



Determination of metals by total reflection X-ray fluorescence and evaluation of toxicity of a river impacted by coal mining in the south of Brazil

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ABSTRACT

Metal (Fe, Mn, Zn, Ni, Cd, and Pb) concentrations in the region of Criciúma (Brazil), a region impacted by coal mining, were determined in water and sediments using total reflection X-ray fluorescence (TXRF) spectroscopy. Samples were collected from the *Mãe Luzia* River (south Brazil) at five different stations, from the source down to the river mouth (Ararangua estuary). Water and sediment toxicity were also evaluated using bioassays with *Daphnia magna* as the bioindicator. The metal present in the highest concentrations both in water (1.3–11 mg L⁻¹) and in sediments (34–142 mg L⁻¹) was iron. Results suggest an influence of coal mining on the aquatic receptors, showing a clear relationship between metal content (mostly Fe) and ecotoxicity.

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1. Introduction

Acid mine drainage (AMD) is one of the most serious environmental pollution problems in the mining industry. It is currently a global problem. All over the world, studies have been conducted in order to remediate or to monitor effluents contaminated with AMD [1–6]. Acid water loaded with toxic heavy metals is generated by the weathering of sulfide minerals (such as pyrite, FeS). Oxidation engenders a series of reactions (S⁻² is converted to SO₄⁻²) that are responsible for acids and metals leaching into the environment, which continue releasing acidic water long after the mine has closed. The effects of AMD on bodies of water can be perceived as far away as 23,000 km [7] and can persist for more than a century [8,9]. Furthermore, the typically low pH values found in AMD can cause metals to be very soluble in water. For instance, concentrations as high as >10 mg L⁻¹ of Fe and up to 50 mg L⁻¹ of Mn have already been reported for AMD [10].

In the south of Brazil (Santa Catharina's department), there are over 1000 abandoned mines. Furthermore, some of the active mines do not have treatment plants for their effluent. Rivers in this region are considered to be dead, since in addition to receiving AMD, domestic effluent and agricultural discharge also increase the toxicity level, causing serious problems for aquatic ecosystems. When

the fact that this pollution has occurred over the last 30 years is accounted for, the rivers' sediments might also have suffered important alterations.

In exploratory studies, the metal concentrations in effluents from this region were measured using atomic absorption spectroscopy. These water samples came from AMD, which had both mining and benefiting processes, and were collected before and after a treatment system. It is worth mentioning that benefiting process of coal has steps of crushing and washing, the latter aiming at removing the coal fine before heating the coal to transform it into coke. Data regarding the pH values, metal concentrations, and sulfate concentrations are shown in Table 1.

According to Table 1, the pH was very low (2.7–3.5). Sulfate levels (1587–8412 mg L⁻¹) and metal concentrations, specifically Fe (69–700 mg L⁻¹), Mn (7.4–47 mg L⁻¹), and Zn concentrations (1.6–5.4 mg L⁻¹), were very high. These results alert researchers to the risk of potential impacts on the aquatic ecosystem in this region's streams. In order to evaluate the degree of contamination in this region, the metal concentration (Fe, Ni, Cd, Mn, Zn, Cr, and Pb) and ecotoxicity of water and sediments collected from the *Mãe Luzia* River were investigated. Samples were collected at five different stations, from the source to the river mouth of the Ararangua estuary (Atlantic Ocean), as shown in Fig. 1. The flow rates roughly vary between 13 (*Mãe Luzia* River) to 142 m³ s⁻¹ (*Fiorita* River). The source (P1) was considered as control sampling point.

Metal contents were determined by total reflection X-ray spectroscopy (TXRF), while ecotoxicity tests were conducted using

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Table 1

Typical values of pH, sulfate, Fe, Mn and Zn before and after treatment plants in three different companies

Parameter	Before treatment ^a	After treatment ^b
pH (25.0 °C)	3.5	8.0 ^c
	2.7	9.0 ^d
	3.1	8.5–8.6 ^c
Sulfate (mg L ⁻¹)	1587	–
	2780	2546–3016 ^d
	8412	4581–4605 ^c
Fe _{total} (mg L ⁻¹)	69	1.5 ^c
	176	0.02–0.4 ^d
	700	1.4–2.1 ^c
Mn (mg L ⁻¹)	7.4	0.55 ^c
	21	0.13–1.3 ^d
	47	2.9–4.4
Zn (mg L ⁻¹)	1.6	0.04 ^c
	3.2	<0.02 ^d
	5.4	0.05–0.07 ^c

^aEffluent consists of ADM, mining and discharge waters; ^btreatment processes of ^calkalization and flotation by dissolved air or by ^dalkalization, flocculation and decantation.

Daphnia magna. This bioindicator has been used to determine the ecotoxicological level of sewage sludge [11], textile [12], and AMD effluents [13].

