

Geogenic factors affecting the selenium(IV) distribution in sediments from Madeira River basin, Brazil

A. da Costa Neto^{*1}, D. M. Bonotto² & F.L.A. Mesquita³

^{*1}*In memoriam, Departamento de Ciências Exatas, Fundação Universidade Federal de Rondônia-UNIR, Brazil.*

²*Departamento de Petrologia e Metalogenia, Instituto de Geociências e Ciências Exatas-UNESP, Rio Claro, Brazil.*

³*Curso de Zootecnia, Universidade Estadual Vale do Acaraú-UVA, Sobral, Brazil.*

Abstract

This investigation was carried out at the Madeira River basin, located in the state of Rondônia, Brazilian Amazon. Sediments from Madeira River between Teotônio and Santo Antônio waterfalls along 25 km upstream from Porto Velho, the capital of Rondônia state, and from nine lakes located around Porto Velho municipality were chemically analyzed for Se (IV) in order to evaluate the main factors affecting the Se(IV) distribution in the environment. Selenite ion was chosen to investigate the selenium behavior in the area, because acid conditions are dominant there. The importance of clays, iron oxides, organic matter and minor refractory minerals was considered in order to explain most of the obtained data.

1 Introduction

Selenium was discovered in 1817 by Berzelius and Gahn who used copper pyrites as a source of SO₂ for the H₂SO₄ manufacture and generated a residue containing a new element that was named from the Greek σελήνη, the moon [1].

In present days, it is used in photocells, xerography, metal rectifiers, for the dehydrogenation of hydroaromatic compounds valuable in elucidating the structure of several natural products, as an oxidizing agent and catalyst in organic syntheses, as oxidation inhibitors in lubricating oils, in shampoos as a

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dandruff inhibitor, as bases for phosphors, for red ceramic and enamel pigments, for coloring glass red or reddish yellow and to neutralize the greenish tints caused by the presence of iron in certain types of glass in railway, marine and other signal lamps.

Selenium is necessary as a trace nutrient to man, but it may also cause toxic effects when ingested in non-appropriate amounts. For instance, hydrogen selenide when breathed in air, even at very great dilutions, causes headache and nausea, and, at high concentrations, acute irritation of the mucous membrane; many selenium compounds cause eczema and inflammation on contact with the skin, being absorbed essentially in the kidneys, spleen and liver when ingested, and only slowly released from the body, causing the subject to have extremely offensive smelling breath and perspiration for a long period [1]. The selenium deficiency and toxicity, mainly in the field of animal nutrition, has been considered elsewhere [2,3], with the problem of seleniferous soils and their effects on animal and human population being reported in Colombia since colonial times [4]. Seleniferous agricultural drainage wastewater has become a new major source of pollution in the world, where, in the USA, large areas of farmland in 17 western states generate contaminated drainage with Se concentrations much higher than the US Environmental Protection Agency water-quality criterion for the protection of aquatic life [5].

Thus, environmental problems involving generated natural and anthropogenic selenium are becoming widespread, being necessary to enhance the knowledge of its behavior in different situations. Selenium predominantly occurs in four forms in the natural environment. The highly soluble selenate (SeO_4^{2-}) is found in alkaline oxidizing environments. In more acidic environments, selenium tends to occur as selenite (SeO_3^{2-}) ion, which is not as soluble as selenate, whereas in more reducing environments, selenium may occur as the metal (Se^0) or the selenide (Se^{2-}) ion [6]. The types of reactions that affect selenium in sediments can be both biotically and abiotically controlled, involving conversions between particulate and dissolved phases and including redox reactions able to change the oxidation state of selenium [7].

This investigation focused the selenium presence in sediments of the Madeira River basin, Brazilian Amazon, an area where special attention has been paid to mercury inputs due to gold mining activities [8]. Because the development of farmlands in Brazilian Amazon is a recent issue that has caused several debates and discussions, it is important to provide information about the selenium behavior there since its content in soils and grasses of cattle farms have induced variable degree of intoxication on animal and human population [4]. Selenite ion, Se(IV) , was chosen to investigate the selenium occurrence in the area, due to the dominance of acid conditions there.

