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STUDY OF SOME ENVIRONMENTAL IMPLICATIONS DUE TO THE DISPOSAL OF ASHES FROM THE SÃO JERÔNIMO POWER STATION - RS

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ABSTRACT

The residues (ash agglomerates from combustion) generated at the São Jerônimo Power Station (UTSJ) were characterized with the main objective of evaluating, in pre-established conditions, the release of Cd, Co, Cu, Pb, Ni, Zn, Mn, Al and Fe to the environment. Results revealed that, at different pH values, Fe, Zn, Mn and Al were present in higher contents. In surface waters, for all sites analyzed, Fe and Al surpass the environmental standards imposed by Brazilian Legislation for class II surface waters. Surface sediments at the sites studied are basically composed by ashes from UTSJ and a cumulative effect of deposition of the metals on the river sediments was verified. The experimental results, are strongly indicative of an imperative need for a change in criteria in relation to the final disposal of residues from UTSJ. Otherwise there is a high risk that the environmental impact in the short term will irreversibly damage the environment.

KEYWORDS: Residue analysis, coal ash, extractable metals, surface waters, sediments.

RESUMO

Os resíduos gerados (cinzas aglomeradas provenientes da combustão) da Usina Termoelétrica de São Jerônimo (USTJ) foram analisados com o objetivo principal de avaliar, em condições pré-estabelecidas, a liberação de Cd, Co, Cu, Pb, Ni, Zn, Mn e Fe ao ambiente. Os resultados mostraram que a diferentes valores de pH, o Fe, Zn, Mn e Al apresentaram teores mais elevados. Nas águas superficiais, em todos os pontos analisados, o Fe e o Al excedem os padrões ambientais estabelecidos pela legislação brasileira para águas de classe II. Os sedimentos de margem dos pontos estudados, se compõem basicamente por cinzas da USTJ e ainda existe um efeito acumulativo de deposição de metais sobre os sedimentos do rio. Os resultados experimentais são fortemente indicativos da necessidade urgente de alteração dos critérios de deposição final dos rejeitos da USTJ. Se providências não forem tomadas, existe um elevado risco de que o impacto ambiental atual se torne, a curto prazo, irreversivelmente prejudicial ao meio ambiente.

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INTRODUCTION

Residues are generally defined as substances present in any environment and whose properties affect environmental characteristics (quality) (ISO - International Organization for Standardization)[1]. In this context, associating this idea to coal processing, it is relevant to report that the major coal application in the state of Rio Grande do Sul (RS) is the combustion in power stations for energy generation. About 2 million ton/year are consumed by thermoelectricity and about 1 million ton/year by cement and petrochemical industries, among others.

Most thermoelectrical power stations (Usinas Termoeletricas - UT) located in Rio Grande do Sul burn pulverized coal, except for Usina Termoelétrica São Jerônimo (UTSJ) that uses a combustion system on grate furnace. This small-sized power station, when compared to others located in Southern Brazil, e.g. Usina Termoelétrica Presidente Medici at Candiota generates agglomerated residues due to ash sintering inside the combustion chamber. Ashes from combustion on grates are generally made up of high contents of organic matter when compared with pulverized coal and this ashes contentmetals (Ni, Co, Pb, Zn, etc..), the concentrations varying according to coal origin[2-4]. The organic matter persists after combustion because the coal is burned without previous processing.

Environmental problems brought about from residue disposal depend on its characteristics and the pH found in the environment. It is well-known that ash agglomerates induce less-critical environmental effects than ash from pulverized coal combustion, which presents smaller particle size and is more readily subjected to the environmental action and subsequent metal release.

Some kind of ashes produce acidic pH values in contact with water, while others result in alkaline ones. Several studies have been done on metallic extraction of ashes from coal combustion, to evaluate metal mobility in these residues. Some of them are outstanding, such as Sanchez et al.[5,6], Teixeira et al.[7], Eary et al.[8] and Roy et al.[9]. These studies establish that the type of process, the nature of ashes, the metallic enrichment on particle surface are factors that contribute to metal mobility.

Environmental problems induced by ash disposal have been observed in certain regions in Rio Grande do Sul, where the presence of significant amounts of this residue, inadequately disposed[10]. In spite of the fact that inadequate disposal of ashes has been verified in the areas of Charqueadas and São Jerônimo, the behavior of the pollutants due to weathering has not been clearly elucidated. The ashes from the two locations present different characteristics that are due to coal type and different combustion processes. Ashes have been used in pavement of highways and as landfill on private properties. Many of the deposits and landfills found in these two areas are within the Jacuí River Flood plain. In both cases, the landfills as well as significant quantities of ashes launched without defined guidelines along roads or highways present serious problems to the environmental[10].