2. Methodology

2.1. Material cleaning procedures

Cleaning solutions were prepared with bi-distilled HNO₃ (Merck). All materials were washed with MilliQ[®] water, followed by washing with bi-distilled acid cleaning solution (5%) and rinsing three times with MilliQ[®] water. Metal solutions for the calibration and dilution of samples were prepared using a Titrisol[®] stock solution (1000 mg L⁻¹) purchased from Merck Co., using the MilliQ[®] water purification system ($R = 18.2 \text{ M}\Omega \text{ cm}^{-1}$ at 25 °C). Polyethylene bottles were decontaminated with HNO₃ solution for 24 h.

2.2. Sampling procedures

Sampling of water and sediments was performed in a plastic container as indicated in the APHA-AWWA-WEF Standard Methods [14]. Water samples (1 L) were preserved with 1.5 mL of bi-distilled HNO₃ and refrigerated at 4 °C until analysis. Water sampling was

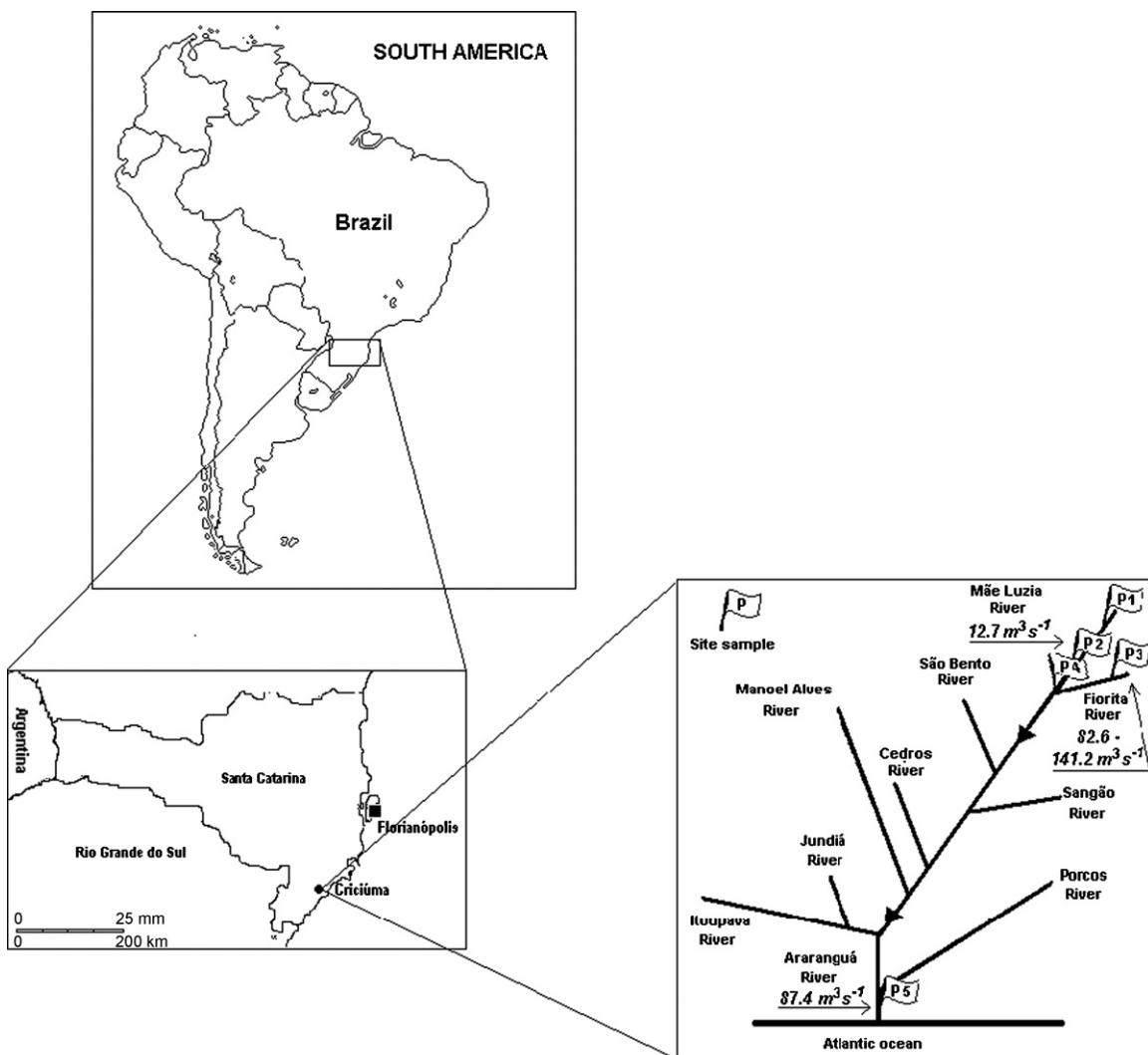


Fig. 1. Sampling sites in the Mãe Luzia River.