2 Material and methods

The Madeira River is one of the largest tributaries of the Amazon River, extending from Bolívia and crossing the city of Porto Velho, capital of Rondônia State in Brazil, which is the most populated site (population approximately

300,000, according to the 1999 census) along it. The Aw-tropical rainy climate (Köppen classification) characterizes Rondônia State, i.e. the relative air humidity ranges from 74.2 up to 90.8% and air temperature from 20.7 up to 32.2 °C [9]. The wet season (average rainfall = 250 mm/month) occurs between October and April, whereas the dry season (average rainfall = 20 mm/month) between May and September [9].

This study provided Se(IV) distribution data for two types of materials: 1) sediments collected by [8] at 12 points along 25 km in the Madeira River between the Teotônio and Santo Antônio waterfalls, upstream from Porto Velho (area of about 260 km²) (Fig. 1); this sector of the river is not suitable for navigation, and fieldwork was performed from a small boat during the dry season in a two-week period in August 1996. Approximately 500 g of sediments were collected from each sampling point with a bottom dredge that slowly trawled upstream and transferred samples to a half-filled thick polyethylene bag. 2) core sediments (20 to 80 cm deep) collected by [9] at nine lakes between Jamari and Ji-Paraná rivers, that are tributaries of Madeira River; the studied area is situated between 8° and 9°S and between 62° and 64°W (Fig. 1), being the fieldwork realized during October 1999 and February 2000, also utilizing a small boat that crossed several *igarapés* in order to have access to the lakes. The lakes exhibited variable dimensions (5 to 10 m deep, 600 to 7000 m long, and 300 to 1200 m wide), occurring clear and black waters depending on the dissolved organic matter content. A 1-m long acrylic tube (10 cm in diameter) adapted to an iron outliner was driven into the sediments preferentially at the middle of each lake, being each profile cut in 5-cm thick slices, that also were transferred to polyethylene bags.

All bags containing the sediments were stored in iceboxes and transported to the laboratory. The material was dried at 60°C, crushed, quartered, sieved for separation of the < 200 mesh (< 74 µm) size fraction, and divided into aliquots for different analyses. The determination of Se(IV) was performed in approximately 0.5 g of dried material, that was immersed in 1 mL of high purity distilled water, being added 2 mL of a 3:1 HCl-HNO₃ mixture for utilizing the acid digestion procedure through heating at 50°C during 15 minutes [10]. The solution was separated from the sediments by filtration, being its volume elevated up to 100 mL with pure distilled water. Standard analytical techniques [11] were used for treating the solution in order to obtain its selenium concentration by spectrophotometry. Diaminobenzidine reacted with all selenium present as selenite (Se⁴⁺) to give a yellow-colored piazselenol complex extracted with toluene, being its color read by Hach DR/2000 spectrophotometer at 420 nm [11]. Table 1 reports all obtained Se(IV) concentration data.



