

COMPARISON OF DIFFERENT ENRICHMENT FACTORS TO ASSESS THE NATURAL ACCUMULATION OF TRACE ELEMENTS IN SEDIMENT CORES FROM NHECOLÂNDIA PANTANAL

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ABSTRACT

Four sediment cores were collected at different lakes of salty water, commonly known as “Salinas”, in the Nhecolândia Wetland. In the collected cores, Salina A, Salina 6, Salina M and Salina V, the elements As, Ba, Co, Cr, Cs, Fe, Hf, K, Na, Rb, Sb, Se, U, Zn and rare earth elements Ce, Eu, La, Lu, Nd, Sc, Sm, Tb and Yb concentrations were determined by instrumental neutron activation analysis (INAA) technique. Aiming to verify the best criterion to evaluate the enrichment factor of minor and major elements in the sediment cores, three different calculations of the enrichment factor was employed. The first one, EF (Enrichment Factor), compares the normalized element concentrations with Upper Continental Crust normalized values, the second one, GNF (Geochemical Normalization Factor) compares the ratio between the element concentration and the normalizer with the depth in the sediment core; for these both factors the element Sc was used as a normalizer element. The third one factor, BEF (Base Enrichment Factor), compares the concentrations determined throughout the core with the results obtained in the base of it. With the results, it was possible to conclude that the best enrichment factor to evaluate the enhancement of elements in natural environments is the one that takes into account the core element concentration obtained in the base of it, BEF.

1. INTRODUCTION

Brazilian Pantanal is the largest wetland in the world, and it is a huge and rich ecosystem. The total area, about 200,000 km² during the rainy season, extends through central-west Brazil, eastern Bolivia, and northeastern Paraguay. Nhecolândia Pantanal, one of the 11 sub-

regions of Brazil Wetlands, is a very complex and sensible ecosystem with a vast vegetation and flora. The Paraguay River and its tributaries run through the wetlands and due to the low declivity of the plains in the North-South and East-West direction take four months or more to cross the entire wetland creating a great ecosystem [1].

The origin of the saline water is not well known and it can be by the evaporative concentration of the fresh water due to the existence of salt deposits and by the soil impermeability [2, 3]. Hence, the Salinas are perennial and forming lakes of saline water at high pH, ranging from 9 to 10 [4, 5, 6]. These wetlands have been affected in last decades by the soil uses and cattle breeding [3].

The sediment of an aqueous system represents an important source of study because it is a deposit of solid material, formed by different sources. Studying the sediment chemical composition in combination with geochemical tools, such as the material source lithology, process of soil formation, pH and sediment color is possible to evaluate the element concentrations during its genesis, permitting inferences about its probable source [7].

Studies performed at Nhecolândia Pantanal showed that the soil and sediment from this region are formed in its majority by sand [8]. Some studies [9, 10] analyzed the sediment chemical composition of the saline lakes from Nhecolândia Pantanal, but without the assessment of the sediment chemical enrichment, by natural or anthropogenic causes.

The enrichment factor has been used in different ecosystems and has proved to be an important tool to evaluate contamination. In this evaluation some elements can be used, as Al and Fe that remains constant during the weathering, or elements that present less variation, as Hf and Sc [11-17].

The main goal of this study was to determine a better instrument to evaluate the enrichment factor of the elements As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, La, Lu, K, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, Yb and Zn in sediment cores collected in Nhecolândia Pantanal using three enrichment factors, and therefore infer a probable human impact in the area. These elements were determined by instrumental neutron activation analysis (INAA) technique.

2. EXPERIMENTAL

2.1 Sampling and Physical and Chemical pre-treatment of the samples

Four sediment cores, from Salina A, SA, Salina 6, S6, Salina M, SM, and Salina V, SV, that are located at Nhumirim Farm, 19° 33' 23.31" S e 56° 4'57.56" W, Fig. 1, were collected in 2010 in Nhecolândia Pantanal, Mato Grosso do Sul. The sampling was performed with a PVC manual sediment sampler and the cores stored in a freezer for preservation.

At the opening of the cores, some observations about the sediment color were made. The SA core, which was 108 cm long, presented in its initial 51 cm a black sediment that was an indicative of organic matter, and from 51 cm to the end of the core a dark gray color, followed by beige and again a dark gray color, indicating alternation of the organic matter presence.

