Biosorption of Heavy Metals by Algae Communities in Water Streams Impacted by the Acid Mine Drainage in the Coal Mining Region of Santa Catarina - Brazil

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Abstract

The acid mine-drainage (AMD), from the ecological point of view, affects the aquatic environments. The low pH and the high concentration of sulphates and dissolved metal ions reduce the biological diversity. These systems can be characterized as simple ecosystems, dominated by acidophilus and acid tolerant organisms. In the coal mining region of Santa Catarina, Brazil, the water streams impacted by AMD can be inhabited by few algae groups including the following genuses: *Microspora*, *Eunotia*, *Euglena*, *Mougeotia*, and *Frustulia*. The aim of this work was to study the metal accumulation by these algae communities (periphyton) and their contribution in the water decontamination. The results showed that the algae biomass presents high concentrations of metals, especially iron. The results showed that is possible to associate the composition of the biofilms with the water chemistry and with the natural attenuation of AMD's environmental impact.

1. Introduction

The water pollution caused by acid mine drainage (AMD) is probably the most significant impact of coal in the coal region of Santa Catarina State Brazil (Alexander *et al.*, 1995). The water derived from coal mining, coal preparation and tailing sites impacts streams from three main watersheds: Araranguá River, Tubarão River and Urussanga River. These watersheds have a total of 20.209,54 kilometers damaged by mining activity.

The low pH values, the high concentration of sulphates and the dissolved metal ions reduce the biological diversity, which are dominated by acidophilic and acid-tolerant organisms (Valente and Gomes, 2007). Despite the extreme physical and chemical conditions, some algae grow in this environment and allow the formation of a periphytic community.

The periphyton is a complex matrix consisting of microscopic algae, heterotrophic microbes, fungi, organic and mineral detritus adhering to a substrate in the photic zone of aquatic environments and thus represent a functional microcosm that supports both autotrophic as heterotrophic processes (primary production, decomposition and nutrient cycling). Most of the biomass in the biofilm, however, is associated with the algal component (Kostel *et al.*, 1999). The division Clorophyta is typically dominant in water streams impacted by AMD, including species such as *Klebsormidium* sp., *Mougeotia* sp., *Zygnema* sp., *Ulothrix* sp. *Euglena mutabilis* Schmidtz, *Pinnularia acoricola* Hust, and *Eunotia exigua* (Niyogi et al., 2002).

The identification of existing algae on acidified waters has been studied in various regions of the world, including Hocking River (Ohio, USA) (Verb and Vis, 2001), Valdarcas (Portugal) (Valente, 2004), Tinto River (Spain) (López-Archilla *et al.* (2000), New Zealand (Bray, 2007) and very recently at the Lake Kirkkoja¨rvi (Finland) (Kihlman and Kauppila (2010) and the coal Mining Region of Santa Catarina (Brazil) (Freitas et al, 2010). In general, these studies highlight the interaction of the biodiversity and primary production with factors such as pH, conductivity, concentration of dissolved metals, and deposition of metal oxides.

The aim of this work was to study the metal accumulation by algae communities (periphyton) and their contribution in the water decontamination in the Coal Mining Region of Santa Catarina - Brazil.

2. Methods

This study was conducted in the coalfield of Santa Catarina State, Brazil, including water streams of third order in the watersheds of Tubarão River, Araranguá River and Urussanga River. The area is bounded by the coordinates 28º11' to 29º03' south latitude and 49º10' to 49º37' west longitude. The climate is subtropical and the rain is well distributed throughout the year with an average annual rainfall of 1600 mm. The annual average temperature is 19°C, with the monthly average temperatures ranging from 15°C in winter to 24°C in summer, with possible occurrence of frost.

The flow rate was measured and water samples were collected in the months of july/2009, october/2009, december/2009, and april/2010 using the water resources database carried out by the "Sindicato das Indústrias de Extração de Carvão do Estado de Santa Catarina" (SIECESC). The water analyses considered the following parameters: pH, conductivity, turbidity, Eh, colour, metals (Fe, Al, Mn and Zn), sulfates, nitrogen and phosphorus. All analyses followed the procedures described in the ''Standard Method for the Examination of Water and Wastewater" (Eaton et al, 2005).

Algae sampling and identification schedule was coincident with the water sampling. The periphyton was collected in an area of 100 cm^2, packed in plastic bottles of high density polyethylene (HDPE), and preserved with Lugol for identification. Taxonomic identification was achieved by optical microscopy, based on morphological features and simple coloration tests (Bold and Wynne; 1985; Bicudo and Menezes; 2006).

For chemical analysis, the periphyton biomass was washed with deionised water, dryed at 60^{o}C, and grounded/sieved to particle below 0,6 mm. The metal analysis of the biomass considered the following elements: Fe, Ca, Mg, Mn, Zn, and Cu. The analyses were carried out by flame atomic absorption spectrometry (AA) following the procedures of the "Official Methods of Analysis of the Association of Official Agricultural Chemists" (AOAC, 1980).

3. Results and Discussion

Table 1 list the averages flow rates and the chemical characteristics in the six sampling places. It is possible to observe that the algae were found in water streams considering different flow rates and metal/sulphate concentrations. However, the pH was in narrow range, varying from 2.9 to 4.1.

Table 1. Summary of the effluent chemistry (average) on sampling places studied in the coalfield of Santa Catarina.