The aim of this study is to characterize residues generated by Usina Termoeletrica São Jeronimo-UTSJ, with the use of different extraction techniques, to evaluate in "pre-established conditions" the release (mobility) of metals (Cd, Co, Cu, Pb, Ni, Zn, Mn and Fe) in the environment. This type of study is important since due to the increase in use of coal, the Environmental Protection Agency of the State of Rio Grande do Sul should encourage the adoption of proper techniques for the disposal of residues generated in all steps of coal processing. The destination of areas for residue disposal, protection of surface and ground waters, coal preparation and processing, damage to the environment and economic issues are all important factors to be considered.

EXPERIMENTAL

Origin of coal ashes and sampling

Ashes studied come from the São Jerônimo Power Station -UTSJ that are disposed in areas surrounding it. Sampling procedures followed the ISO Norm [11]. The sampling site is shown in Figure1. Samples were carried to the laboratory (in Porto Alegre, RS-Brazil) in suitable polyurethane bags. A manual quartering followed, until four equal one-kilogram portions, representative of the global sample, were obtained. Finally, samples were comminuted to a particle size smaller than 149 µm (total fraction).

Water and sediments were collected according to standard procedures[12]. Water samples were placed in adequate bottles, cold-stored (in a box with ice) until arrival to the laboratory. There, they were stored in cold chamber at - 4°C up to the time of analysis. Samples destined for analysis of specific elements were preserved adequately in the moment of sampling, to maintain the activity of each element. Sediment samples were packed in plastic bags at low temperature and transported to the laboratory for further homogenization, quartering, drying (temperature up to 60°C) and size reduction in porcelain mortar (< 149 µm particle size).

Sampling points for water are shown in Figure 1 and are the following: Point 1: Porteirinha Stream, under the bridge of the RS Road 105; Point 2: Jacuí River, close to the coal discharge site; Point 3: water put in puddles close to the point of embarkation of the boat to General Câmara, along the RS Road 105.

Figure 1 also illustrates sampling sites for sediments: on the banks of Porteirinha Stream, close to the bridge of the RS Road 105 (Point 1) and in the Jacuí River's bank, by the site of coal discharge (Point 2).

Methodology

Ashes : Total extractions were made with hydrofluoric and hydrochloric acids. Partial extractions were done with a preliminary calcination of 1 g sample at 450°C for 24 hours. Afterwards, the sample was dissolved in 5 ml of concentrated HNO_3 (analytical grade, Merck) and taken to dryness in a water bath. Again it was dissolved in 5 ml aqua-regia ($HCl:HNO_3$, 3:1) and dried (T = 250° C). The residue was dissolved in 5ml of HNO_3 (conc.) and diluted to a volume of 50ml. To check the chosen method, another aliquot of sample was dried at 85°C for 12 hours. From it, 1g was weighted and digested with 10ml of aqua regia. The solution was heated at 250°C and evaporated to dryness. A second 10-ml aliquot of aqua regia was added. This procedure was followed until the complete elimination of coal matter from the sample. Three blanks were prepared, containing the same concentration of acids used in the sample preparation for both digestion methods.

Dissolution of metallic elements. Two methodologies of analysis were applied for this test:

1°) method A – was proposed for the characterization of residue's harmfulness by EPA-USA and corresponds to the ABNT 10005 Norm and to the Leaching Test - CETESB[13];

2°) method B – was proposed by the Instituto of Pesquisas Hidráulicas of the Universidade Federal of Rio Grande do Sul (IPH-UFRGS) to determine the behavior of a determined residue when disposed in a natural environment. [14]

In both methods the samples of residues (ashes) were tested also "in natura" as in size range < 149 µm. This smaller particle size aimed to increase the surface of contact and to make the residues characteristics more uniform. We tested the two procedures described below to determine the more adequate conditions for analysis.

The following procedures were adopted for both size ranges:

1) Without agitation : a) For a relatively short period of time (48 hours) to avoid that bacterial cultures develop in the test medium or other effects, and b) For a long period of time (7, 14, 30, 60 days) to achieve conditions of better equilibrium;

2)With agitation: The adopted systematics was the same as described in the item above for 12 hours at 60°C, using a portion of 1g of sample;10ml deionized water at a constant pH value (= 5) during the test [13]. The other consisted of 25g of sample in 125ml of distilled deionized water (20% pulp); the pH wasn't adjusted, its changes were monitored.

In each step, after the adequate interval of time, an aliquot was taken for the analysis of dissolved metals.

