THE STATISTICAL APPLICATION ON ASSESSMENT OF THE BALANCE ENVIRONMENTAL RESTORATION OF THE RIVER MURUCUPI – BARCARENA – PA –AFTER THE RELEASE OF RED MUD

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Abstract - *The Murucupi River forms an important tributary of the Marajó bay, within complex basin of the Amazon region, where the local population uses the river water as a food source (fish) and transport. In April 2009, the Murucupi River received a large amount of toxic waste that leaked from containment basins of red mud of the industrial hub in Barcarena, where does the processing of bauxite to produce alumina by the Bayer process. After pouring, the biota of the Murucupi River was completely affected, leading to death of fish, plants and microorganisms. Whereas the Murucupi River suffers direct influence of the tide that enters in his bed, this study aims to evaluate from studies of seasonal chemical and physical parameters of metal concentrations in the Murucupi riverbed, the reestablishment of the environmental balance by applying the statistical model to interpret the results.*

Index Terms - Red Mud, Murucupi River, Environmental Impacts.

INTRODUCTION

The water contamination by toxic chemicals in water bodies is a major environmental concern around the world. Several authors have investigated the influence on the presence of heavy metals such as Cd, Pb, Cr, etc., in aquatic ecosystems and the harmful effects that these elements cause in the biota and humans [1], [2] [3] and [4]. Furthermore, heavy metals present a high tendency to biomagnification [5].

The red mud, also known as a by-product of the Bayer process, is an industrial process residue from refining of bauxite and characterized by a high alkalinity with a pH varying between 12 and 13, which complicates its reusing and disposal. Their composition varies according to the nature of bauxite and technique used in these refining of bauxite.

There are reports of various methods of neutralization of the red mud, including infiltration of atmospheric CO2 [6], the use of strong acids to neutralize the red mud being the pH 8 a great one, which the toxic metals are insoluble [7].

The production of red mud varies according to the bauxite used as raw material, and it can vary from 0.3 to 2.4 tons of red mud per ton of alumina produced. Brazil is the 3rd largest world producer of alumina, where the estimated annual production attention to the dimension of the environmental problem that the red mud represents [8] considering the existence of trace elements with a high toxic potential such as Cd, Pb, Mn , Cr and As

Al is an element present in high concentrations on the red mud, and as a consequence of this, it is extremely toxic to animal and vegetable organisms. Fe, Zn, Na, are also elements present in the composition of red mud that is in a high concentration levels and are also harmful to animal and vegetable organisms.

In industrial area of Barcarena the red mud-PA is stored in containment basins in the open air, which offers a huge risk because of high rates of rainfall in the Amazon region, which has caused leakage of red mud from the river containment, leading to various environmental impacts throughout the ecosystem which, directly or indirectly is related to the industrial area.

Over the last decades, the aquatic ecosystems have been modified in a significant manner due of multiple environmental impacts coming from human activities such as mining, construction of dams and reservoirs; making straight ways and deviation of the natural course of rivers; domestic sewage discharge and industrial not treated, deforestation and a inappropriate soil use in riparian areas and floodplains;

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overexploitation of fishing resources, introduction of exotic species, among others.

As a result of these activities, it has been observed a significant decrease in water quality and loss of aquatic biodiversity, due to the disruption, the chemical and physical environment and modification of natural dynamics of biological communities.

The river Murucupi (Figure 1) comprises an import affluent of the Marajó bay inside a complex basin of the Amazon region. The aquatic environments are used around the world with different purposes, among which stands out the water supply, power generation, irrigation, navigation, aquaculture and the harmony landscape [8].

