ	<LQ
P6	<LQ	<LQ	0.09	0.12	0.57	69.75	<LQ	<LQ	<LQ
2014									
P1	<LQ	0.11	2.20	2.27	6.67	156.81	0.84	5.07	16.84
P2	0.48	<LQ	1.99	1.27	5.76	131.34	0.80	4.20	5.36
P3	<LQ	0.14	4.77	1.35	9.43	<LQ	1.19	11.11	15.98
P4	0.06	0.14	1.80	0.53	2.67	171.25	<LQ	5.01	3.47
P5	0.41	<LQ	1.11	1.58	13.05	<LQ	<LQ	4.27	7.27
P6	<LQ	<LQ	1.04	0.58	3.21	<LQ	<LQ	3.56	2.54
TEL	5.90	0.60	–	43.40	31.60	–	22.70	35.80	121.00
PEL	17.0	4.90	–	111.00	149.00	–	48.60	128.00	459.00
Interstitial water (µg L⁻¹)									
2013									
P1	<LQ	<LQ	6.5	25.3	3.0	321.3	8.7	<LQ	<LQ
P2	<LQ	<LQ	5.4	13.9	5.8	1125.5	3.7	<LQ	<LQ
P3	<LQ	<LQ	8.9	36.1	17.9	368.5	16.7	<LQ	<LQ
P4	<LQ	<LQ	6.2	31.0	55.9	4955.3	18.9	17.3	<LQ
P5	28.5	<LQ	11.8	116.5	68.5	6641.2	28.2	<LQ	<LQ
P6	<LQ	<LQ	6.6	62.3	17.5	7808.5	15.1	<LQ	<LQ
2014									
P1	<LQ	<LQ	<LQ	89.5	50	367.9	<LQ	<LQ	129.7
P2	<LQ	3.4	<LQ	43.1	30.7	606.4	<LQ	<LQ	24.5
P3	24.5	9.8	20.7	151.3	67.7	302.7	<LQ	475.7	164.2
P4	116.9	8.7	103.1	303.4	281.5	3254.9	109.4	112.4	<LQ
P5	<LQ	<LQ	<LQ	80.0	59.8	632.3	<LQ	<LQ	116.6
P6	37.2	<LQ	33.2	196.7	95.1	3748.6	51.9	<LQ	<LQ
LQ	22.50	3.26	14.98	2.54	3.32	0.26	41.60	89.66	5.71

LQ: limit of quantification; <LQ: below the limit of quantification; –: no limit established

was no toxicity. It should be emphasized the acute toxicity of metals in hard water to *C. dubia* can be greatly affected by sample pH, with toxicity displaying large variations with a change of 1 pH unit (Schubauer-Berigan et al. 1993), as shown in Table 2. It should be noted that metal concentrations were not measured in the overlying water which has not allowed to make direct comparisons between water column concentrations and test organism tolerance values.

The highest percentage of organic matter (OM) occurred in the second season, especially at points 2 and 5, which had 37.1% and 32.7% OM, respectively (Table 3). With the exception of point 4, the Itupararanga sediment was organic, with OM values higher than 10%. This characteristic had already been observed by Beghelli et al. (2012) and Tani-waki et al. (2013) in other studies carried out in this system.

At the point P3 in both years, there were the highest concentrations of N. In 2014 the P1 point showed high concentrations of N and P, these concentrations may be a consequence of the intense agricultural activity practiced in the region (Sardinha et al. 2010; Conceição et al. 2011). In the first sampling period, 50% of the points had higher clay content than the other inorganic fractions. In the second sampling period, more than 80% had higher clay content, with 56.2% clay at point 3 and 55.7% at point 2; the data are presented in Fig. 3. In both sampling periods, the beginning of the system (P1) presented the lowest clay proportions, which can be explained by the greater water turbulence and drag fractions with finer granulation.