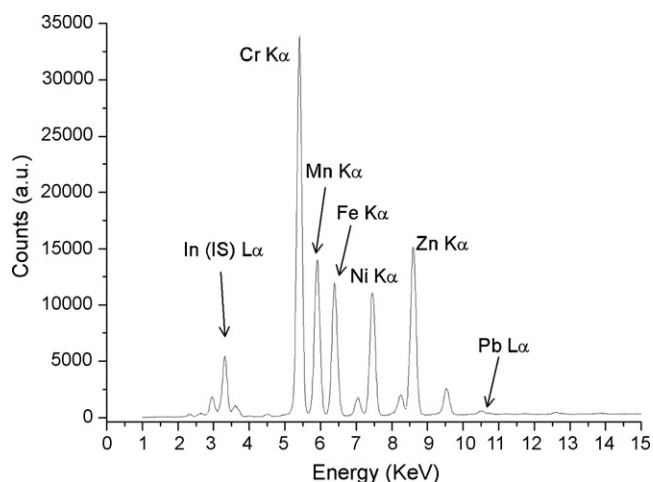


Fig. 2. Typical spectrum of the calibration standard (25 mg L⁻¹).

performed by collecting 1 L of water in polyethylene bottles preserved with 1.5 mL of HNO₃. The samples were collected in the middle of the river from the depth of ca. 10–20 cm with the bottle bore directed to the river source. Sediment samples were collected with van Veen dredge (0.0428 m²), stored in plastic bags at -5 °C. Prior to treatment, the sediment samples were kept in a hood for 48 h to remove excess water, then dried for 24 h at 110 °C and finally pulverized before acid digestion.

2.3. Sample digestion

Sample aliquots of water (10 mL) were acid digested in a water bath with bi-distilled HNO₃. Sediment (ca. 1 g) was digested as described for water, but HClO₄ (Merck) was added and stirred for 12 h at 95 °C. Extract from acid digestion (sediment and water) was transferred into a volumetric 100 mL flask, internal standard (IS) was added, and the solution was diluted to the final volume.

2.4. Metal determination by TXRF

Metal (Cr, Mn, Fe, Ni, Zn, and Cd) concentrations were determined by Total reflection X-ray fluorometry (TXRF), using the XRF line at the National Synchrotron Light Laboratory (LNLS) located in Campinas (Brazil). Water and sediment samples were analyzed in quadruplicate. From samples in which IS was added, a 5 μL aliquot was taken and deposited on an acrylic reflector surface. This reflector was left in a hood overnight to dry. The experimental XRF signals were corrected using the IS Lα fluorescence line. A typical XRF spectrum is shown in Fig. 2, which shows the analytical lines of Cr Kα, Mn Kα, Fe Kα, Ni Kα, Zn Kα, and Pb Lα. In was used as the internal standard.

Table 2

Metal concentration in water samples from P1 (source of Mãe Luzia River) to P5 (river mouth at Araranguá River estuary)

Site of sample	Metal Concentration ^a						
	Cr	Mn	Fe	Ni	Zn	Cd	Pb
P1 (mg L ⁻¹) ± D ^b	<LD ^{c,d}	0.17 ± 0.01	3.1 ± 0.15	2.2 ± 0.23	0.14 ± 0.02	0.16 ± 0.01	<LD ^e
P2 (mg L ⁻¹) ± D	<LD	0.75 ± 0.06	4.5 ± 3.73	2.0 ± 0.18	0.097 ± 0.05	0.079 ± 0.04	<LD
P3 (mg L ⁻¹) ± D	<LD	0.39 ± 0.01	8.5 ± 1.6	1.1 ± 0.20	0.22 ± 0.33	0.18 ± 0.01	<LD
P4 (mg L ⁻¹) ± D	<LD	1.8 ± 0.04	11 ± 6.5	3.1 ± 0.28	0.25 ± 0.13	0.20 ± 0.01	<LD
P5 (mg L ⁻¹) ± D	<LD	0.17 ± 0.01	1.3 ± 0.56	0.80 ± 0.10	0.098 ± 0.02	0.039 ± 0.03	<LD
Typical values for stream water ^f (mg L ⁻¹)	0.4–1.1 × 10 ⁻³	2.0 × 10 ⁻⁴	1.7 × 10 ⁻²	5.6–1.7 × 10 ⁻⁴	1.0–45 × 10 ⁻⁴	3.0–4.0 × 10 ⁻⁵	0.00004–0.00075

^a Metal concentration = average calculated from quadruplicate; ^b D = t sd/(n)^{1/2}; where Student's t, 90% of confidence where sd = standard deviation and n = degrees of freedom; ^c LD = (3sd)/(angular coefficient); ^d LD_{Cr} = 0.0226 mg L⁻¹; ^e LD_{Pb} = 1.02 mg L⁻¹; ^f from Ref. [15].