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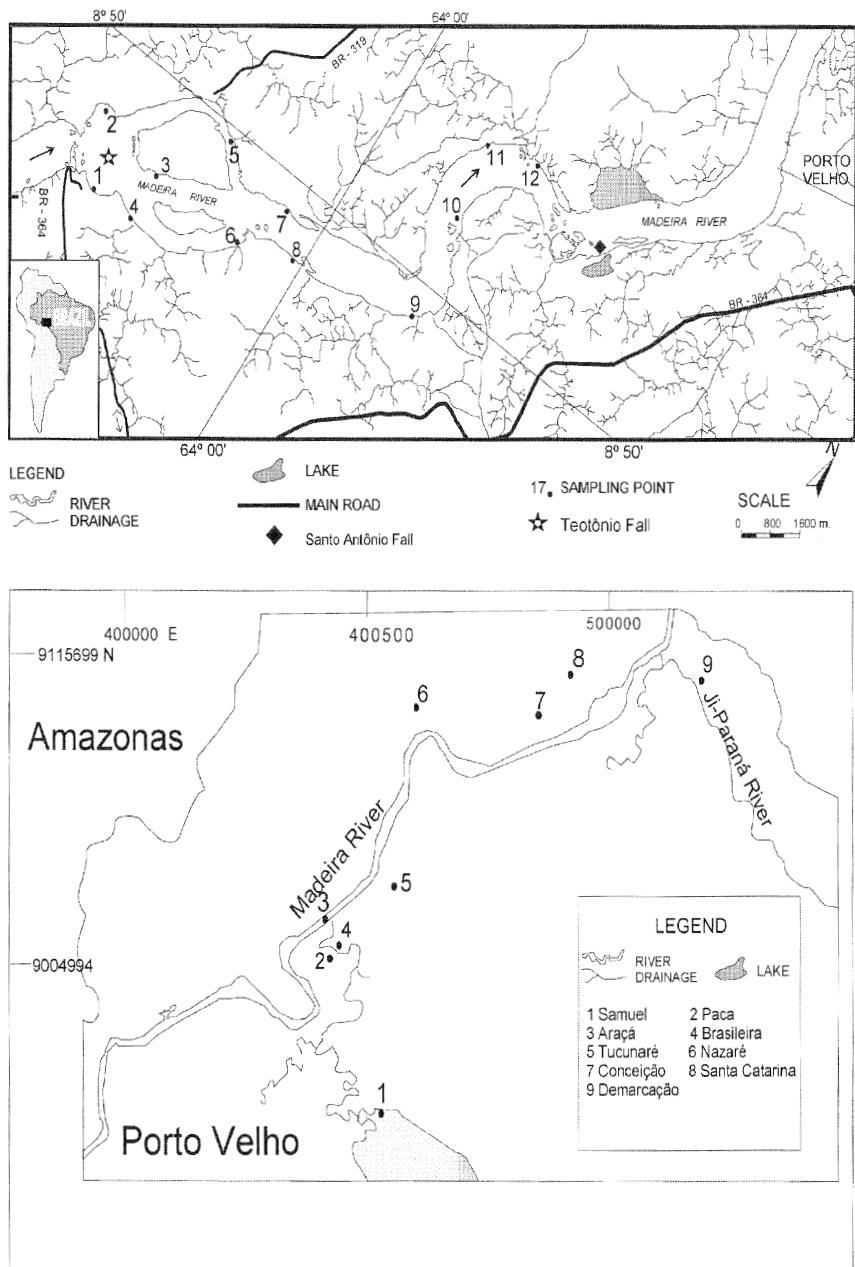


Figure 1: Location of Porto Velho city and sampling points for bottom sediments at Madeira River basin, Rondônia State, Brazil [8,9].

Table 1: Se(IV) content (in ppm) of sediments from a) Madeira River between Teotônio and Santo Antônio falls and b) lakes.

(a)	Sampling Point No.	1	2	3	4	5	6	7	8	9	10	11	12	Mean
	Value	12	6	2	2	< 1	2	2	6	4	6	6	8	4.8

(b)	Depth Range (cm)	Samuel	Paca	Araçá	Brasileira	Tucunaré	Nazaré	Conceição	Santa Catarina	Demarcação
	0-5	6	16	2	2	16	4	12	4	18
	5-10	2	16	2	6	22	6	10	2	4
	10-15	8	16	2	6	18	2	18	6	2
	15-20	4	4	< 1	12	8	6	10	6	2
	20-25		10	2	8	8	8	4	14	4
	25-30			4	10	14		2	6	2
	30-35			4	14	10		4	4	10
	35-40			8	16	4		2	6	
	40-45			4	14	6		6	8	
	45-50			4	8	6		2	6	
	50-55			2	18	2				
	55-60			6		2				
	60-65			4		2				
	65-70			4						
	70-75			6						
	75-80			10						
	Mean	5.0	12.4	4.1	10.4	9.1	5.2	7.0	6.2	6.0

3 The importance of weathering processes

Rock weathering processes often cause chemical changes in soils and sediments. In lateritic soils, silica may be eliminated from silicates, forming free Al-Fe hydroxides [12]. Intense weathering conditions favor the occurrence of laterisation, enhancing the Al-Fe content and diminishing the Si concentration in relation to simply kaolinized rock matrices [13]. In general, the evolution of laterisation processes is related to the nature of the original rock matrix and involves all Al-silicates rock types, with their occurrence affecting very intensively the crystalline rocks of the studied area. The chemical composition of the analyzed lake sediments [9] reflects these aspects, as demonstrates the generalized inverse significant correlation between SiO_2 and Al_2O_3 (Fig. 2). Thus, Si-poorer sediments are more Al-enhanced, suggesting the occurrence of more prolonged/intense weathering processes, with the opposite also being probable.