Extractable metals (those that are not a part of the crystalline lattice) were determined from ashes. The procedure of analysis adopted consisted of changing the pH to 6.0, 4.0 and 1.5. For these tests, 25g of "in natura" sample were treated with a solution of aqua regia and sufficient HNO_3 to achieve the desired pH value. This solution was left for 3 hours under agitation in a semi-turbulent flow regime. Samples were prepared in duplicate for analysis of metals (final volume of 100ml). Afterwards 5% (volume proportion) of nitric acid was added and concentrated to complete dryness. Finally the residue was dissolved in 20 mL of a 10% HNO_3 solution.

The determination of metals (Ni, Pb, Fe, Cu, Zn) in all extracts was performed by Flame Atomic Absorption Spectrometry (FAAS).

Waters: parameters determined were: pH, Hg (cold vapor technique), and Cd, Co, Pb, Fe, Ni, Zn, Mn, Al and Mg, by FAAS techniques. These elements were determined in both dissolved and total forms, following procedures recommended by Standard Methods[12].

Sediments: chemical analyses on "margin sediments" were performed for the determination of extractable metals in a certain level of acidity, at pH values of 6.0, 4.0 and 1.5. The technique applied was the treatment of a solution, 1g sample in 10 ml distilled deionized water, with HNO_3 up to the desired acidity, followed by stirring in a semi-turbulent regime for 3 hours. After heating (250°C) up to almost complete dryness, 2.5 ml of HNO_3 were added and the solution was again heated to a small reflux. It was then diluted to a volume of 25 ml for the determination of Cd, Co, Cu and Pb.

At the present time, the poor sensibility of FAAS for the determination of such levels of metals is widely known. However, the time when the experimental part of at this study was done (1987), this was the only technique available at the institution where it was carried out. Today, in the particular case of analysis of metals in sediments, exist scientifically safer methods that permit a study of metallic mobility. They are recognized by ISO Scientific Committees for their analytical rigor. They were given certified reference materials (CRM) specific for the study of metallic mobility in sediments [15,16].