Eight points calibration curves for Cr, Mn, Fe, Ni, Zn, Cd and Pb had the following R²: 0.9607, 0.9996, 0.9889, 0.9986, 0.9761, 0.9972 and 0.9901, respectively.

2.5. Ecotoxicity tests with *D. magna*

D. magna (IRCHA clones) was cultivated in the laboratory and maintained in culture medium at 20 °C, within 16-h light:8-h dark photoperiod. Ecotoxicity tests were performed in acute exposition (24–48 h), with reconstituted (hard) and diluted water, which had been prepared according to ASTM 8711 (APHA-AWWA-WEF, 1998) [14]. These tests were performed in triplicate with five organisms from 2- to 26-h-old neonates. The neonates were exposed to increasing dilution factors (DF) of water samples (DF = 1, 2, 4, 8, 16, and 32). The sediment sample (0.05–1.5 g) used was mixed with diluted water (20 mL). The stock culture sensitivity was tested with K₂Cr₂O₇, and the results showed suitable values of LC50 to K₂Cr₂O₇ to be between 0.6 and 1.7 mg L⁻¹. Results were expressed in terms of the mortality percentage. The organism was considered not motile (mortality) when the neonates remained static for 15 s or more. The control also had five neonates in diluted water as described in the Standard Methods (APHA-AWWA-WEF, 1998) [14]. The light cycle was 16 h and the temperature was kept at 20 ± 2 °C. The *D. magna* culture was fed with *Scenedesmus subspicatus*.

3. Results and discussion

Table 2 shows the metal concentrations of the six metals evaluated in water samples collected at the five points, as represented in Fig. 1.

According to Table 2, Cr and Pb were not detected in the river. In P1, a high concentration of Fe and Ni were detected (3.1 and 2.2 mg L⁻¹). Mn, Zn, and Cd concentrations in P1 were much lower: 0.17, 0.14, and 0.16 mg L⁻¹, respectively. The Fe concentration increased up to P4, the station at which all the metals showed the highest concentrations. Mn was 1.8 mg L⁻¹; Fe was 11 mg L⁻¹; Ni was 3.1 mg L⁻¹; Zn was 0.25 mg L⁻¹; and Cd was 0.20 mg L⁻¹. It is worth mentioning that P4 is an artificial lagoon formed by effluents from coal mining, which can justify the higher values found for these metals at this site. At P5, metal concentrations are similar to those found in the source sample (P1), probably due to dilution from other rivers and principally due to the large amount of dilution at the estuary. The high dispersion found in the measurement of Fe and Zn at P2, Zn at P3, Fe and Zn at P4 in the water samples could be attributed to the high flow rate in these stations.

According to Table 2, values of metal concentration found in the present study, if compared to those reported in the literature for stream water, are higher for Mn, Fe, Ni, Cd and Pb. This behavior is observed in P1, P2 and P5, which in principle are considered as non-polluted sites. Such results may suggest a geogenic origin for this concentration. Nevertheless, higher values are observed for

Table 3
Metal concentration in sediment samples from P1 (source of Mãe Luzia River) to P5 (river mouth at Araranguá River estuary)

Site	Metal Concentration ^a						
	Cr	Mn	Fe	Ni	Zn	Cd	Pb
P1 (mg kg ⁻¹) ± D ^b	0.15 ± 0.013	1.1 ± 0.0086	34 ± 1.4	8.7 ± 0.048	0.59 ± 0.017	3.6 ± 0.0099	51 ± 0.0053
P2 (mg kg ⁻¹) ± D	0.047 ± 0.0071	0.30 ± 0.0039	61 ± 0.39	0.73 ± 0.0064	0.61 ± 0.0094	3.5 ± 0.025	103 ± 0.014
P3 (mg kg ⁻¹) ± D	0.16 ± 0.0695	0.085 ± 0.0033	142 ± 3.7	7.1 ± 0.27	0.41 ± 0.011	1.8 ± 0.0128	108 ± 0.0132
P4 (mg kg ⁻¹) ± D	0.13 ± 0.058	0.18 ± 0.00715	106 ± 6.16	7.9 ± 0.22	0.94 ± 0.027	1.16 ± 0.0083	53 ± 0.0026
P5 (mg kg ⁻¹) ± D	0.098 ± 0.015	0.27 ± 0.0061	68 ± 5.8	2.0 ± 0.032	1.3 ± 0.047	nd	66 ± 0.0093
Typical values on stream sediment (mg kg ⁻¹) ^c	64–161	<20–77	2098–6784	<6	80–209	1.8	26–195
TEL ^d (level 1) (mg kg ⁻¹)	37.3	nc	nc	18	123	0.6	35
PEL ^e (level 2) (mg kg ⁻¹)	90	nc	nc	35.9	315	3.5	91.3