Two series of counting were made: the first one, after one-week decay and the second one, after 15-20 days. The counting time was 1.5 hours for each sample and reference material. Gamma spectrometry was performed using a coaxial Be-layer HPGe detector with 22% relative efficiency, resolution of 2.09 keV at 1.33 MeV and associated electronic devices. The spectrum was acquired by multichannel analyzer SpectrumMaster and for the analysis WinnerGamma [20] software was used. The methodology validation was performed by measuring the reference materials San Joaquin Soil and SL1.

2.4 Assessment of the Sediment Enrichment

In the present study, the Enrichment Factor – EF, the Basis Enrichment Factor - BEF and the Geochemical Normalization Factor – GNF were used to assess the sediment enrichment and verify which trace element is enriched [21, 22]. The parameters used for this assessment follow the range described in Table 1 by Sutherland [23].

Table 1: Evaluation of the sediment contamination by its enrichment factor [23]

Classification	EF
Low enrichment	< 2
Moderately enriched	> 2 to 5
Very high enrichment	> 5 to 40
Extremely enriched	> 40

2.4.1 Enrichment factor - EF

The enrichment factor in sedimentology points out the element enrichment when compared to background values. In the present work values from the Upper Continental Crust (UCC) [24], were used as background and the element Sc was used as normalizer element. The enrichment factor was calculated by the equation (1) [18].

$$EF = \frac{(C_i/C_n)_{\text{sample}}}{(C_i/C_n)_{\text{background}}} \quad (1)$$

Where:

- EF: Enrichment factor;
- C_i : concentration of the interest element;
- C_n : concentration of the normalizer element.

2.4.2 Basis enrichment factor - BEF

The basis enrichment factor takes into consideration the values obtained in the basis of the core as normalizer [14]. In an environment, such as the Nhecolândia Pantanal, some elements tend to present unique characteristics, which are strongly correlated with the studied site. The equation used is described in (2).

$$BEF = \frac{C_i}{C_b} \quad (2)$$

Where:

BEF: Basis Enrichment Factor;

C_i : concentration of the interest element;

C_b : concentration of the element in the basis of the core.

2.4.3 Geochemical normalization factor - GNF

Another enrichment factor used was the geochemical normalization factor (GNF), which is utilized in environmental studies to evaluate the human impact of metals in aquatic settings [14]. The normalizer element used was also Sc, due to its low mobility throughout the sedimentary column, equation (3).

$$GNF = \frac{C_i}{C_n} \quad (3)$$

Where:

C_i : concentration of the interest element;

C_n : concentration of the normalizer element in the same slice of the core.

3. RESULTS AND DISCUSSION

Table 2 shows the enrichment values, EF, BEF and GNF, for the studied Salinas, SA, S6, SM and SV.