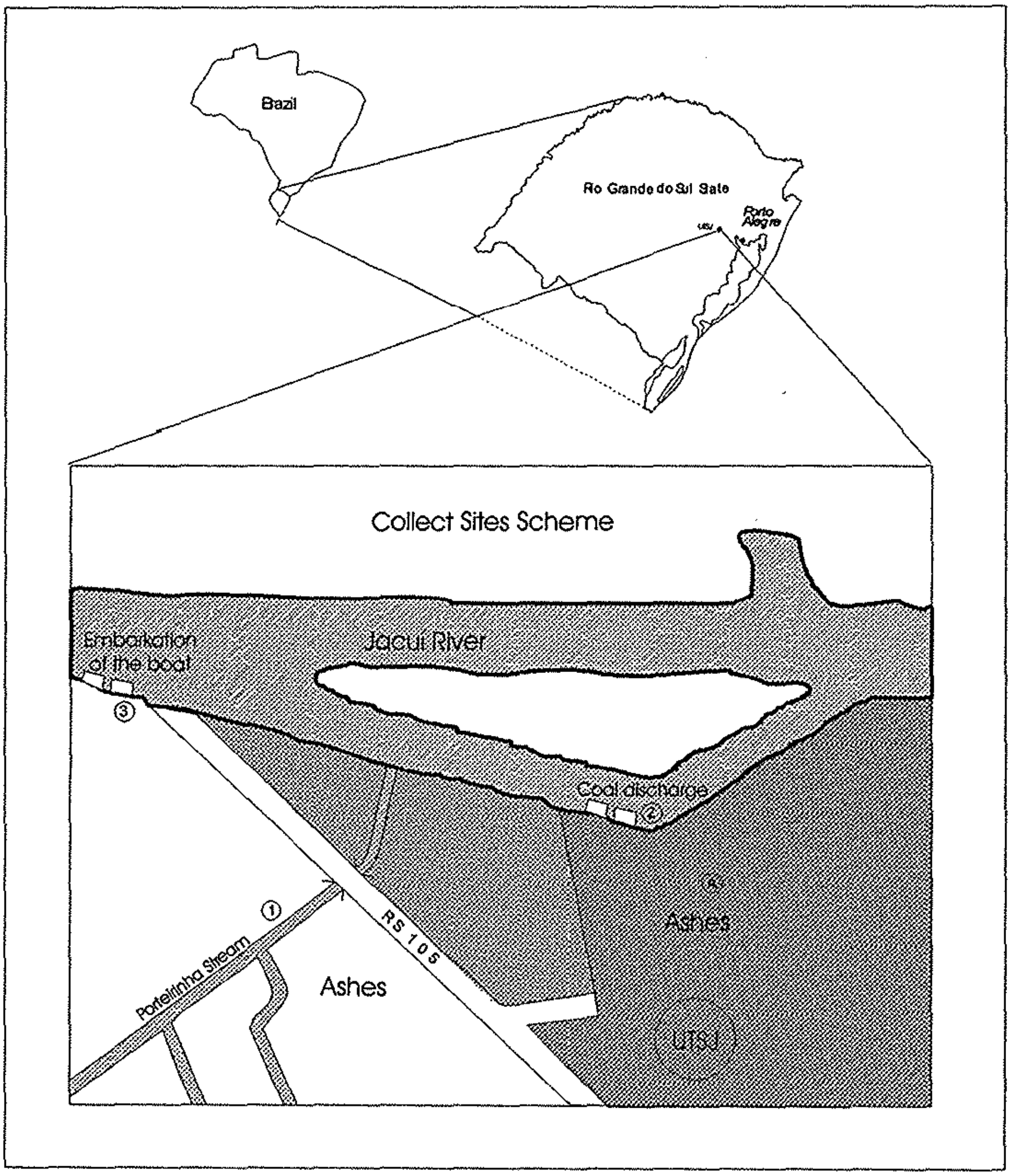

Figure 1. Scheme of the sampling points

RESULTS AND DISCUSSIONS

Ashes

Table I presents the results of total and partial extraction of metallic elements (Cd, Co, Cu, Pb, Fe, Ni, Zn and Mn) present in ashes produced by Usina Termoelétrica São Jerônimo. The difference between those values obtained in total and partial extractions can be explained by distinct associations of metals to the residual organic and inorganic fractions that, depending on environmental conditions, release them in greater or lesser degree in the environment. Nearly 40% results showed low indices of partial extraction (< 20% in relation to the total fraction) indicating that the elements Mn, Cd, Pb, Fe and Co are mostly likely to be associated to the aluminossilicate fraction. However, the other elements (Ni, Zn and Cu) showed a higher degree of dissolution. This indicates that they are present in greater amount in the form of oxides and sulfates, and more significant concentrations of them are likely to appear in aqueous environment [17].

Ashes from UTSJ present basic pH values (pH~9), confirming data reported by other authors that reported an alkaline character for residues from coal combustion [5].

Table II shows the concentration of metals extracted from ashes, varying the pH of the extracting solution. Data revealed a more significant mobility of metals in ashes in extremely acidic medium (pH=1.5), in agreement with results presented by other authors[6,7,9,18,19]. Meanwhile, it was verified that elements presented, even at pH=1,5, low mobility when compared to results obtained in the total extraction. With pH values of 4 and 6, extraction is practically negligible, because metals are below the analytical detection limit of the method (see explanation above referring to analysis of sediments).

Table I: Concentration and partial extraction percentage of metallic elements in ashes

	Concentration ($\mu g g^{-1}$)		%
	Total Extraction (TE)	Partial Extraction (PE)	PE/TE x 100
Cd	2.0	0.3	15
Co	8.0	3.0	38
Cu	29	22	76
Pb	37	7.0	19
Fe	12000	4000	33
Al	--	5000	--
Ni	28	16	57
Zn	26	15	58
Mn	107	12	11

Table II : Concentration of metals from ashes as a function of the pH of the extracting solution.

	Concentration of metal ($\mu g g^{-1}$)		
	pH = 6.0	pH = 4.0	pH = 1.5
Cd	< 0.002	< 0.002	< 0.003
Co	< 0.006	< 0.006	0.092
Cu	< 0.004	0.005	0.275
Pb	< 0.012	< 0.012	0.073
Al	< 0.111	< 0.111	36.4
Fe	0.064	0.141	85.9
Ni	< 0.006	< 0.006	0.302
Zn	0.014	0.017	0.407
Mn	0.004	0.006	1.28

Figure 2 a, b, c, d shows the results of the mobility studies for Zn, Ni, Mn and Fe from ashes in different systems (in aqueous medium as a function of time, using different methods of extraction). Method A presented a higher efficiency for the extraction of Mn, Zn, Ni from "in natura" ashes in relation to method B. This can be attributed to the pH correction and the maintenance of an acidic medium (pH=5), favoring the release of these elements. Meanwhile, method B with agitation was the most efficient in the 20-day period of iron extraction. The mobility curves for Ni and Zn show two subsequent increases. This can be explained by the stirring to which the sample was submitted, that could lead to fragmentation of the residue and a subsequent growth in the surface area allowing a closer contact of the aqueous medium with the unreleased metals.

Method A without agitation was also more efficient in the release of metals in the aqueous medium, when 24 hours was the period used for maximum solubilization, while for method B a longer period was required (10 days). In both cases, Ni, Zn and Mn presented similar behaviors.