Parameters	Ronco D'água	Santa Líbera	Barro Branco	Colonial	Afl. Sangão River	Morozini River
Flow rate (L/s)	420	181	5.6	23	386	0.45
pH	4.1	3.3	3.5	2.9	3.7	3.2
Eh (mV)	175	246	210	235	225	222
Colour (Hazen)	14	98	191	1227	234	156
Turbidity (NTU)	1.4	31.6	31.6	88.8	36.0	3.3
Conductivity ($\mu S/cm^2$)	381	1720	418	1791	814	1148
Acidity (mg of $CaCO_3$/L)	64.6	2007.9	230.4	1767.7	396.7	838.4
Sulphate (mg/L)	587	3609	639	1703	811	1435
Fe (mg/L)	5.3	104.1	9.3	137.7	6.2	5.0
Al (mg/L)	12.3	66.8	11.2	94.9	14.3	25.6
Mn (mg/L)	0.74	3.85	0.35	2.34	1.63	4.87
Zn (mg/L)	0.44	4.67	0.53	2.64	1.90	1.15
Algae presence	Low	Low	Abundant	Abundant	Moderate	Moderate

Table 2 summarizes the communities of acidophilic algae found in the coalfield of Santa Catarina. Periphytic community was represented by five taxa at the genus level, divided into three classes: Chlorophyceae (*Microspora* and *Mougeotia*), Bacillariophyceae (*Eunotia* and *Frustulia*) and Euglenophyceae (*Euglena*). Figure 1 shows the photomicrographs of the identified algae. Figure 2 shows a picture of the algae community at Colonial's, the sampling place with the greatest diversity of acidophilic species. The dominant genus at all sampling places was of the filamentous green algae *Microspora*. This genus demonstrated the best adaptation, being present in a wide range of pH (between 2.9 and 4.1) and with different levels of concentration of iron and sulphate.

Table 2. Algae on acidic aquatic environments in the coal production region of Santa Catarina.

Place	Watershed	Division	Class	Genus	Dominant Genera
Ronco D´Água	Urussanga River	Chlorophyta	Chlorophyceae	*Microspora*	*Microspora*
Santa Líbera	Araranguá River	Chlorophyta Euglenophyta	Chlorophyceae Euglenophyceae	*Microspora* *Euglena*	*Microspora*
Barro Branco	Tubarão River	Chlorophyta Heterokontophyta	Chlorophyceae Bacillariophyceae	*Microspora* *Eunotia*	*Microspora*
Colonial	Araranguá River	Chlorophyta Chlorophyta Heterokontophyta Heterokontophyta Euglenophyta	Chlorophyceae Chlorophyceae Bacillariophyceae Bacillariophyceae Euglenophyceae	*Microspora* *Mougeotia* *Frustulia* *Eunotia* *Euglena*	*Microspora*
Afluente Rio Sangão	Araranguá River	Chlorophyta Heterokontophyta	Chlorophyceae Bacillariophyceae	*Microspora* *Eunotia*	*Microspora*
Rio Morozini	Araranguá River	Chlorophyta Chlorophyta Heterokontophyta Heterokontophyta	Chlorophyceae Chlorophyceae Bacillariophyceae Bacillariophyceae	*Microspora* *Mougeotia* *Frustulia* *Eunotia*	*Microspora*

Figure 1. Photomicrographs showing the algae identified in the coalfield of Santa Catarina. Scale: increase of 1000X.

Figure 2. Presence of algae biomass at Colonial's sampling place.

The metal concentration in the periphyton is at all sampling places is resumed in Table 3. The results showed that the algae species accumulates metals in their biomass. The iron concentration is especially significant, reaching values that can reach 6.3% of the biomass. Among the metals elements studied, the levels of accumulation followed the order Fe > Ca ≈ Mg > Zn > Mn ≈ Cu in all sampling places.

Tabela 3. Metal concentration in the peryphiton biomass (dry basis).

	Ronco D'água	Santa Líbera	M. Barro Branco	Colonial	Afl. do Rio Sangão (PP)	Morozini
Fe (%m/m)	0.22	3.8	3.9	6.3	3.6	3.5
Ca (%m/m)	0.17	0.02	0.13	0.05	0.20	0.17
Mg (%m/m)	0.04	0.03	0.11	0.07	0.10	0.10
Mn (mg/kg)	16.5	<2.00	29	17	82	94
Zn (mg/kg)	82	16	59	39	159	109
Cu (mg/kg)	22	6	17	22	109	70

The most significant productivity, expressed as accumulated biomass, was in the winter where the biomass of periphyton can reach up to 14 g/m^2. The amount of biomass reduces in the spring with, in some places, a complete absence in the summer. The algae mats were found on unconsolidated sediments (like clay and sand), rocks and even in concrete, playing an important role in natural attenuation of stream waters degraded by AMD (Lawrence *et al.*, 1998). These organisms ensure primary production interfering with the mobility of chemical species dissolved in the aquatic medium, like metals and sulfates (Valente and Gomes, 2007) being the pioneer species in the natural recovery of water courses impacted by AMD. The results obtained in this work are in agreement of the work of Lawrence et al (1998), which demonstrated the capacity of algae communities in reducing the levels of metals by sorption in water streams impacted by mining operations.

4. Conclusion

The watersheds in the carboniferous region of Santa Catarina, Brazil, are extensively impacted by the AMD. The results showed that the aquatic environment impacted by AMD can be inhabited by few algae groups. The genuses identified were: *Microspora*, *Eunotia*, *Euglena*, *Mougeotia*, and *Frustulia*. The dominant genus was the filamentous green algae *Microspora*. It was observed that the acidophilic algae grown in water at the pH range between 3.2 and 4.1, and in places with a pH below 2.8 or above 4.2 there was no algae growth. The algae communities present high concentrations of metals, especially iron. The results showed that is possible to associate the composition of the biofilms with the water chemistry and with the natural attenuation of AMD's environmental impact.

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