Table 2: Mean values and range of EF, BEF and GNF, for SA, S6, SM and SV

Elements		Salina A			Salina 6			Salina M			Salina V		
		EF	BEF	GNF	EF	BEF	GNF	EF	BEF	GNF	EF	BEF	GNF
As	Mean	14	1.8	2.7	9.4	0.4	1.3	11	1.4	1.5	79	0.8	11
	Range	6.9 - 49	0.6 - 4.0	0.9 - 6.7	29 - 3.5	0.2 - 1.0	0.5 - 4.0	5.7 - 46	0.7 - 5.8	0.8 - 6.3	108 - 62	0.7 - 1.0	8.5 - 15
Ba	Mean	3.2	0.8	197	2.8	1.4	169	3.4	1.0	206	16	0.9	970
	Range	2.5 - 4.2	0.6 - 1.3	152 - 256	0.9 - 5.8	0.8 - 2.5	53 - 351	0.3 - 4.8	0.1 - 1.4	19 - 291	11 - 19	0.6 - 1.1	670 - 1130
Ca	Mean	0.05	1.7	0.4	0.04	0.7	0.5	0.03	1.6	0.3	0.1	0.9	1.6
	Range	0.01 - 0.1	0.2 - 3.5	0.1 - 0.9	0.03 - 0.1	0.4 - 1.0	0.3 - 0.9	0.01 - 0.05	0.8 - 2.8	0.2 - 0.6	0.1 - 0.2	0.5 - 1.1	0.9 - 2.2
Co	Mean	3.4	0.3	2.5	2.7	1.6	2.4	2.2	1.5	2.0	6.9	0.7	5.4
	Range	0.9 - 4.0	0.1 - 0.5	0.8 - 3.6	1.5 - 4.8	0.7 - 3.4	1.4 - 4.4	1.3 - 4.5	0.9 - 3.0	1.2 - 4.1	3.8 - 9.3	0.4 - 1.0	3.5 - 6.9
Cr	Mean	1.6	0.5	5.3	7.2	1.2	6.6	10	0.8	8.8	3.8	1.2	12
	Range	1.1 - 4.1	0.3 - 1.3	3.6 - 13	3.4 - 20	0.5 - 3.9	3.1 - 18	4.5 - 17	0.4 - 1.4	4.1 - 16	2.7 - 5.2	1.0 - 1.7	8.7 - 16
Cs	Mean	1.3	0.4	0.4	0.1	1.0	0.3	2.4	1.0	0.3	1.7	0.8	0.6
	Range	1.0 - 1.6	0.2 - 0.5	0.3 - 0.6	0.1 - 0.2	0.5 - 1.7	0.2 - 0.6	1.9 - 3.5	0.8 - 1.5	0.3 - 0.5	1.5 - 1.9	0.6 - 1.0	0.5 - 0.6
Fe	Mean	1.0	0.3	0.3	3.8	1.1	0.3	0.6	1.1	0.3	2.4	0.7	0.8
	Range	0.4 - 1.3	0.2 - 0.5	0.1 - 0.4	2.9 - 6.3	0.5 - 2.3	0.2 - 0.5	0.4 - 1.2	0.7 - 2.2	0.2 - 0.5	1.6 - 2.9	0.4 - 1.0	0.5 - 0.9
Hf	Mean	2.7	1.6	2.2	11	0.7	3.7	20	0.8	6.5	7.2	1.3	3.8
	Range	1.5 - 9.4	0.6 - 3.6	0.8 - 4.9	2.8 - 30	0.3 - 1.4	0.9 - 9.4	5.8 - 28	0.2 - 1.1	1.8 - 9.0	4.6 - 9.7	1.0 - 1.8	2.4 - 5.1
K	Mean	1.1	0.6	0.5	0.7	1.0	0.4	1.0	1.4	0.5	<2	<2	<2
	Range	0.7 - 1.4	0.3 - 0.8	0.2 - 0.7	0.2 - 1.1	0.8 - 1.3	0.1 - 0.6	0.7 - 1.4	1.0 - 2.1	0.3 - 0.7	<2	<2	<2