Al_2O_3 is a constituent often used to identify gains and losses during chemical weathering [14,15]. Such oxide is assumed to remain constant in soil profiles, despite its variability in concentration against depth [15]. $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios have been utilized by geochemists as weathering indices [16,17], with the highest values indicating less prolonged/intense processes. Each sediments profile

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plotted in Fig. 2 exhibited different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, thus, characterizing more/less prolonged/intense weathering processes. For instance, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios corresponding to 3-4.1 and 4.6-5 were found, respectively, for Brasileira and Santa Catarina lake sediments. The mean $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of each sediments profile was: Samuel=2.5, Paca=3.8, Araçá=3.8, Brasileira=3.2, Tucunaré=5.7, Nazaré=5.1, Conceição=4.3, Santa Catarina=4.8, and Demarcação=4.

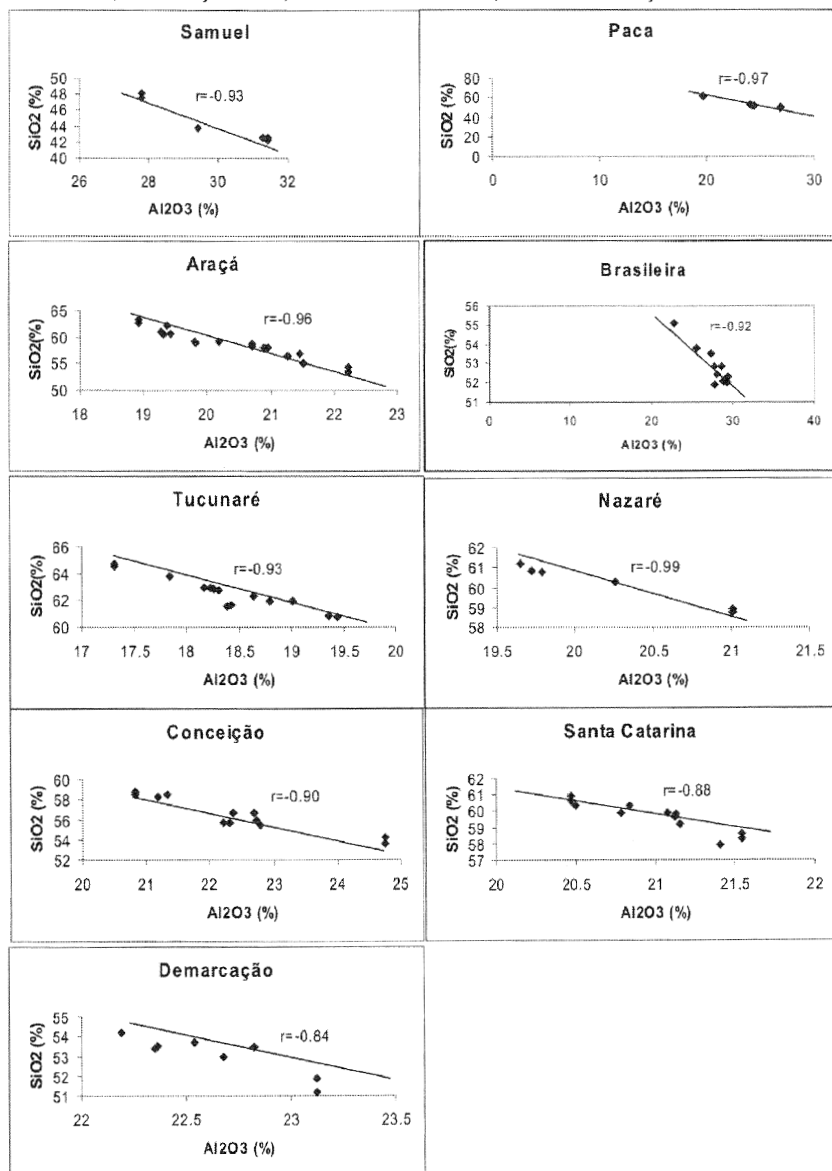


Figure 2: Relationship between SiO_2 and Al_2O_3 for core sediments of lakes at the Madeira River basin, Rondônia State, Brazil. Data reported by [9].