^aMetal concentration = average calculated from quadruplicate; ^bD = $t \text{sd}/(n)^{1/2}$; where Student's t , 90% of confidence where sd = standard deviation and n = degrees of freedom; ^cfrom Ref. [15]; ^dTEL, "threshold effect level" from Ref. [16]; ^ePEL, "probable effect level" from Ref. [16].

expected polluted sites (P3 and P4), therefore, suggesting probably an anthropogenic origin.

The visual aspect of samples collected in P3 and P4 suggests some alteration in metal concentration from natural conditions. Comparing the color from P1 to P4, the reddish color gradient increases in intensity. This variation is accompanied by the increase in Fe, as shown in Table 3.

According to Table 3, all the metal contents, excepting for Mn, were higher than those determined in water samples. Cr and Pb were detected at each of the five stations. Taking into account PEL reported values, most of the analytes are found in lower levels, excepting for Cd and Pb. It is worth noting that higher concentrations could be expected for Mn and Fe, especially at stations which are directly influenced by coal mining activities (P3 and P4). Meanwhile, at these points, acidic conditions (low pH) might have favored Mn and Fe dissolution, together with other metals. If one considers the solubility product (K_{sp}) values for Mn^{2+} and $\text{Fe}^{2+/3+}$ ($K_{sp} \text{FeL}_2 = 7.9 \times 10^{-16}$; $K_{sp} \text{FeL}_3 = 1.6 \times 10^{-39}$; $K_{sp} \text{MnL}_2 = 1.6 \times 10^{-13}$) [17], a hypothetical limitation of solubility can be calculated if 1 mg L^{-1} of each metal (Mn^{2+} and $\text{Fe}^{2+/3+}$) precipitated as generic anions (L). In this case, only when the pH reaches 10.5 will Mn precipitate. Depending on the speciation of Fe (Fe^{2+} or Fe^{3+}), two situations must be taken into account: Fe^{3+} precipitates at pH 2.7, while Fe^{2+} needs a pH of at least 8.8 to precipitate. Both Fe^{2+} and Mn^{2+} will precipitate only at an elevated pH (>8.5). These considerations can be depicted from the diagram of metal hydroxide precipitation (Fig. 3).

Fig. 3 shows that the precipitation of each metal in its hydroxide form depends on the pH. Thus, probably, levels of Mn and Fe were relatively low in the sediment samples. This happens because the acidic conditions found in P3 and P4 might be dissolving both Fe^{2+}

and Mn^{2+} , while only Fe^{3+} is precipitated. These results suggest that Mn might be present in the water but practically absent from the sediments.

In spite of the possible presence of Mn in the water column, its concentration in water ($0.17\text{--}1.8 \text{ mg L}^{-1}$) was still very low when compared to the LC50 (concentration that is toxic to 50% of test organisms) for *D. magna* ($16\text{--}19.5 \text{ mg L}^{-1}$) reported in the literature [19]. On the other hand, $\text{Fe}^{2+/3+}$ levels in water ($1.3\text{--}11 \text{ mg L}^{-1}$) demand more concern since this value reached the threshold reported for LC50 to *D. magna* ($8.6\text{--}13 \text{ mg L}^{-1}$) [20]. Equally Ni and Cd showed some influence in ecotoxicity to bioindicator as discussed further in Fig. 6. It is worth mentioning that under the present conditions the other metal (Cr, Zn and Pb) concentrations in the aqueous medium do not seem to engender potential ecotoxicity.

In order to better evaluate these measured metal concentrations at the five points and their influence on living organisms, ecotoxicity tests were carried out on neonates of *Daphnia magna*. Data were expressed in terms of the dilution factor (DF) necessary to extinguish mortality of the bioindicator, as shown in Fig. 4.