The second sampling point, more upstream of the reservoir, presented higher organic matter loading in both

Table 2 Mean lethal concentrations (LC50) of metals for *Ceriodaphnia dubia* in 48 h exposure and respective ph values reported in the literature

	LC50 (µg L^{-1})	pH	References
As	1448	7.8–8.3	Spehar and Fiandt (1986)
Cd	560	6–6.5	Schubauer-Berigan et al. (1993)
	350	7–7.5	
	120	8–8.5	
Co	#	#	#
Cr	144	7.8–8.3	Spehar and Fiandt (1986)
Cu	9.5	6–6.5	Schubauer-Berigan et al. (1993)
	28	7–7.5	
	200	8–8.5	
Mn	14,500	8–8.2	Lasier et al. (2000)
	9100	7–7.6	Boucher and Watzin (1999)
Ni	200	6–6.5	Schubauer-Berigan et al. (1993)
	>140	7–7.5	
	13	8–8.5	
Pb	280	6–6.5	Schubauer-Berigan et al. (1993)
	>2700	7–7.5	
	>2700	8–8.5	
Zn	>530	6–6.5	Schubauer-Berigan et al. (1993)
	360	7–7.5	
	95	8–8.5	

[#]No values reported in the literature

collection periods and higher toxicity in relation to the other points showing acute and chronic toxicity. The sediments of the reservoir have characteristics (clayed and organic) that facilitate the adsorption and accumulation of contaminants and nutrients. The results of the toxicity tests show that the reproduction of the organisms tends to be reduced in the samples obtained at the beginning of the system (Fig. 2). The direct influence of the forming rivers that flow into the dam can justify this fact, as well as the large amount of P found at P1 in the year 2014.

At sampling sites very similar to those in this study, Taniwaki et al. (2013) performed genotoxicity analyses in 2010 and showed that there was an increase in the index of chromosomal alterations when compared to the negative controlin all seasons, with the point in the center of the system (P4) presenting the highest index. A study by Beghelli et al. (2016) that evaluated the community of benthic macroinvertebrates identified species that were bioindicators of organic enrichment and tolerant to pollution.

The PCA was performed with the following variables: IMs, CMs, OM, pH and inorganic fraction. The IMs and CMs were expected to be directly correlated in the principal component analysis (PCA), but this situation was not so clear. In 2013, Axis 1 highlighted the roles of the CMs As, Cd, Co, Cr, Cu and Ni in addition to the percentages of silt and OM, while the IMs As, Co, Cr, Cu, Mn, Ni and Pb were highlighted on axis 2 (Fig. 4). There were correlation of the Mn and Cu IMs with clay and the Co, Cr and Cu CMs with OM that can be justified by the formation of aggregates and complexes. In 2014, there were greater contributions of the

Fig. 2 Results of chronic toxicity tests obtained on the basis of reproductive parameter, presentation of average of neonates per individual
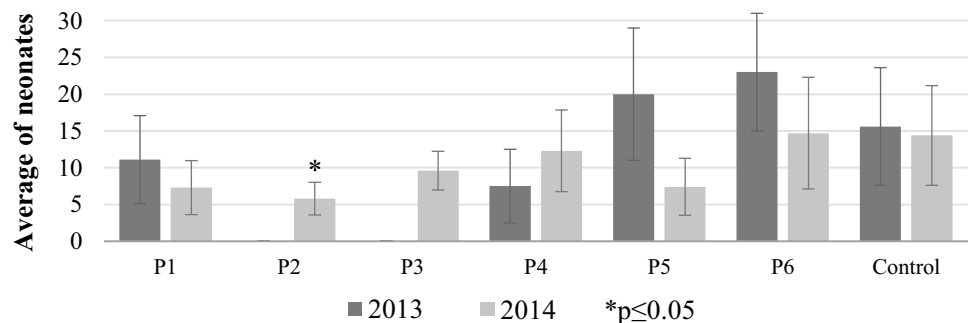
Table 3 Concentrations of organic matter (OM), Nitrogen (N), Phosphorus (P) and pH of crude sediment found in the Itupararanga Reservoir in the samplings held in September (2013) and in March (2014)