4 The presence of Se(IV) at the Madeira River basin

The mean Se(IV) content (4.8 ppm) of sediments between Teotônio and Santo Antônio falls is about 100 times higher than the average Hg content (0.047 ppm) [8], with non significant correlation being found between Se(IV) and other parameters analyzed for these sediments [8]. The average Se(IV) content of most of the core lakes (4-7 ppm) is practically equivalent to the value found for sediments from Madeira River, whereas those determined for Paca, Brasileira, and Tucunará lakes (9.1-12.4 ppm) correspond to the highest values reported for soils close to the border of streams recognized as carriers of seleniferous sediments in Colombia [4].

Partial hydrolysis developed under slow flow conditions may occur in several intensity degrees during weathering in tropical regions characterized by hot and wet climate. X-ray diffraction of sediments from Madeira River between Teotônio and Santo Antônio falls [8] identified quartz, mica, feldspars, pyrophyllite, gibbsite, ilmenite, amorphous Fe-Mn oxides, kaolinite and chlorite-vermiculite mixed layers, and some of these minerals represent alteration products of granitoids (i.e. feldspars yield kaolinite). The presence of kaolinite was also confirmed on the study of the stability relations of mineral phases in the systems $K_2O(CaO, Na_2O)-Al_2O_3-SiO_2-H_2O$ [8].

An aspect frequently emphasized in literature [5,7] is that the Se(IV) selenite ion, as $HSeO_3^-$ and SeO_3^{2-} , exhibits a great tendency to be absorbed by clay minerals and Fe oxi-hydroxides. Several direct significant relationships reflecting this aspect were found when the data reported by [9] were correlated with the measured Se(IV) content, as plotted in Figs. 3-5, i.e. $Al_2O_3-CaO-MgO-Na_2O-K_2O-TiO_2-Fe_2O_3$ vs. Se(IV). The inverse significant correlation between SiO_2 and Se(IV) (Fig. 3) is related to the general inverse relationship between SiO_2 and Al_2O_3 (Fig. 2).

Beyond the typical $Al_2O_3-Fe_2O_3$ accumulations during chemical weathering, other constituents also are present in resistates/minor refractory minerals more resistant to weathering (such as apatite, zircon, and sphene, among others) that are incorporated intact in the coarser grained fraction of the analyzed sediments, becoming additional sorbents for selenite ion. A good example for this is the direct significant relationship between P_2O_5 and Se(IV) for core sediments from Paca, Conceição, and Tucunará lakes, as plotted in Fig. 4.

Organic matter as well has been considered an important complexing agent for selenite ion [5,7], and a direct evidence for this was found for sediments of Demarcação lake (Fig. 6). Since the Loss on Ignition (LOI) expresses the organic matter + adsorbed water + water in crystal lattices and fluid inclusions + CO_2 of carbonates + SO_2 of sulfides, it is a parameter related with organic matter, thus, justifying the significant relationships between LOI and Se(IV) plotted in Fig. 6.

Hg absorption by organic matter was identified on the analyzed sediments [9], so that the significant relationship between Hg and Se(IV) plotted in Fig. 6 for core sediments of Nazaré and Demarcação lakes is certainly related to the organic matter influence on the heavy metals absorption. However, in the case of core sediments of Brasileira lake, the significant relationship between Hg and

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Se(IV) (Fig. 6) may be justified by the presence of clays, amorphous Fe-Mn oxides, and minor refractory minerals, rather than organic matter. An opposite trend between Hg and Se(IV) was found for core sediments of Conceição lake (Fig. 6), being related to the contrary behavior of these constituents with the core depth, i.e. Hg increases with depth, whereas Se(IV) decreases with depth [9] (Fig. 6); neither Hg nor Se(IV) are correlated with organic matter in this sediments profile. Another significant relationship expressing the decrease of Se(IV) with depth was verified for core sediments of Tucunaré lake (Fig. 6).