Conditions were considered to be toxic to *D. magna* when the mortality was higher than 12.5% [13]. Fig. 4 shows that there are no toxic effects on *D. magna* at P1 (DF 1). For P2 and P3, several dilutions were necessary until no residual toxicity could be detected (DF 8 and 16, respectively). For P4, only after DF 64 was no toxicity observed. This indicates an effect on the bioindicator and possibly some influence of the trophic level of *D. magna*, i.e., a primary consumer. According to Fig. 4, at P5 (an estuary of the Araranguá

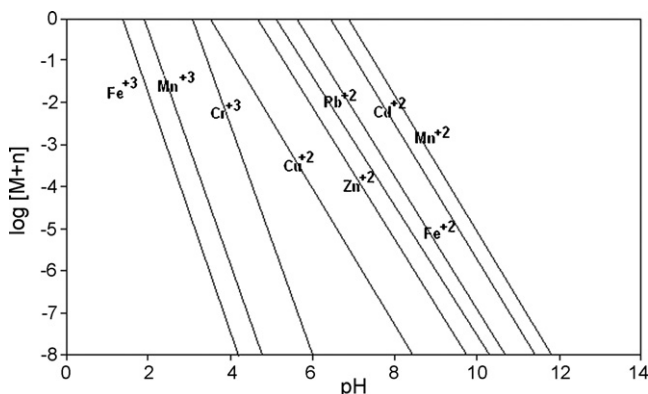


Fig. 3. Diagram of metal hydroxide precipitation. Adapted from Ref. [18].

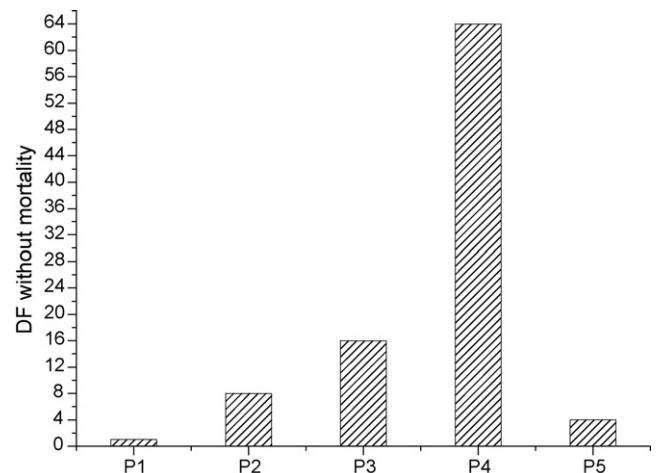


Fig. 4. Ecotoxicity test results of water samples using *D. magna* along the river from P1 up to P5 (DF = dilution factor).