	OM (%)		N (mg Kg^{-1})		P (mg Kg^{-1})		pH (crude sediment)	
	2013	2014	2013	2014	2013	2014	2013	2014
P1	20.72±0.02	30.60±3.45	1.95	31.90	2.31	145.12	6.93	7.05
P2	29.91±0.11	37.11±1.12	11.01	5.10	3.64	2.32	6.55	6.26
P3	23.9±0.05	24.90±0.98	26.72	36.91	4.12	14.70	6.49	6.51
P4	8.20±0.13	9.23±0.02	5.20	17.10	1.74	3.45	7.36	6.43
P5	26.01±1.10	32.70±1.47	5.71	6.20	1.27	0.98	6.79	6.75
P6	14.20±0.09	14.10±0.07	2.40	5.12	1.25	1.46	6.68	6.90

Fig. 3 Results of inorganic fractions in sediment samples, obtained in 2013 and 2014

Fig. 4 Principal component analysis of the correlation of measured variables for the sediments: [#]interstitial metals (IMs), [*]bioavailable metals (BMs), OM, pH and inorganic fraction

interstitial metals As, Cd, Co, Cr, Cu, Mn and Ni and the percentages of sand and clay on axis 1 and the interstitial metals Cd, Pb, Zn and the metals in crude sediments Cd, Co, Ni, Pb and Zn on axis 2 (Fig. 4). There was a correlation between the metals in crude sediments and the Mn, Pb and Zn IMs, likely due to the higher concentrations of IMs and their bioavailability as a consequence. The metals Pb and Zn are usually found to be associated in nature, and a correlation between them is commonly reported (Allaby 2008; Charriau et al. 2011). The correlation of the clay with the IMs occurred in the two PCAs. Several authors report the possibility of metals forming colloids and aggregates with clay and OM (Luoma and Rainbow 2008; Charriau et al. 2011; López et al. 2012).

The sediment in this system presents high capacity for the retention of pollutants, which can contribute to the occurrence of system toxicity and impairment of water quality. Although we did not notice a direct influence of CMs and IMs on the water column, additively acting metals may explain the toxicity in the sediment of the system.

After conducted acute and chronic toxicity tests with *C. dubia*, *Pimephales promelas* and *Oncorhynchus mykiss* to determine the effects of metals combined as mixtures (As,

Cd, Cr, Cu, Hg and Pb), Spehar and Fiandt (1986) observed that the joint action was nearly strictly additive for *C. dubia*. In the literature the additive effects of metals mixtures on toxicity are often reported (Norwood et al. 2003; Alsop and Wood 2013; Traudt et al. 2016; Lari et al. 2017).

There was no correlation of the metals in the crude sediment and in the interstitial water with the acute and chronic toxicities detected. It should be noted that Lira et al. (2017) drew attention to the constant proliferation of cyanobacteria, potentially producing cyanotoxins in the reservoir in question. Thus, considering the toxicities found and the intense agricultural activity, it would be interesting to evaluate the possible agricultural pesticides, drugs and cyanotoxins, which may contribute to the toxicity found in the sediments of this system.

The results showed a marked presence of clay and organic matter, demonstrating a high capacity for the adsorption of metals and organic pollutants. There was no direct correlation between IMs and CMs. Although the PEL model SQGs considered the sediment as having low potential to cause damage to benthic organisms in this study, we noticed damage to nektonic organisms. Considering that there was no correlation between the metals analysis of the crude

sediment and the toxicity, even adopting the criterion of the SQG, there was also no correlation between the metals in the interstitial water and toxicity to the organisms of the water column. These results indicate that these are weak analyses, leading us to affirm that in such a complex matrix, it is essential to carry out ecotoxicological tests, which may reflect all of the dynamics of the interaction of pollutants with biological systems. This work concluded that the metal values described in the Canadian SQG to classify sediment toxicity may not guarantee the protection of the nectonic organisms. The *C. dubia* trials presented acute and chronic toxicities that may be related to the bioavailability of the metals or other possible contaminants in the sediment, such as cyanotoxins, agricultural pesticides, drugs and endocrine disruptors, which were not evaluated in the present study.

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