Table 2 continued

Elements		Salina A			Salina 6			Salina M			Salina V		
		EF	BEF	GNF	EF	BEF	GNF	EF	BEF	GNF	EF	BEF	GNF
Na	Mean	50	1.7	360	89	1.2	601	139	1.3	933	149	1.1	1003
	Range	6.2 - 197	1.0 - 5.4	75 - 1323	20 - 308	0.6 - 4.0	133 - 2072	36 - 645	0.5 - 6.2	241 - 4338	108 - 239	0.8 - 1.7	727 - 1610
Rb	Mean	1.4	0.4	14	1.1	1.0	12	1.3	0.9	13	1.9	1.1	19
	Range	1.1 - 1.8	0.3 - 0.6	11 - 18	0.7 - 1.7	0.7 - 1.5	6.7 - 17	0.6 - 1.9	0.5 - 1.3	5.5 - 19	1.5 - 2.1	1.0 - 1.3	15 - 21
Sb	Mean	6.9	0.7	0.1	4.6	0.6	0.1	5.1	1.0	0.1	9.4	0.9	0.2
	Range	4.9 - 11	0.4 - 1.1	0.1 - 0.2	1.6 - 8.7	0.4 - 1.0	0.0 - 0.2	3.6 - 6.3	0.7 - 1.3	0.1 - 0.1	5.9 - 13	0.6 - 1.1	0.1 - 0.2
Ta	Mean	1.0	0.9	0.2	1.2	0.7	0.2	2.0	0.8	0.4	1.3	0.8	0.3
	Range	0.6 - 2.3	0.4 - 1.8	0.1 - 0.5	0.6 - 2.2	0.3 - 1.0	0.1 - 0.4	0.6 - 2.7	0.3 - 1.0	0.1 - 0.5	0.9 - 1.5	0.6 - 1.0	0.2 - 0.3
Th	Mean	1.2	0.5	1.2	1.4	0.7	1.3	1.8	0.7	1.7	1.5	1.0	1.4
	Range	0.9 - 1.8	0.3 - 0.7	0.8 - 1.7	0.9 - 2.1	0.4 - 1.1	0.9 - 2.0	0.9 - 2.3	0.4 - 1.2	0.9 - 2.1	1.3 - 1.8	0.9 - 1.2	1.2 - 1.7
U	Mean	2.5	0.9	0.5	1.5	0.6	0.3	2.7	0.9	0.6	2.0	1.0	0.5
	Range	1.5 - 4.4	0.6 - 1.3	0.2 - 1.0	0.4 - 3.2	0.2 - 1.0	0.1 - 0.7	1.4 - 3.5	0.4 - 1.2	0.3 - 0.8	1.4 - 2.4	0.7 - 1.3	0.3 - 0.5
Zn	Mean	1.3	0.3	9.2	1.1	1.2	7.0	0.9	0.6	6.1	1.7	1.0	11
	Range	0.8 - 2.4	0.1 - 0.5	4.9 - 15	0.8 - 1.7	0.5 - 2.6	5.0 - 11	0.5 - 1.7	0.4 - 1.2	3.5 - 11	1.5 - 2.1	0.8 - 1.2	10 - 13
Ce	Mean	1.4	0.4	8.4	1.6	0.6	9.5	2.0	0.8	11	1.7	0.9	10
	Range	1.0 - 1.9	0.3 - 0.6	5.9 - 15	1.0 - 2.6	0.3 - 1.1	5.7 - 15	1.3 - 2.6	0.5 - 1.4	7.6 - 15	1.5 - 1.9	0.8 - 1.0	8.5 - 11
Eu	Mean	1.6	0.3	0.1	0.5	0.7	0.2	0.3	0.7	0.2	2.1	0.9	0.2
	Range	1.4 - 2.1	0.2 - 0.4	0.1 - 0.2	0.3 - 0.8	0.2 - 1.4	0.1 - 0.3	0.2 - 0.4	0.5 - 1.3	0.1 - 0.2	1.7 - 2.5	0.7 - 1.1	0.1 - 0.2
La	Mean	1.3	0.3	3.8	1.4	0.7	4.0	1.6	0.8	4.5	1.5	0.9	4.0
	Range	1.0 - 1.9	0.2 - 0.5	2.8 - 5.1	0.7 - 2.5	0.2 - 1.8	1.8 - 6.9	1.0 - 2.3	0.5 - 1.5	2.8 - 6.3	1.2 - 1.6	0.8 - 1.1	3.4 - 4.3
Lu	Mean	2.3	0.7	0.1	2.7	0.6	0.1	4.9	0.8	0.1	3.3	1.0	0.1
	Range	1.6 - 5.5	0.4 - 1.3	0.0 - 0.2	1.2 - 6.4	0.3 - 1.0	0.0 - 0.2	2.1 - 6.1	0.3 - 1.1	0.1 - 0.2	2.2 - 4.0	0.8 - 1.3	0.1 - 0.1
Nd	Mean	1.2	0.5	2.8	1.1	0.5	2.5	1.8	0.8	4.3	1.2	0.9	2.9
	Range	1.0 - 1.5	0.3 - 0.6	2.3 - 3.4	0.2 - 1.8	0.1 - 1.2	0.5 - 4.4	0.4 - 2.8	0.2 - 1.5	1.1 - 6.6	0.5 - 2.4	0.4 - 1.6	1.1 - 5.8
Sm	Mean	1.6	0.3	0.8	2.0	0.7	0.8	2.3	0.8	1.0	2.0	0.9	0.8
	Range	1.4 - 2.3	0.2 - 0.5	0.6 - 1.3	1 - 2.9	0.2 - 1.5	0.3 - 1.2	1.6 - 3.1	0.5 - 1.5	0.6 - 1.3	1.6 - 2.3	0.7 - 1.1	0.7 - 0.9
Tb	Mean	1.6	0.3	0.1	2.2	0.7	0.1	2.6	0.9	0.2	2.6	0.8	0.2
	Range	1.1 - 2.8	0.2 - 0.4	0.1 - 0.2	1.0 - 3.9	0.2 - 1.3	0.1 - 0.2	1.4 - 3.5	0.5 - 1.2	0.1 - 0.2	1.7 - 3.1	0.5 - 1.0	0.1 - 0.2
Yb	Mean	2.2	0.7	0.5	2.6	0.6	0.5	4.6	0.8	0.9	3.5	1.5	0.7
	Range	1.5 - 5.0	0.4 - 1.3	0.2 - 1.0	1.2 - 5.5	0.2 - 1.0	0.2 - 1.1	1.8 - 5.9	0.3 - 1.2	0.4 - 1.2	2.0 - 4.6	1.0 - 2.0	0.4 - 0.9

<2 – Low enrichment

3.1. Enrichment factor – EF

Fig. 3 shows the results obtained of EF for values greater than 2.0, in the four Salinas, which considers the sediment as moderately enriched, and the fine fraction proportion determined in each of the Salinas.

