STUDY OF METAL CONCENTRATION: AL, Na, Fe AND Zn IN FISHES AFTER RED MUD SPILL IN MURUCUPI RIVER, BARCARENA-PA

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Abstract *- In April 29, 2009, during the period of higher rainfall in the Amazon region, there was a rupture in the red mud containment basin of the company, which the undertaking by the Bayer process, bauxite benefits in alumina production, producing as a waste, the red mud, for containing highly toxic waste in their composition a large concentration of NaOH and trace elements with toxic potential. As result of leakage of red mud in the Murucupi River, there was the death of a great multitude of fishes, reptiles and phytoplankton that formed the biota. This work was carried out to evaluate metal concentration in fish killed in Murucupi River, collected soon after the environmental accident. The goal is to perform statistical comparison of the metal concentration in fish and water to assess the impact caused by toxic waste receiver that has polluted the ecosystem of the do pant material.*

Index Terms – Heavy metals, fishes, Murucupi River, Environmental impacts.

INTRODUCTION

The introduction of toxic elements into aquatic systems occurs naturally through the geochemical processes in the weathering and the contribution attributed to human activity is a reflection of its extensive use by the industry [1]. The pollution of an aquatic ecosystem can cause changes of the physical, physicochemical, and / or biological characteristics, which see compromise the multiple uses that water is intended for [2]. The assessment of metal pollution is an important aspect of most programs to control water quality. These programs include elements such as Al, Cd, Cr, Cu, Fe, Hg, Ni, Mn, Pb, and Zn. The concentration of different elements can vary in a wide range (0.1 to 0.001 mg L^{-1}) in non-polluted areas and can reach levels which are hazardous to human health in areas where waters are influenced by anthropogenic activities [3].

The main sources of trace elements to the aquatic environment continental are weathering of rocks and erosion of soils rich in these materials. More recently other sources of trace elements are assuming a large importance: industrial activities through solid effluents are released directly into the atmosphere and liquids that are released in small streams or directly into rivers and lakes, mining activity, domestic sewage and surface waters from areas where pesticides are used [4].

All life forms on earth depend on water for survival. It should be remembered that all the water on the planet is only 3% freshwater, of which 79% of this total is in the form of glaciers and icebergs, 20% as groundwater, and only 1% is directly available for human use [5]. Despite this the natural reservoirs have been depositories of a wide variety of products from human activity. The presence of potentially toxic elements is responsible for adverse effects on the environment, with repercussions on the economy and public health. The introduction of toxic elements into aquatic systems occurs naturally through the geochemical processes in the weathering and the contribution attributed to human activity is a reflection of its extensive use by the industry [1].

The pollution of an aquatic ecosystem can cause changes of the physical, physicochemical, and/or biological characteristics, which undermines the multiple uses that water is intended for [2].

Some metals such as manganese, copper and zinc, when present in minimum quantities is important for the physiological functions of living organisms and regulate many biochemical processes. The same metals, however, when discharged into natural waters in high concentrations by sewage, industrial effluents and mining can have severe toxic effects in the aquatic environment and subsequently in humans [3].

Pollution by trace elements in rivers has become a matter of great concern in the last decades not only by the threat to the public water supply, but also the risks to human consumption of fish stocks. Heavy metals from natural and anthropogenic sources are continuously released into the rivers, and they are serious threats due to their toxicity, long

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persistence, bioaccumulation and biomagnification in the food chain [6], [7], [8] and [9]. The heavy metal contamination in water and its absorption by fishes is a direct consequence of urban and industrial pollution [10] and [11].

There is an increasing awareness of potential hazards which exist due to contamination of freshwater impoundments by toxic metals associated with mining and quarrying [12]. The reason is the global demand for minerals, which intensified the exploitation of natural resources. The tailings from the mining and milling operations are released in settlements and dams or waste treatment lagoons. Containment basins or dams may contain significant concentrations of toxic metals [13] which may be released to the environment.

Many of the dissolved metals which enter into rivers are adsorbed on the colloidal particles. Also in high alkalinity, metals, particularly lead and cadmium, precipitate in the form of complexes, thus influencing forceful the metal toxicity [14]. Therefore, the precipitation and sedimentation of cadmium and lead, to a lesser extent, copper and alkaline zinc may be greater in containment basins for sedimentation processes, which act as a sink for metals [14].

The cautions in relation to heavy metal pollution have focused on the property that most of them have to accumulate in the environment and allowing transport of contaminants through the food web for different trophic levels of the food chain. This effect culminates with the occurrence of the highest rates of contamination at the highest levels of the trophic web.