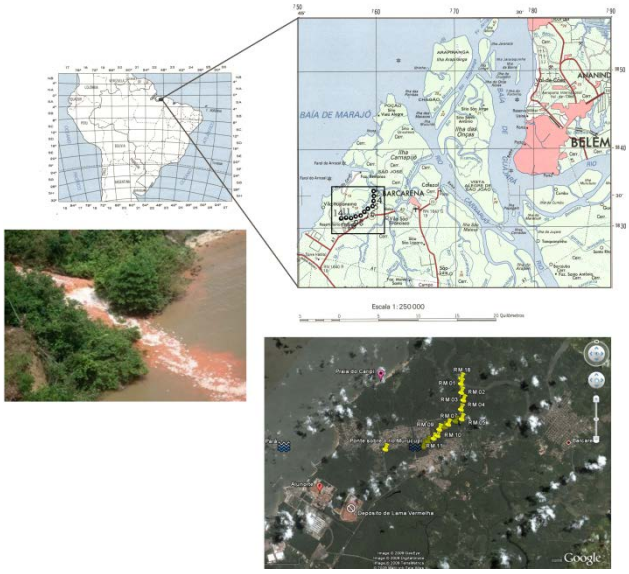

FIGURE 1
MAP OF THE STUDIED AREA
FONT: PEREIRA ET AL, 2007

FIGURE 2
A DEAD FISH ON MURUCUPI RIVER (APRIL 29TH, 2009)

The Amazon has the largest and the most complex river basin on the planet, being important to consider that the river Murucupi is a component river of this complex water system. In April, 2009, the river Murucupi received a large amount of toxic waste leaked from containment basins of red mud from the industrial area of Barcarena-PA, where makes the beneficiation of bauxite to produce alumina. After the pouring, River Murucupi biota was completely affected, leading to death of fishes, plants and microorganisms (Figure 2).

Whereas the Murucupi River is under direct influence of the tide that enters in its riverbed hauling a large volume of water that acts as diluents of chemical contaminants present waters of the Murucupi River, this study aims to assess based on studies of seasonal the physicochemical parameters and concentrations of metals on the riverbed of Murucupi River restoring the environmental balance by applying statistical analysis to interpret the results.

METHODOLOGY

Collects and treatment of samples

The collection of water samples were performed with the help of a boat on site, a day after the leak which the analyses were made from the amplitude of the tide. The locations (Table 01) of sampling were georeferenced using a GPS (global positioning system).

Table 01. Sample locations

Sample	Time	Location
RM 01	10:25	01°29’39,0’’ S 48°40’06,6’’W
RM 02	10:35	01°29’53,9’’ S 48°40’06,0’’W
RM 03	10:45	01°30’06,8’’ S 48°40’02,4’’W
RM 04	10:55	01°30’22,4’’ S 48°40’06,2’’W
RM 05	11:00	01°30’38,7’’ S 48°40’04,9’’W
RM 06	11:15	01°30’42,7’’ S 48°40’15,4’’W
RM 07	11:20	01°30’48,1’’ S 48°40’27,4’’W
RM 08	11:25	01°30’52,8’’ S 48°40’34,5’’W
RM 09	11:30	01°30’56,6’’ S 48°40’42,5’’W
RM 10	11:40	01°31’07,2’’ S 48°40’45,3’’W
RM 11	11:45	01°31’12,2’’ S 48°40’51,8’’W
RM 12	11:51	01°31’17,9’’ S 48°41’01,5’’W
RM 13	12:00	01°31’23,6’’ S 48°41’06,7’’W
RM 14	12:05	01°31’26,0’’ S 48°41’09,5’’W

There were used polyethylene bottles, previously decontaminated with 10% nitric acid for 48 hours, which they were washed with distilled water, and ultrapure water and in the collection site to the sample itself. From each point two samples were taken, one for the testing of elements and another for storage as counterevidence, both were stored at 4 ° C, but only the second was acidified to pH <2 with concentrated nitric acid (about 1 ml to 500 mL sample) after filtering.

The treatment of samples was conducted in the LAQUANAM; the samples were pre-screened and filtered through a membrane type GFF (0.22 μm Millipore) for subsequent analysis of chemical elements by ICPOES.