For SA, the elements that presented EF higher than 2 were As, Ba, Co, Hf, Lu, Na, Sb, Sm, U and Yb.

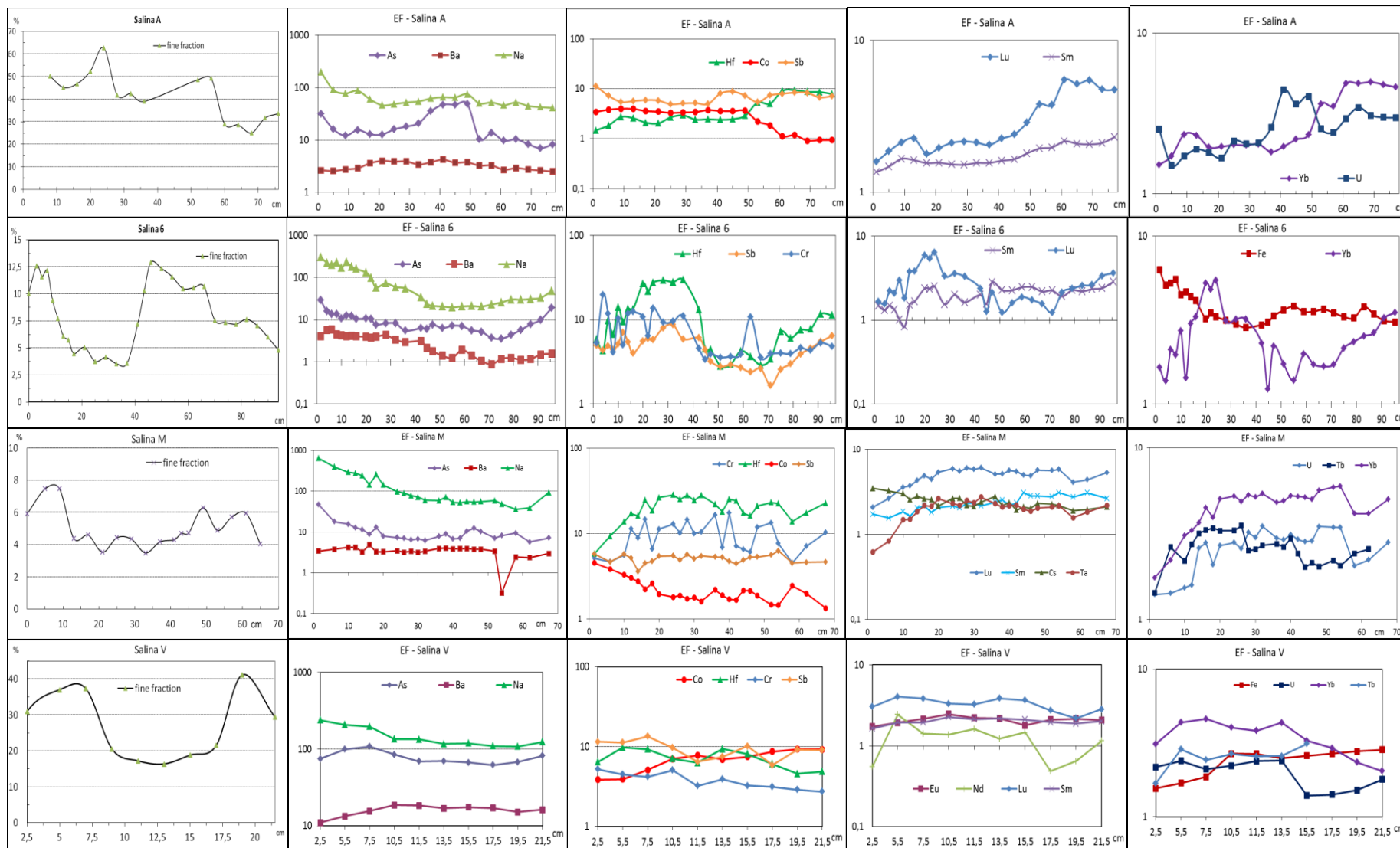


Figure 3: EF values for trace elements and fine fraction proportion determined in Salina A, Salina 6, Salina M and Salina V.