Metals perform beneficial or harmful functions to human health, mainly depending on its concentration. It is known that food is one of the main ways to ingest these metals, but it must be observed that these foods are ready for consumption [15]. The fish is a rich food in high quality protein and easy digestibility, such as the lysine. It is an excellent source of vitamins A and D, which are present in their fat and also contains thiamine, riboflavin (vitamin B1 and B2) and is rich in essential minerals for the metabolic processes of the human organism [16]. Among the essential elements, there are potassium, calcium, zinc, phosphorus, magnesium and other forming part of the animal diet.

METHODOLOGY

The samples (Table 1) of fish were collected alongside the Murucupi River (Figure 1); early in the state of decomposition, due to the time elapsed between the environmental accident that caused the mortality of fish (Figure 2) and time of sample collection (24 h). Treatment of samples was conducted to the LAQUANAM and refrigerated for later analysis of the chemical elements by ICPOES. Were analyzed the following metals (Al, Fe, Zn and Na) by atomic emission spectrometry with inductively coupled plasma (ICP OES).

A program of analytical quality control with the use of reference standards and DORM 2 and was used for the purpose of provide reliable data and calibrate the equipment to the matrix fish, being the recoveries of elements between 72.21% -99.01% the descriptive statistical analysis and comparison of averages was performed using the statistical program BioEstat 5.0.

TABLE 1
THE FISH BIOMETRY COLLECTED ON MURUCUPI RIVER IN MAY 5TH, 2009

Sample	Specie	Size (cm)	height (kg)	Collected material
A1	Peacock bass	60	5	Muscle
A1	Peacock bass	60	5	Gills
A2	Peacock bass	55	4	Muscle
A2	Peacock bass	55	4	Gills
A3	Peacock bass	30	1	Muscle
A3	Peacock bass	30	1	Gills
A4	Eigymania Sp.	30	0,7	Muscle
A4	Eigymania Sp.	30	0,7	Gills
A5	Eigymania Sp.	30	0,2	Muscle
A5	Eigymania Sp.	30	0,2	Gills
A6	Angelfish	20	0,04	Muscle
A6	Angelfish	20	0,04	Gills
A7	Angelfish	15	0,2	Muscle
A7	Angelfish	15	0,2	Gills
A8	Mandi	80	2	Muscle
A8	Mandi	80	2	Gills
A9	Piaba	10	0,15	Muscle
A9	Piaba	10	0,15	Gills
A10	Angelfish	15	0,1	Muscle
A10	Angelfish	15	0,1	Gills
A11	Angelfish	25	0,3	Muscle
A11	Angelfish	25	0,3	Gills
A12	Peacock bass	70	4	Muscle
A12	Peacock bass	70	4	Gills

FIGURE 1
MURUCUPI RIVER

FIGURE 2
DEAD FISHES COLLECTED ON MURUCUPI RIVER IN APRIL 04TH, 2009

RESULTS AND DISCUSSIONS

After the red mud spill from the containment basin of the company through the process of beneficiation of bauxite to the production of alumina which generates the red mud as a residue, was observed in the river Murucupi by riverside residents and during the collection performed on the day 29/04 / 2009 a large amount of dead fish, giving an intense foul smell of decaying organic matter.

The results for the metals Al, In, Fe and Zn in the musculature, in the gills of the fish and in the water are described in Table 2.

TABLE 2
RESULTS OF CHEMICAL ELEMENTS ON RIO MURUCUPI RIVER (PPM)

Sample	Al	Fe
Average April 04th, 2009 on water	5588,27± 1683,78	798,34± 137,98
Average in fishes (muscle)	146546,01± 171863,43	24960,16± 31927,87
Average in fishes (gills)	134543,40± 162202,30	20929,19± 6167,82
Sample	Zn	Na
Average April 04th, 2009 on water	52,52 ± 19,49	35,78± 119,07
Average in fishes (muscle)	183,32± 2138,87	420,16± 488,79
Average in fishes (gills)	125,92± 152,60	172,61± 191,42

The results of chemical analysis for Al in the musculature of the fishes were on average 26 times higher in muscle and in the gills about 24 times higher than those found in the water indicating that the red mud supersaturate the musculature and the respiratory structures of fishes, this being the probable cause of fish deaths considering that at high pH values characteristic of the red mud, Al shows precipitation forming $Al(OH)_3$, blocking the respiratory pathways of fishes causing them to death by suffocation. Studies have reported values of Al in media ranging from 8 to 20 ppm in fish musculatures [17] from non-impacted areas, values seven times smaller, it was found in impacted fishes in the Murucupi River, indicating that fishes from the Murucupi River were contaminated by Al at levels that exposes the risks to the fish population that depends on the region's rivers impacted. This fact becomes worrisome due to the Al is associated with diseases such as encephalopathy, osteomalacia, dementia, behavioural changes and speech disorders [17]