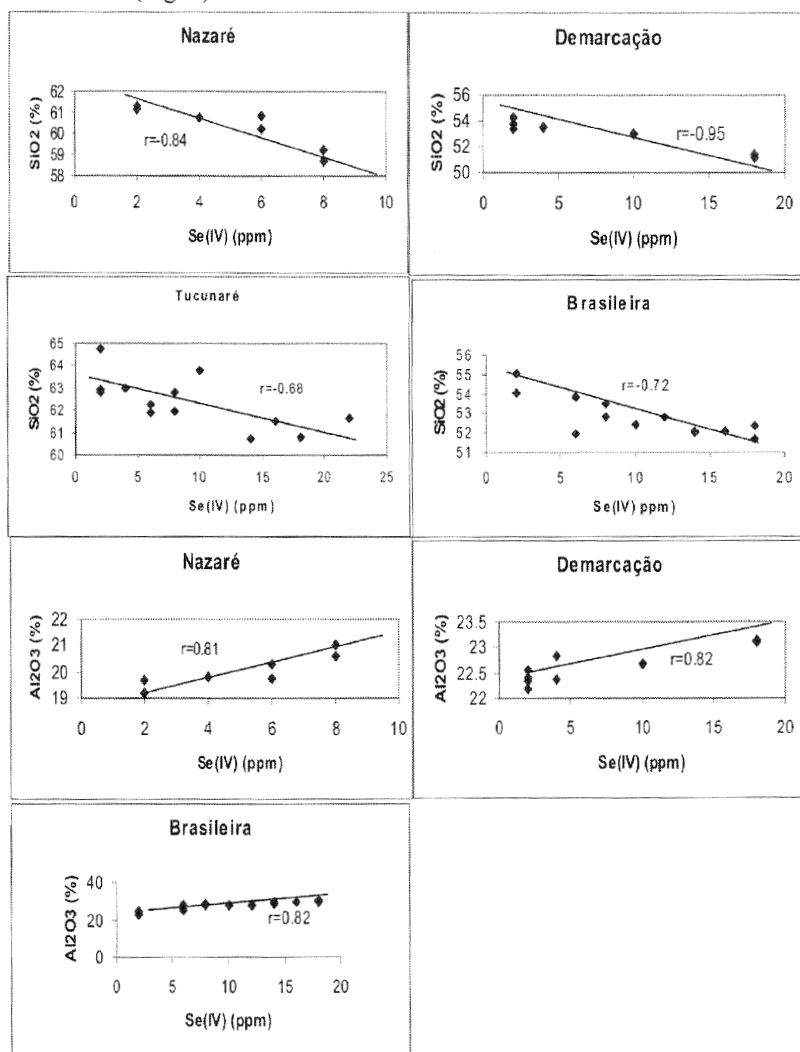


Figure 3: SiO_2 - Al_2O_3 vs. Se(IV) relationships for core sediments of lakes.

The Se mobility in the environment is dependent of biogeochemical, physical and chemical parameters, that are expressed, for instance, by temperature, pH, redox potential, dissolved oxygen and sulfur in the water column, phytoplankton composition, bioturbation occurrence, and biological activity intensity, among others [7]. Despite their importance on the Se(IV) migration, they were not properly evaluated during the development of this investigation. Therefore, some of them possibly may be important/responsible for explaining the significant relationships reported in Table 2 for several lakes of the studied area, which are opposite to those plotted in Figs. 2-6.