The highest values were determined for the element Na, which presented values about 100, but decreasing with depth. The second element with highest values was As, with values of about 50, in the depths from 40 cm to 50 cm, where a black sediment color was found, which is an indicative of high organic matter content. The elements Co, Lu, and Yb also presented in some slices of the core higher values, the results for Lu and Yb are probably related to the grain size of the sediment and the result for Co to the organic matter content. The other elements, Hf, Lu, Sm, and U showed a homogeneous behavior throughout the core, with a few variations.

In S6, the elements that presented EF higher than 2 were As, Ba, Cr, Fe, Hf, Lu, Na, Sb, Sm, and Yb.

The highest values were determined for the elements As and Na; the elements Hf and Yb showed higher values from 20 cm to 40 cm, due to a probable increase of organic matter content; and in the end of the sedimentary column, from 70 cm to 97 cm, the values also increased. The EF values for the elements Hf and Yb showed an opposite behavior to the one showed by the silt and clay fraction. The other elements presented values almost constant throughout the core.

For SM, the elements that presented EF higher than 2 were As, Ba, Co, Cr, Cs, Hf, Lu, Na, Sb, Sm, Ta, Tb, U, and Yb. The highest values of EF were determined for the elements As and Na, with higher values at the beginning of the core, where an increase in organic matter content can be inferred by the presence of a black color of the sediment. The element Hf presented values above 10 throughout the sedimentary column; the other elements presented a few variations.

For SV, the elements that presented EF higher than 2 were As, Ba, Co, Cr, Eu, Fe, Hf, Lu, Na, Nd, Sb, Sm, Tb, U and Yb. The highest EF was determined for the elements As and Na; the other elements presented an homogeneous behavior throughout the core, due to the uniform black color of the sediment core. The elements Eu and Nd presented EF values higher than 2 only for this Salina, SV.

3.2. Basis enrichment factor – BEF

The obtained results of BEF in the four Salinas are presented in Fig.4 for the trace elements that presented enrichment superior to 2.0, what is considered as moderately enriched sediment, and the fine fraction proportion determined in each of the Salinas.

For SA, the elements that presented BEF higher than 2 were As, Ca, Hf and Na. The elements As and Na presented BEF values decreasing with depth, however As presented an increase of these values from 35 to 50 cm, which is probably related to the increase of the fine fraction observed at this depth. The elements Ca and Hf presented a similar behavior from 0 to 50 cm, but different from 50 cm to the end of the core where only Ca followed the silt + clay content.

In S6, the elements that presented BEF higher than 2 were Ba, Co, Cr, Fe, Na, and Zn. The elements Ba, Co, Cr and Fe, presented an increase of the enrichment values from 43 cm until the end of the core, as the same behavior was observed to the fine fraction content in this core. The elements Na and Zn presented higher values of BEF in the beginning of the core.