The concentrations of iron in the fishes musculature were detected on average 32 times higher than in the river Murucupi and in the gills about 27 times greater, and 10 times higher values than those reported for fish musculature in not affected areas [18]. Even the Fe being an essential element, the iron contamination draws attention due to high levels that the Fe is responsible for a broad spectrum of diseases, among them hemochromatosis, such as cancer, liver and heart disease, diabetes, hormonal and the immune system disorders and even chronic degenerative diseases [17], [19] and [20]. The contribution of Fe in fishes and Murucupi River who served as the receiving body of toxic waste leaked from the containment basin was incorporated into the biota, thus increasing the natural levels of this element available to plants and animal species that reproduce in the Murucupi River, and are consumed by the local population of the region, placing the population in danger of exposure to excess of this element..

The results for the Na analysis shown concentrations in muscle and gills of the fishes considerably larger than in the Murucupi River, confirming the effected observation for the metals Fe and Al, that the high concentration of metals in water caused a super concentration of these metals in fishes in the river affected by red mud, Na is not a restrictive element by the current legislation, however, the high sodium levels in fishes are worrisome due to be in an element directly related to cardiovascular diseases like high blood pressure and maintenance of high levels in the Murucupi River, focus on high levels of Na in fishes to be consumed endanger the population that consumes them.

Zn concentrations were on average three times higher than the levels of Zn in the water, which is consistent with other studies that assessed Zn in fish musculature where they were detected values ranging from 17 to 150 ppm.

The zinc is a trace element which is essential for human health. The mineral is found throughout the body and is involved in many metabolic processes that affect the immune system function, brain and sexual development.

When people absorb zinc, some individuals may experience a loss of appetite, decreased taste and smell, slow healing of wounds and ulcers. Although humans can handle high concentrations of zinc, some people may develop major health problems such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause atherosclerosis. The continued exposure to zinc chloride can cause respiratory disorders. Zinc may be a

danger to unborn children and newborn infants. When mothers absorb large concentrations of zinc, children may be exposed to it through blood or breast milk (ELISA, 1988).

Some fishes can accumulate zinc in their bodies when they live in streams contaminated by zinc. When zinc enters in the bodies of these fishes can biomagnifies the food supply chain.

The correlation analysis of the results indicate a positive correlation (0.662, sig= 0.019) between the concentrations of Al in fishes and in the water, indicating that the Al detected in fishes has probably the same source of Al in water, which is in accordance with what was observed during the environmental accident origin of all impacts in the Murucupi river and the ecosystem composed by it.

The same observation is made for Zn where the correlation between Zn in fishes and in the water in a positive correlation was 0.636 (sig = 0.026), indicating that the uptake of Zn in the Murucupi River also is the origin of Zn detected in the musculature of fish. A strong correlation is observed between the Na found in water and the Na concentrations found in fish (0.739, sig = 0.006), these data show that red mud is directly related to the death of fishes in the Murucupi River, considering the Na as a macro component in the chemical composition of the red mud. The correlation between Na and Fe in the water found in fish (0.668, sig = 0.018) indicates that these elements have the same origin, probably the toxic waste carried to the river bed impacted.

Conclusion

Studies in the Murucupi River at the moment after the red mud spill (red mud); demonstrate the high degree of impact caused by the toxic waste carried to the water body under study. These observations are confirmed by the large amount of dead fish found in the Murucupi River which coupled with the strong characteristics of foul smell from decaying fish has become an unhealthy environment for the riverside residents who depend on the river for their daily maintenance activities, such as shipping, subsistence fishing, recreation, among others. The metal concentrations in fishes show that these elements have undergone a process of concentration in dead animals, indicating that the red mud was largely responsible for the environmental imbalance found in the Murucupi River.

These observations are of great concern because the Murucupi River over the years act as receiving body of industrial wastes from the Industrial Pole of Barcarena, where the accumulation of metals, including the trace elements can be occurring at worrying levels, exposing the population to risks , population that depends both directly and indirectly by Murucupi river. Another worrisome fact, is related to the origin of contribution of these elements, that originates in industrial waste from chemical processes, and this fact calls attention due to reports in the literature correlated in leukaemia cases in women exposed to industrial waste, in addition other cancers related to the exposure of trace elements, which may naturally be in the composition of this waste generated in the chemical process developed in the industrial pole located in the region where the study was developed and where occurred the leakage of red mud that triggered the great environmental impact observed in the Murucupi River.

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