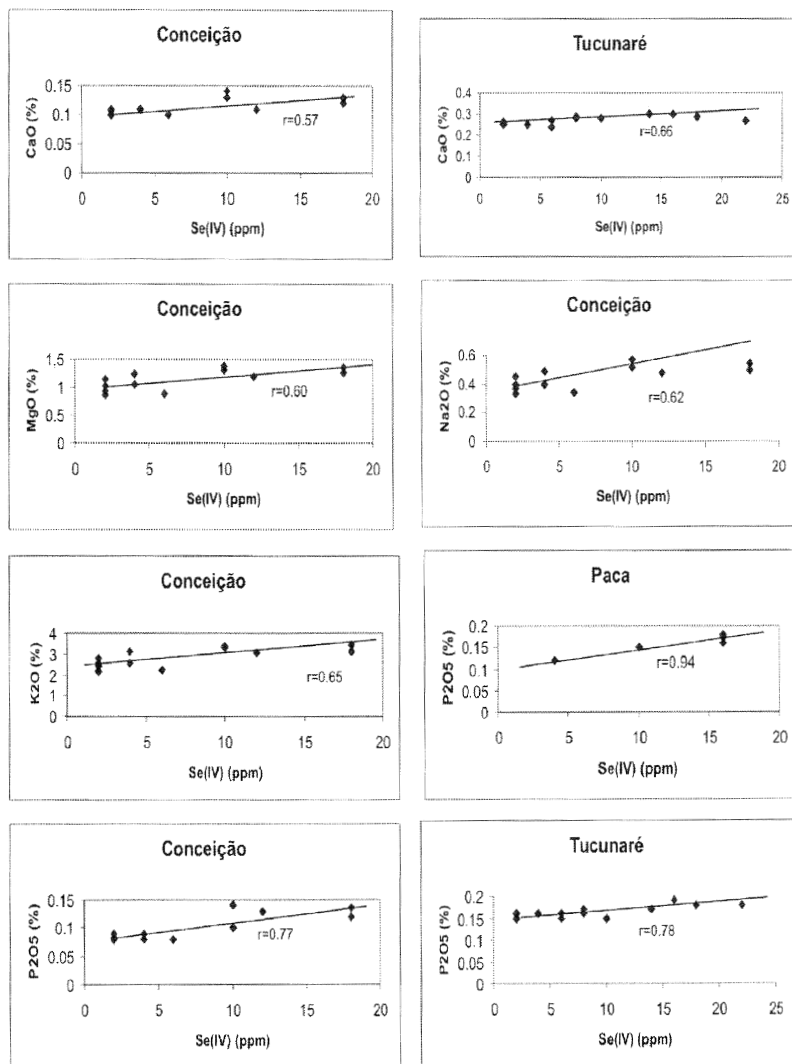


Figure 4: CaO-MgO-Na₂O-K₂O-P₂O₅ vs. Se(IV) relationships for core sediments of lakes.

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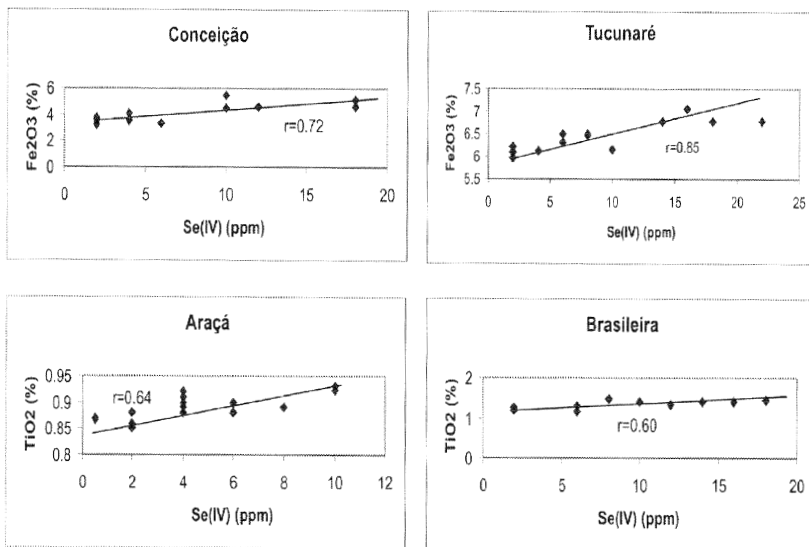


Figure 5: Fe₂O₃-TiO₂ vs. Se(IV) relationships for core sediments of lakes.

In general, national standards [18,19] provide maximum Se permissible concentration limit in drinking water, not establishing Se concentrations in sediment quality guidelines for the protection of aquatic life. Despite this, it is important the Se monitoring on these materials due to the possibility of its assimilation by biosphere and recognized health hazards caused to animals and humans. The results of this investigation constituted a contribution to improve the knowledge about the Se distribution in the Brazilian Amazon, generating useful information for researchers/decision makers interested on its adequate management for agricultural purposes.

Table 2: Significant correlation coefficient among Se(IV) content (ppm) and other parameters evaluated by [9] for lake sediments of Madeira River basin.