In relation to particle size, the fraction with size < 149 µm presented a higher index of release of metals in the aqueous medium, generally showing higher concentrations than "in natura" ashes for both methods (Figure 3 a, b, c, d). These results can be attributed to the finer particle size that enhances metallic release in aqueous medium in more significant amounts.

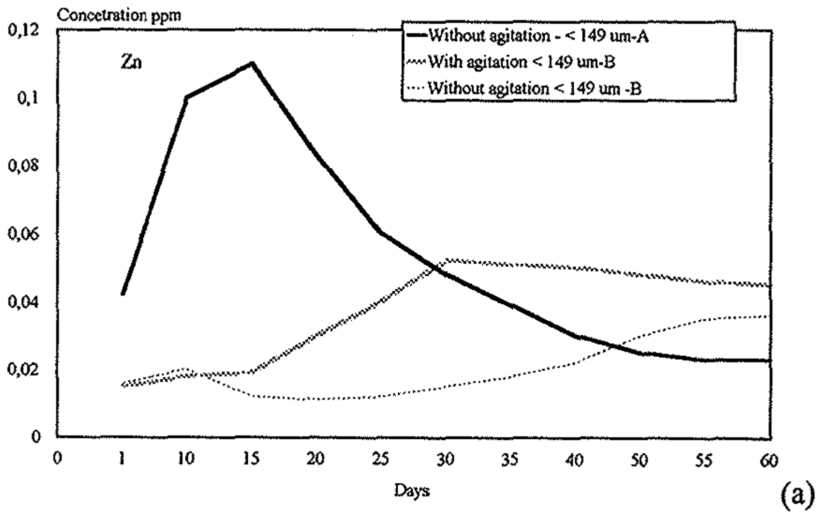

Figure 2a : Study of the mobility of Zn in ashes in function of time in different systems.