To evaluate the results of the tidal influence was used the tide chart provided by DHN - Tide Table ref. Vila do Conde Port - Latitude: 01 º 32'0, 4S, Longitude: 048 º 45'0, 2W.

Analytical methodology

The physicochemical analyzes were performed in place using a multiparameter sonde - YSI Manufacturer - Hexis Brazil - Model 6600 - which assessed the OD, pH, conductivity, turbidity, and chloride, calibrated with an appropriate solution before the field trip.

We analyzed the following metals (Al, Cr, Fe, Pb, Mn, Zn and Na) by optical emission spectrometry with inductively coupled plasma (ICPOES). Software of analytical quality control with the use of reference standards NIST 1643e was used for the purpose of providing reliable data and calibrates the equipment for the river water matrix, being the recoveries of elements between 77.21% - 105.91%. The descriptive statistical analysis and comparison of averages was performed using the Statistica software.

RESULTS AND DISCUSSIONS

The analyzes of the physicochemical parameters performed in the Murucupi River on April 29th, 2009, after the leak of red mud from the sump the industrial area of Barcarena describe the large variation in the natural conditions of environmental balance of the ecosystem formed by the Murucupi River.

The average results of chemical analysis for the parameters OD, turbidity, pH, conductivity, metals and chloride, performed on day April 29th, 2009; May 2nd, 2009 and March 10th, 2010 are described in Table 1 and 2 respectively.

TABLE 1
RESULTS OF AVERAGES FOR THE PHYSICOCHEMICAL PARAMETERS.

	OD mg/L	***Turbidity UNT***	***pH***
CONAMA	>5	<100	6,0 a 9,0
Average I	2,91± 0,75	287,69± 35,80	7,20± 0,21
Average II	2,69± 0,19	34,13± 1,35	6,58± 0,01
	Cond µS/cm	***Cl^- mg/L***	
CONAMA	-	<250	
Average I	181,07± 40,33	513,19± 261,52	
Average II	133,67± 2,84	237,50± 49,88	

I – on April 29th, 2009; II – on May 2nd, 2009

The results for OD are lower than the recommended by legislation in force [9], possibly being the cause of mortality of fishes. The chloride is above the maximum allowed by CONAMA 357-05, probably indicating the addition of a neutralizing agent, most likely hydrochloric acid, in order to reduce the caustic nature of the red mud [10]. The addition of acids can have triggered exothermic chemical reactions with the consequence of a decreasing of solubility of oxygen in water.

The results obtained for turbidity express a wide variation of chemical analyzes performed on different dates on which they gave the collection campaigns, observing a reduction of approximately 4 times the values found for the turbidity between the days April, 29th and May 02nd 2009, showing that the plume of pollution composed by the red mud, clay material with a low soil gradation, with the major constituents Al_2O_3 and Fe_2O_3, suffered a dilution during the time interval elapsed between the collection campaigns..

A The same observation applies to the results of chloride concentration (Figure 3) which the high levels found for the analysis of the day April 29th, 2012 confirm the use of the red mud neutralizer being the neutralization used a strong acid, most likely HCl or the addition of ocean waters [11], which also contribute to the increase of chloride concentration in the river analyzed.

It is observed that between the day May 2nd, 2009 the chloride concentration was approximately 4 times lower which a also contributed to the reduction of electrical conductivity in the river water, due to the decrease in the ionic charge, confirming the debugger effect of intrusion on tidal waters of the Guajará bay into the Murucupi River the average variation of the metals Al, Cr, Fe, Pb, Mn, Zn and Na are shown in the Figures 4-9 which describe the debugger effect of the intrusion of the tidal water in the river Murucupi River.