Parameter	Lake					
	Conceição	Santa Catarina	Demarcação	Tucunaré	Araçá	Brasileira
Depth					0.68	0.78
SiO ₂		0.64			0.62	
TiO ₂	-0.68		-0.70			
Al ₂ O ₃					-0.58	
Fe ₂ O ₃					-0.64	-0.74
MnO			-0.83			-0.67
MgO		-0.61	-0.85		-0.66	-0.68
CaO		-0.57				-0.72
Na ₂ O				-0.73		-0.68
K ₂ O			-0.88			-0.64
P ₂ O ₅					-0.59	-0.72
LOI		-0.73				

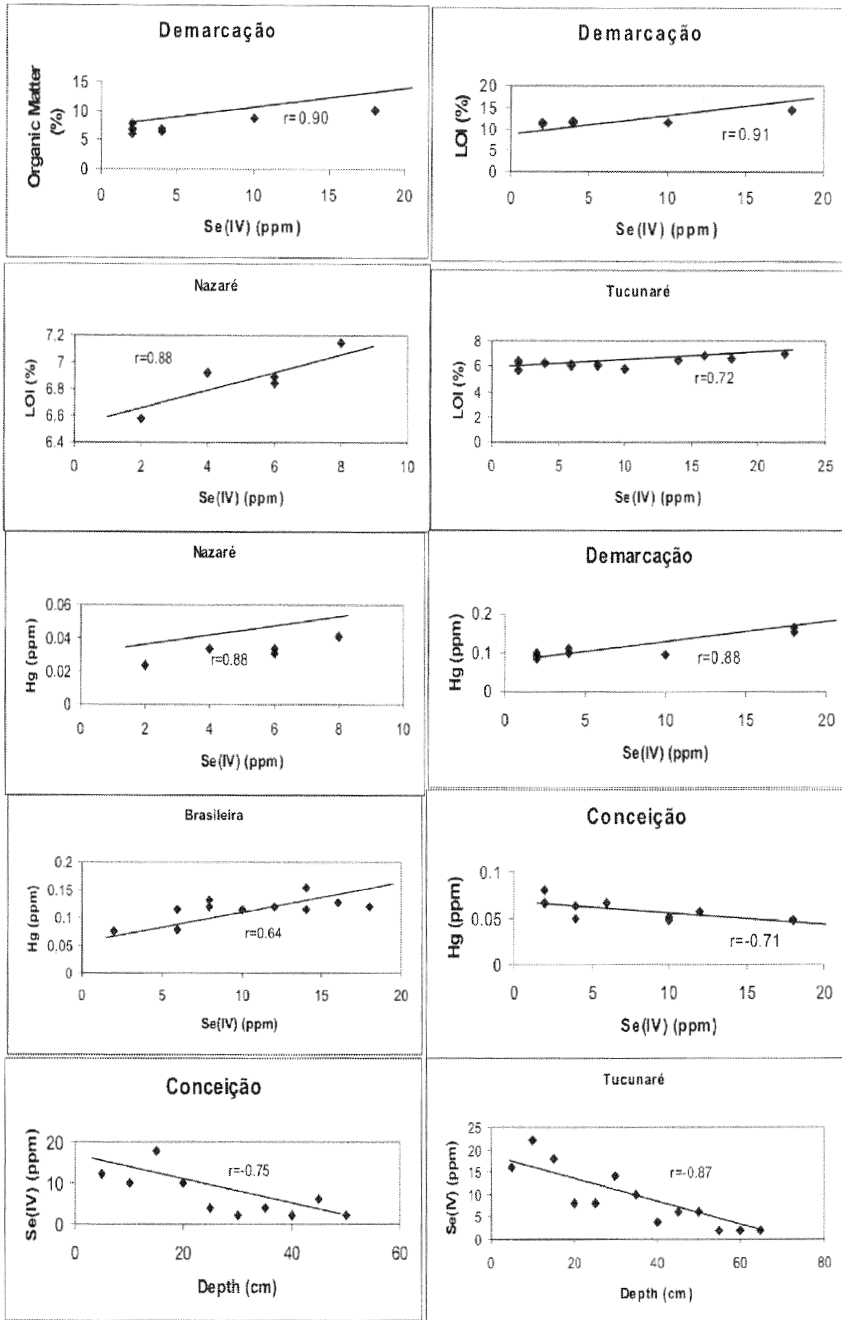


Figure 6: Organic Matter-LOI-Hg vs. Se(IV) and Se(IV) vs. depth relationships for core sediments of lakes.



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