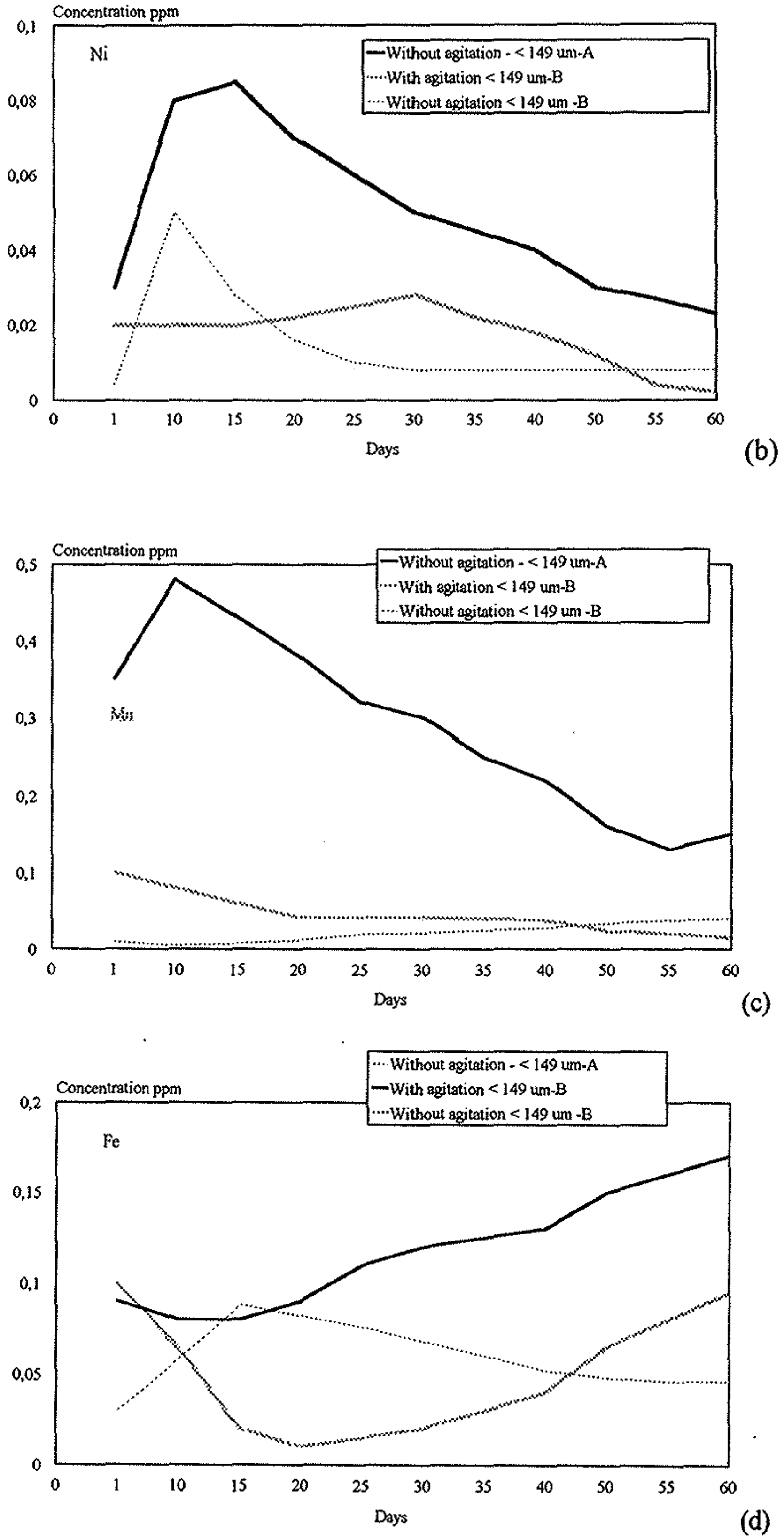

Figure 2 b,c,d: Study of the mobility of Ni, Mn and Fe in ashes in function of time in different systems.

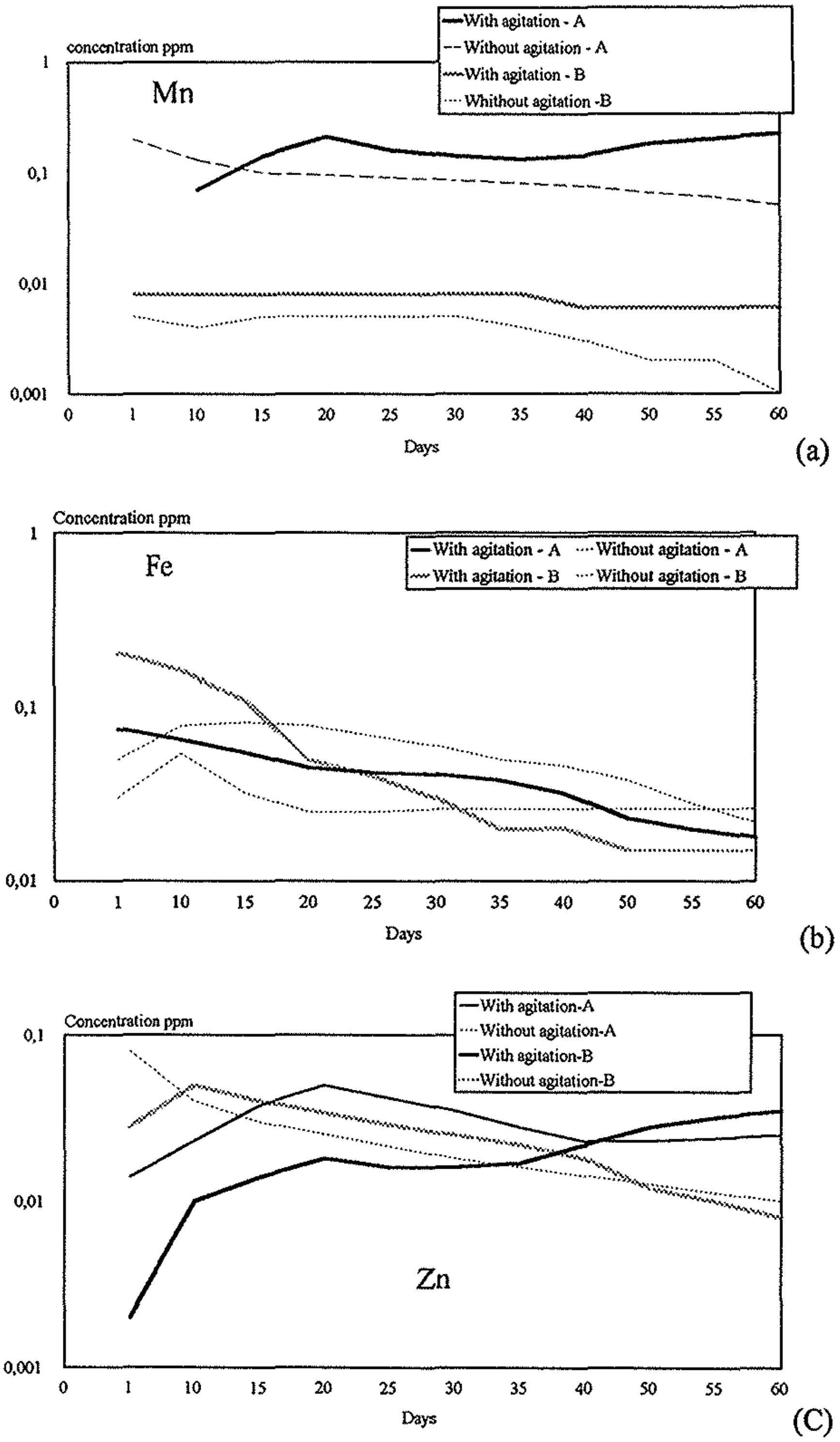

Figure 3 a, b, c : Study of the mobility of Mn, Fe and Zn in ashes of particle size less than 149 µm as a function of time, using two different methods of extraction.