TABLE 2
RESULTS OF CHEMICAL ELEMENTS ON MURUCUPI RIVER (WITH NO RAIN) (µg/L)

	Al	***Cr***	***Fe***	**Pb**
CONAMA	100	50	300	10
Average I	5588,27±1 683,78	7,32±1, 12	798,34± 137,98	7,83± 4,69
Average II	4437,54± 251,48	8,25± 1,11	750,58± 45,38	4,40±4, 71
AverageIII	14948,8± 8500,90	5,0± 2,58	495,4± 177,44	4,61±2, 50
	Mn	**Zn**	**Na**	
CONAMA	100	180	-	
Average I	61,46± 21,74	52,52 ± 19,49	35974,78± 11940,07	
Average II	5,39±0,63	21,83± 29,94	34403,72± 1948,46	
AverageIII	5,3± 2,86	5,3± 12,01	1469,4± 754,09	

I – on April 29th, 2009; II – on May 2nd, 2009; III – on March 10th, 2010

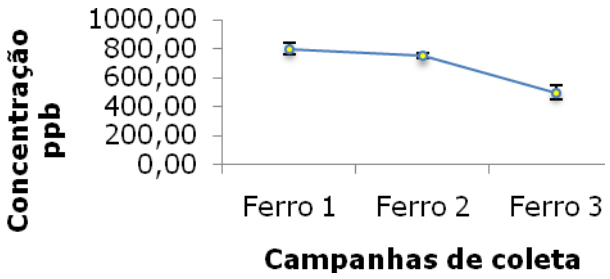

FIGURE 3
IRON CONCENTRATION ON MURUCUPI RIVER (mg/L)

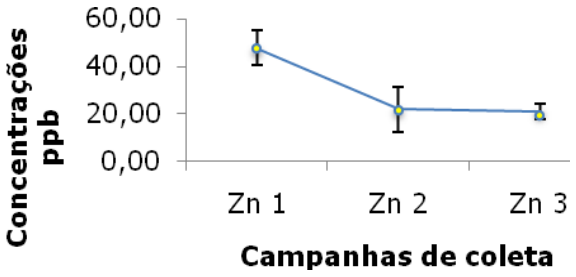

FIGURE 4
ZINC CONCENTRATION ON MURUCUPI RIVER (mg/L)

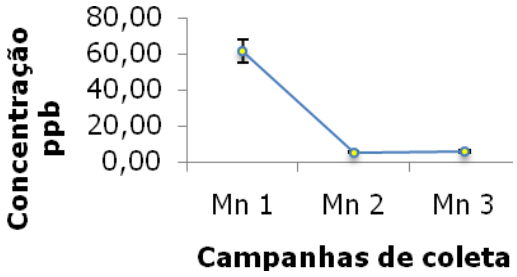

FIGURE 5
MANGANESE CONCENTRATION ON MURUCUPI RIVER (mg/L)

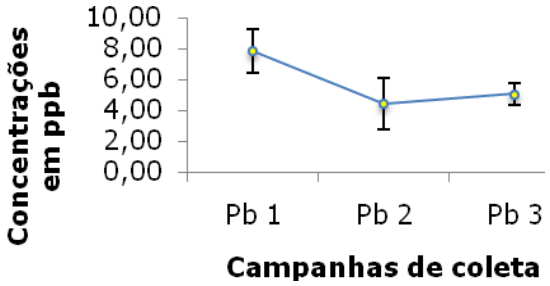

FIGURE 6
LEAD CONCENTRATION ON MURUCUPI RIVER (mg/L)

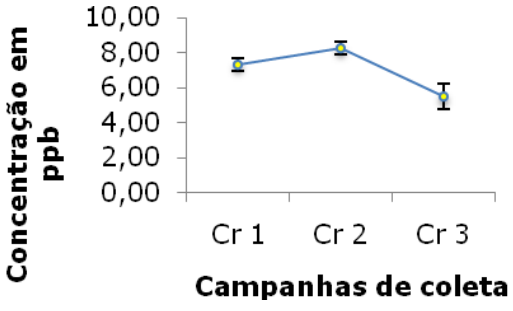

FIGURE 7
CHROME CONCENTRATION ON MURUCUPI RIVER (mg/L)

The analysis of the curves that describes the behaviour of variations of the averages of aluminium, shows that the concentration of this component increases over time elapsed between the chemical analyses. This observation can be explained due to the high pH of toxic waste, and higher pH values the Al suffers precipitation from the hydroxide form.