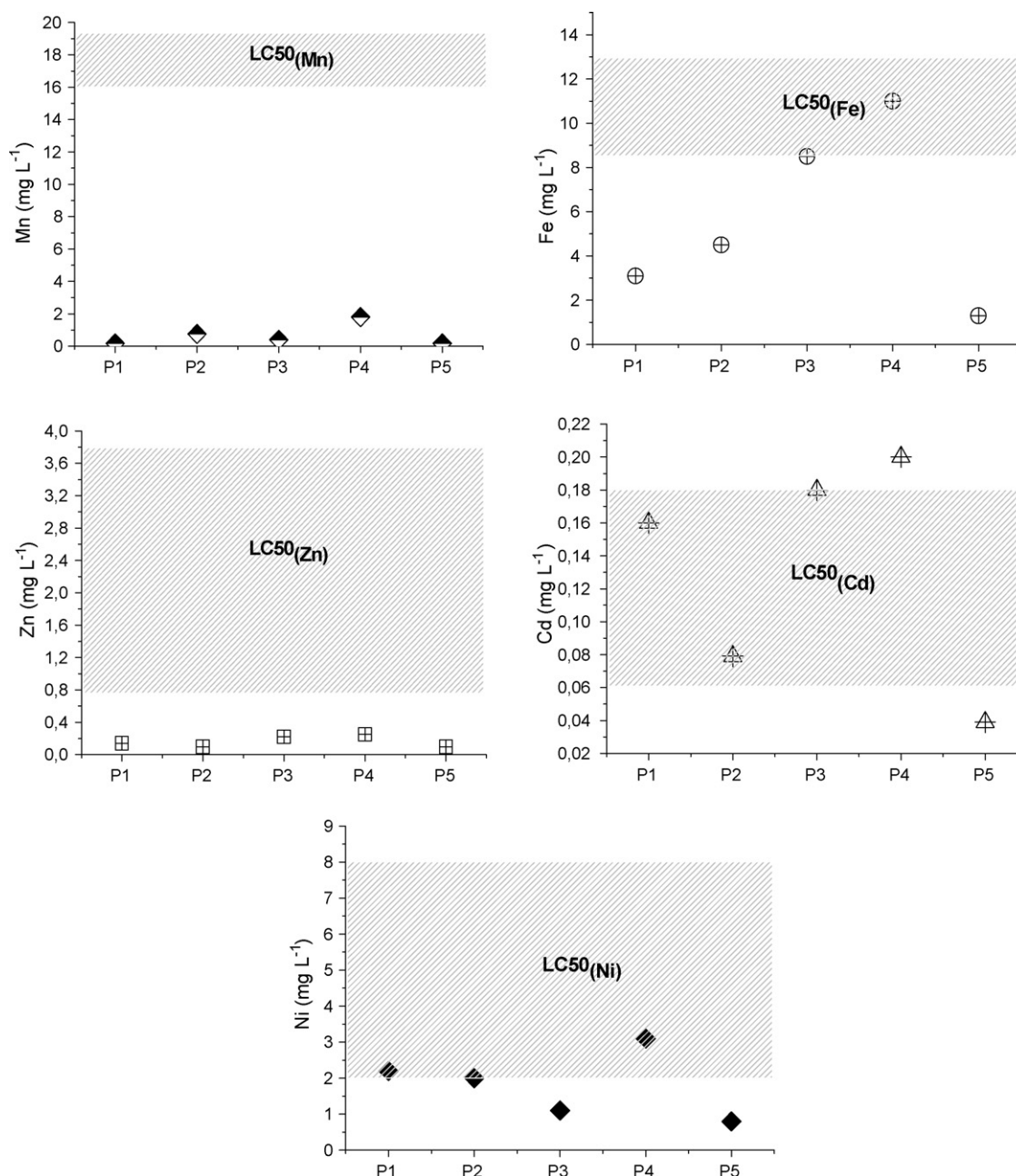


Fig. 5. Metal concentrations at P1–P5 versus the LC50 reported in the literature. Cd: 0.026–0.120 mg L⁻¹ [18], Ni: 2.0–8.0 mg L⁻¹ [20], Mn: 16–19.5 mg L⁻¹ [19], Fe: 8.6–13 mg L⁻¹ [20], and Zn: 0.78–2.8 mg L⁻¹ [22,23].

River) ecotoxicity is not as low as levels observed at the source (P1), although the metal concentrations at these two points are very similar. One cannot neglect the influence of sea water at this point, which might alter the salinity and conductivity, affecting other physicochemical parameters. Such conditions might be unsuitable for the bioindicators used, since *D. magna* is adapted to fresh water. It would be better to compare these results with LC50 data from the literature [19–23]. Fig. 5 shows the maximum detected concentration for each metal quantified, compared to the respective LC50 for the *D. magna* bioindicator. Cr and Pb were not compared since they were not detected in water samples. It is worth noting that this comparison has to be taken into account with caution, since the metals in the water of the river are present in a complex mixed with other organic compounds, metals and nutrients that modify

the possible effect in the *D. magna*. Nevertheless, some clues can be provided by this relationship.

Comparisons between Mn and Zn versus LC50 in terms of lethality indicate that the metal level is far from those values reported for *D. magna*, suggesting that these metals in these concentrations might not exert any influence on this bioindicator. The difference between LC50 and metal concentration is even larger in the case of Mn. For Cd and Ni, the metal concentration was within the range of LC50 at P1, P2, and P4. Similar behavior was found for Cd at P1–P4, and P3 and P4 were even above the reported LC50 values. One cannot neglect the possible adaptation of *D. magna* to Cd [21], which could explain the lack of toxicity observed for this bioindicator for stations P1 and P2 (see Fig. 4). Meanwhile, even organisms that have adapted to Cd have shown a LC50 maximum at 0.18 mg L⁻¹

[21]. Therefore, Cd concentrations found in P3 and P4 would still be higher than this value, thus suggesting potential toxicity. In the case of Fe, metal concentrations which exceeded the LC50 to *D. magna* were reached in both P3 and P4. Nevertheless, the increase in the Fe concentration from P1 to P4 might somehow affect the toxicity to *D. magna*. An attempt to correlate the Fe concentration and the ecotoxicity, expressed in terms of the dilution factor, is shown in Fig. 6.

A correlation between dilution factor and Fe concentration was found, suggesting a relationship between ecotoxicity and Fe concentration. However, one cannot neglect the fact that in this correlation there might be the influence of other metals, especially Ni and Cd. The latter have been reported as presenting low LC50 levels to *D. magna* ($0.86\text{--}6.3\text{ mg L}^{-1}$ [24] and $0\text{--}4.0\text{ }\mu\text{g L}^{-1}$ [25], respectively) when compared to Mn and Fe ($16\text{--}19.5$ and $1.3\text{--}11\text{ mg L}^{-1}$, respectively). Also, these metals must have influenced the sediment in the Benton community. No bioindicator representing Benton was employed. Nevertheless, some clues can be obtained by using *D. magna* to evaluate the influence of the precipitated metal on the organisms living in the water column. The results of dry sediment samples' ecotoxicity on *D. magna* are shown in Fig. 7.