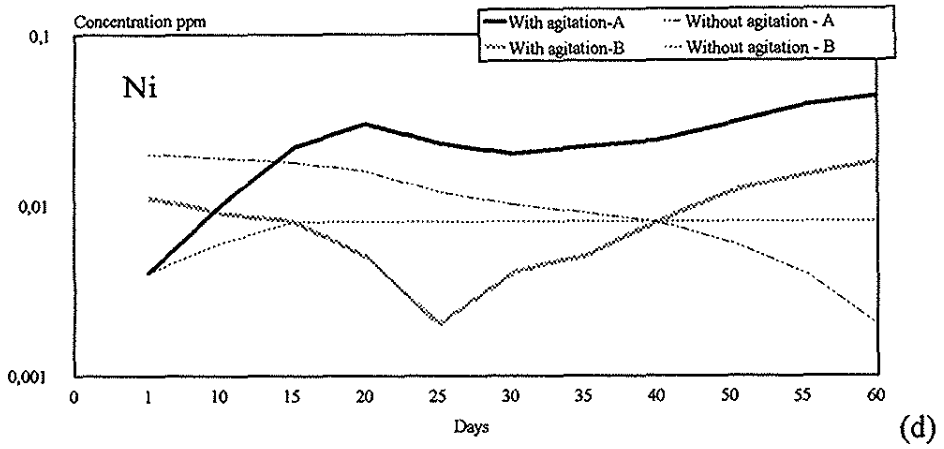

Figure 3 d : Study of the mobility of Ni in ashes of particle size less than 149 µm as a function of time, using two different methods of extraction.

Surface waters

In three sites close to the São Jerônimo Power Station, where the contamination by ashes was visible, pH and total and dissolved metals (Cd, Co, Cu, Ni, Pb Zn, Cr, Mn and Fe) were determined in surface waters (Figure 4). The pH at these sites was close to neutral, ranging between 6.2 and 6.4. The results of metallic contents were below the detection limit of the method for Cd, Co and Ni. The concentrations of the other elements, except for Fe, were inferior to the values recommended by Brazilian Legislation of the Conselho Nacional de Meio Ambiente (CONAMA) for class II water courses (CONAMA, Resolution n°020/86). These elements did not present variations between total and dissolved concentrations, except for Pb and Mn, because of the ease with which these elements associate to suspended particles and Fe because of its elevated content in ashes (Figure 2) and also in sediments of the Jacuí River [20].

Sediments

In sites of the Jacuí River banks, metals extractable from sediments were determined, with variations in pH and the results are shown in Figure 4. A relation between these data and those obtained for metals extractable from ashes (Figure 5) is verified, leading to the conclusion that the collected sediments are basically made up of residues from the power station, as visually observed.

The elevation of pH from 6.0 to 6.4 and from 4.0 to 6.3 at sampling points 2 and 3, respectively, indicates the presence of ashes in these sites, with alkaline characteristics. At low pH (1.5) the concentrations of metal ions is much higher indicating again that that the coal ashes are alkaline in character.

When the results of extractable metals from sediments (Figure 5) and ashes (Table I) are compared, one can notice that data from the latter are lower than those values obtained for sediments. This can be attributed to a cumulative effect of element deposition in sediments at the sampling point 1, and to this effect the presence of coal fines should be added, as it's visually confirmed at the point 2