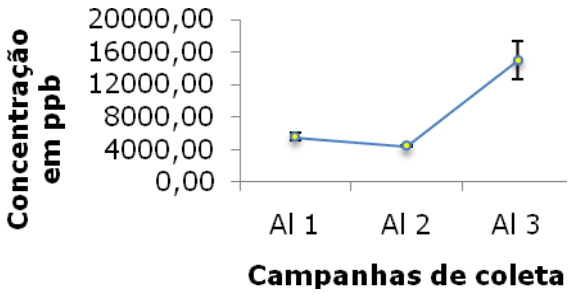

FIGURE 8
ALUMINIUM CONCENTRATION ON MURUCUPI RIVER (mg/L)

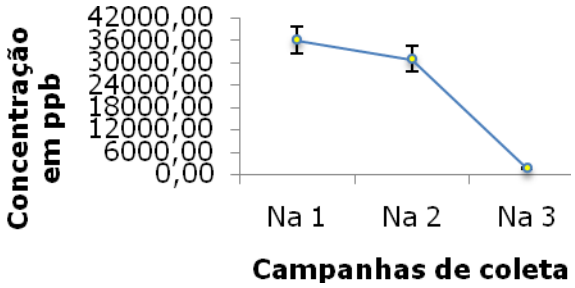

FIGURE 9
SODIUM CONCENTRATION ON MURUCUPI RIVER (mg/L)

To the depurative effect of the tidal waters the natural equilibrium conditions on Murucupi River where the pH varies around 5.5 and is therefore slightly acidic and at such conditions of pH the aluminium is released from the hydroxide form to the form of ions free. Another likely explanation for the observation of this increasing of the concentration of aluminium is the river Murucupi River continue receiving the contribution of waste from the industrial process of beneficiation from bauxite.

The Fe also showed a little variation, which can be explained by the fact that this element is a natural constituent from geochemistry of the area and also be a macro element within the composition of the red mud, being these two key factors contributing to the intake of iron into the on Murucupi River.

The Na, element not restricted by the legislation in force, perfectly describes the depurative effect exerted by the intrusion of the tide on Murucupi River its concentration declines over time between the sampling campaigns.

The Na, although not being restrictive, their high concentration on the occasion of the red mud leak draws attention as a consequence of the impact that this element causes the longing of the animals, also interfering in the chemical balance of substances into the plant organisms.

The Pb, although the values found do not exceed the limit established by the legislation, draws attention to this element does not exert any physiological role, so the availability of this element in environments used by humans as a source of water, food or any other activity directly , is extremely worrying from the standpoint of public health.

Conclusion

The comparison between the results of analyzes of chemical and physicochemical parameters on Murucupi River, the river demonstrate that the natural conditions spontaneously tends to equilibrium, which can be observed by the reestablishment of the natural conditions of pH and the decrease of the dissolved metals in the water concentrations.

It is important to note that these values of the concentrations of aluminium, it is observed that the Murucupi River continues acting as the receiving body of domestic and industrial wastes from the community on its surroundings, which can be a factor that makes the recovery from biota affected by the red mud.

Regarding the reestablishment of the natural conditions of the Murucupi River the intrusion of waters of the Guajará bay acts as a determining factor for the re-establishment, working with an debugger agent to step into the body of the river Murucupi promotes the dilution of contaminants and with the low tide the plume of pollution of the river dragged out Murucupi being dispersed in the Guanabara bay, the major constituent of the Amazon basin.

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