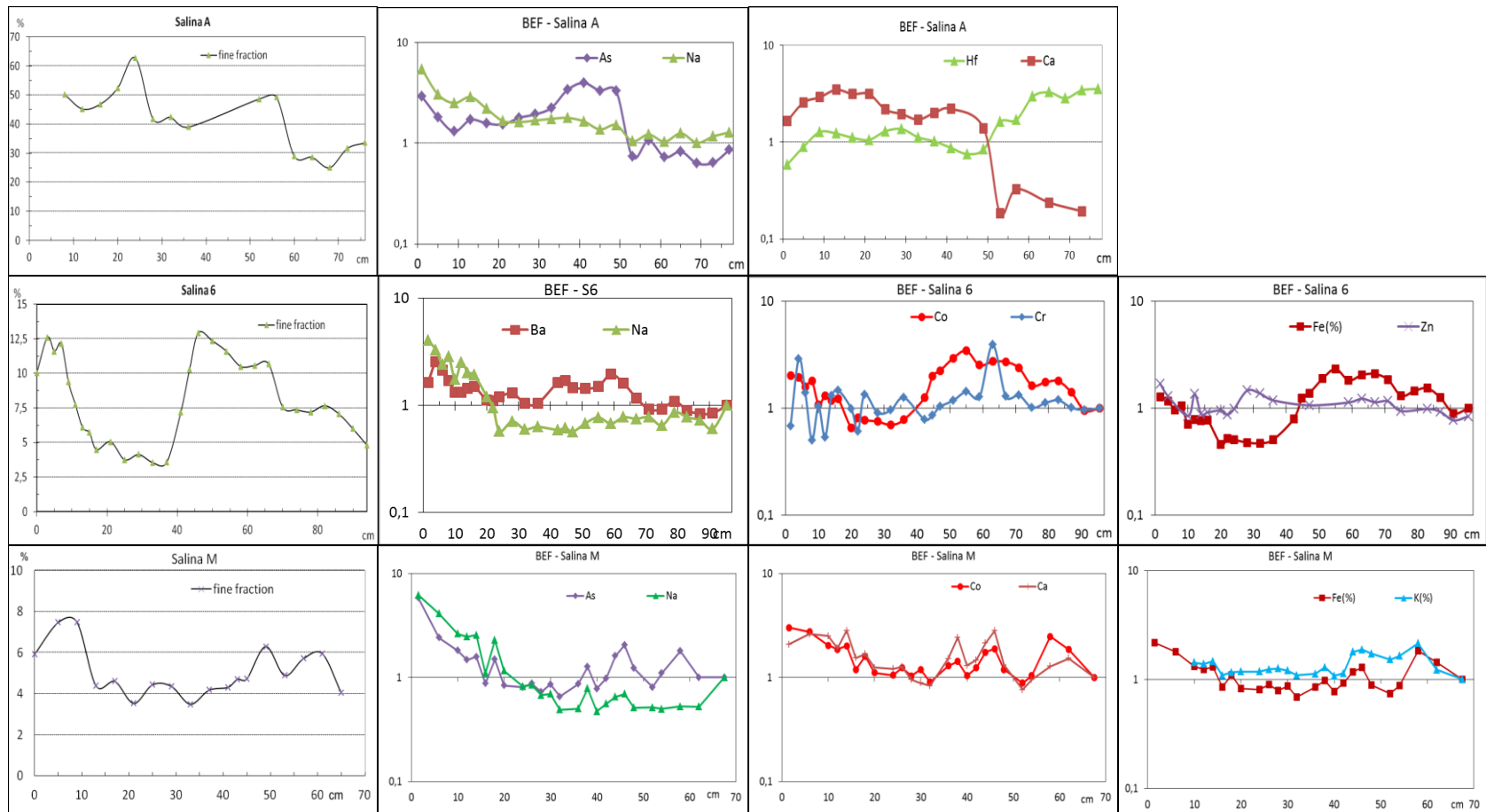


Figure 4: BEF for trace elements and fine fraction proportion determined in Salina A, Salina 6 and Salina M.

In SM, the elements that presented BEF values higher than 2 were As, Ca, Co, Fe, K, and Na. These elements presented higher values of BEF, from 0 to 15 cm, coincident with the higher percentage of silt + clay. It can be verified that the BEF values presented variations from 15 cm to 70 cm for these elements, also following the fine fraction content.

None of the BEF determined in SV core were higher than 2.

3.3. Geochemical normalization factor - GNF

The obtained results of GNF in the four Salinas are presented in Fig. 5 for the trace elements that presented enrichment superior to 2, what is considered as moderately enriched sediment, and the fine fraction proportion determined in each of the Salinas.

For SA core, the elements that presented GNF higher than 2 were As, Ba, Ce, Cr, La, Na, Rb, and Zn. The elements As, Ce, Cr, La, Rb, and Zn presented a few variations throughout the core. The element As presented lower enrichment values when compared to the other enrichment factor used in these study, suggesting that for the present studied environment the previous results, EF, and BEF, cannot be considered as an enrichment.

For S6 core, the elements that present GNF higher than 2 were Ba, Ce, Cr, Hf, La, Na, Rb, and Zn. The elements Cr and Hf presented a similar behavior with higher values from 0 to 40 cm. The element Cr presented constant values of GNF from 40 cm to the end of the core, only one peak was observed at the depth of 63 cm, due to a slight increase of silt + clay. For the element Hf, an increase of GNF values can be observed from 75 cm to the end of the core. The elements Ba, Na, and Rb presented lower GNF values where the dark color was observed, from 42 cm to 69 cm, suggesting that these elements did not have an affinity with the organic matter in this particular environment. The other elements presented a few variations throughout the sedimentary column.

In SM core, the elements that presented GNF higher than 2 were As, Ba, Ce, Cr, Hf, La, Na, Nd, Rb, and Zn. The elements Rb and Zn presented a decrease in the GNF values from 40 cm to 60 cm, and the other elements presented a homogenous behavior, with a few variations through the core.

For SV, the elements that presented GNF higher than 2 were As, Ba, Ce, Co, Cr, Hf, Na, Nd, Rb, and Zn. The elements As, Ce, Co, Cr, Hf, Nd, Rb and Zn presented an approximately homogeneous behavior throughout the core, due to probably the uniform color of the sediment core from this Salina.