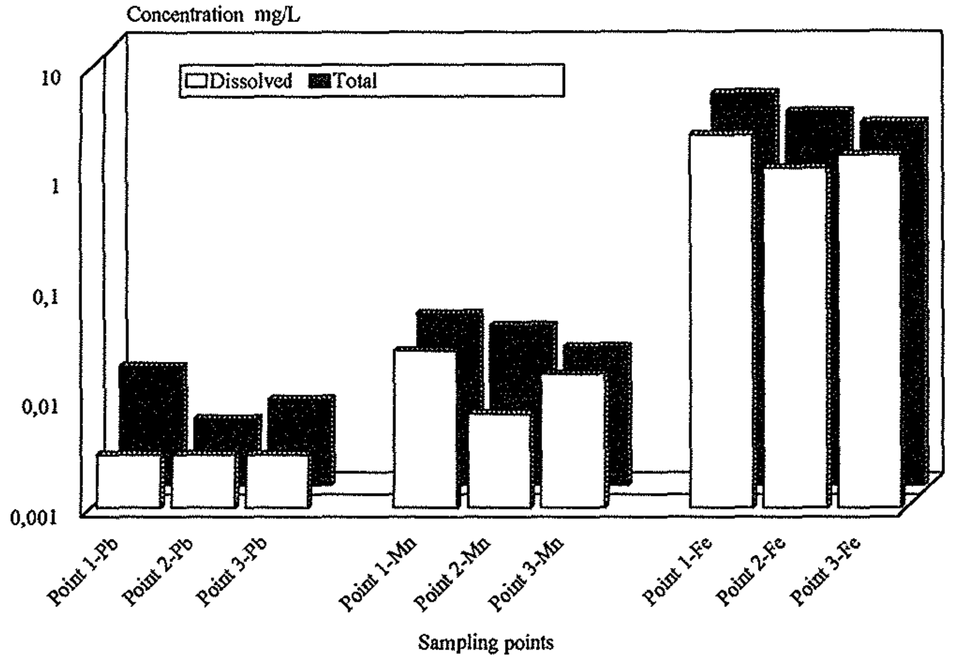

Figure 4 : Concentration of dissolved and total metals in surface water

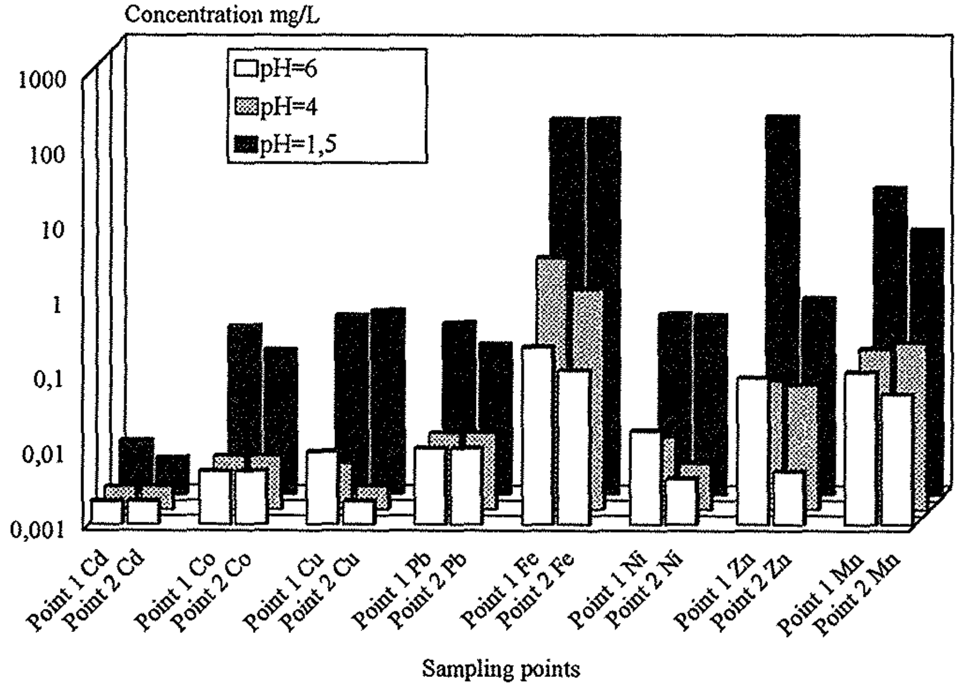

Figure 5: Efficiency of extraction of metals from sediments with variation of the pH of the medium

The experimental results obtained permit us to conclude that the bottom ashes from the São Jerônimo power station present a basic character and the release of Ni, Pb, Cd, Zn, Cu, Mn and Fe from this residue is much more significant at low pH.

From the methods studied in this work, that in which an acidic pH in the medium is corrected and maintained throughout all the experiment (method A), favored the release of Zn, Ni and Mn. The concentrations of such elements increased with the time of extraction, reaching a maximum value in 20 days, while Fe presented a highest value in the earlier phase of the experiment, 24 hours.

At Jacuí River's banks, metals in water were below those values established by the Brazilian law, except for Fe and Al. Contamination by ashes from the power station was verified in the sediments. A cumulative effect of deposition in "marginal sediments" of Jacuí River was found, since values of extractable metals from sediments surpassed those found in ashes.

Based on the exposition we suggest that the final disposal of power station residues should be conducted under adequate criteria and conditions, so that they do not cause more severe environmental problems.

A systematic study is recommended to obtain more technical subsidies with relation to residues from power stations. This will make possible the creation of norms that technically define the specific use of ashes.

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