Results of ecotoxicity tests with sediment samples showed a higher toxicity to bioindicators for samples collected in P3 and P4. In P1, the highest mortality percentage was 13.3%, which was very close to the lower limit of toxicity considered for this test (toxicity is reported for mortalities $>12.5\%$). In P2, a site where there is AMD discharge, mortality values were 53.5% from 0.5 g of sediment and 100% from 1 g of sediment. Similar behavior was observed at P3 and P4, even when a lower sediment mass was used. These samples (P3 and P4) have been shown to be toxic to *D. magna* in a test with 0.05 g of sample. In P4 with 0.05 g, 100% mortality was observed, while in P1, the highest mortality (13.3%) was obtained with 0.5 g of sample. The P5 sample exhibited toxicity only after 1.5 g of sediment.

Fe concentrations of the sediments (Table 3) were in the range of $100\text{--}150\text{ mg kg}^{-1}$ for stations P3 and P4, i.e., practically three or four times higher than those at the source. These results, combined with ecotoxicity tests, suggest that Fe might contribute to the observed toxicity for the bioindicator. In addition, the presence of other metals can increase the toxicity due to a combination of elements, as recently discussed by Kim and co-workers [13]. Then, although the reported criteria to polluted identification showed in Tables 2 and 3 suggest nonconcern levels for water sample have been attained, we believe that somehow it might engender an eco-

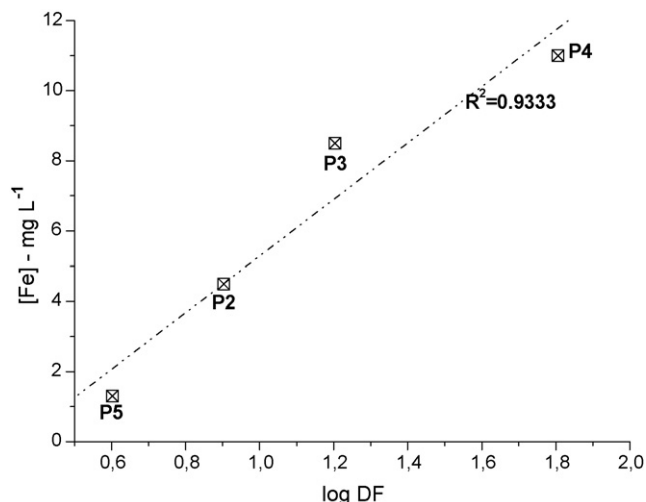


Fig. 6. log DF versus Fe concentration along P1–P4.

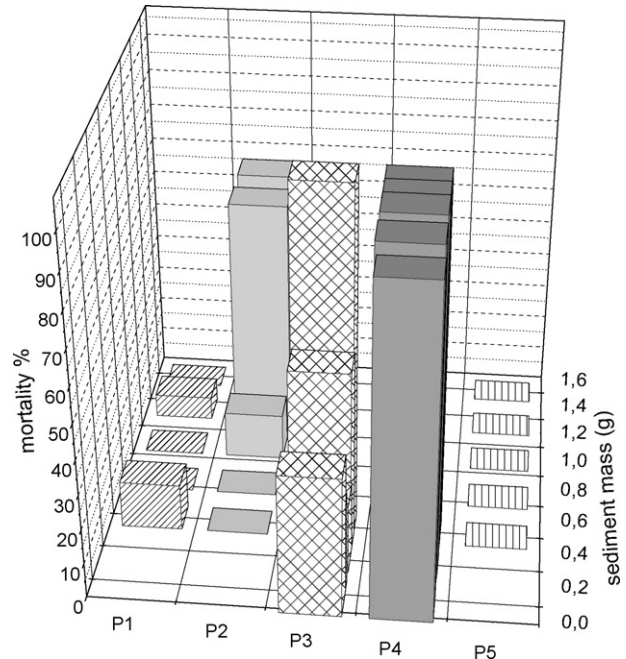


Fig. 7. Toxicity to neonates of *Daphnia magna* from sediment samples in an acute test (48 h). Effect of the sediment mass at each of the five stations.

toxicological alteration, interfering in the living conditions in the evaluated rivers.

In summary, it seems that these metals might engender some effect on the bioindicator. These behaviors of metals in the samples analyzed suggest that the aqueous body was affected by the AMD discharge in the water as well as in the sediment matrix. One cannot neglect the fact that the sediment tests were carried out with purified water in the laboratory, while water in the river might have a toxicological effect on living organisms.

4. Conclusions

Water and sediment collected from the *Mãe Luzia* River (south Brazil) at five different stations, passing by a region impacted by coal mining processing, had different metal concentrations, depending on the proximity to the source, the AMD discharge regions, or the river mouth. In the samples evaluated, sediments affected by AMD discharge, which had a high concentration of metals, were shown to be toxic to the bioindicator. A combination of TXRF analysis and ecotoxicity tests with *D. magna* was shown to be a potential tool for monitoring and mapping the levels of pollution in aquatic bodies and their sediments.

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