The highest values of GNF were observed for the elements Ba and Na in the four Salinas studied. These values can be explained because the normalizer element used, Sc, presented much lower concentration than these two elements, therefore increasing their enrichment considerably.

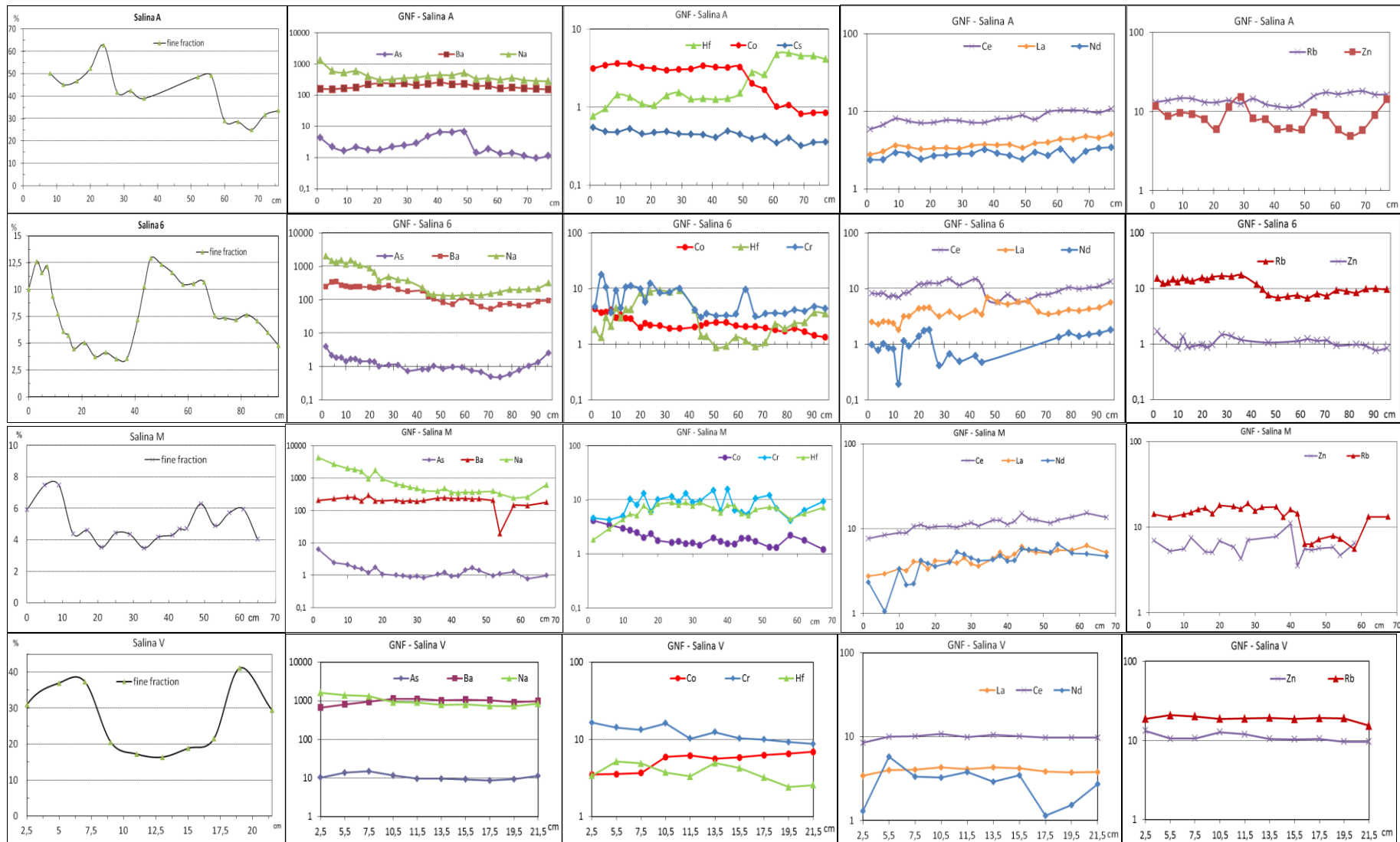


Figure 5: GNF for trace elements and fine fraction proportion determined in Salina A, Salina 6, Salina M and Salina V.

3. CONCLUSIONS

The present paper used three different enrichment factors to evaluate the enrichment of trace elements determined in sediment cores collected in Nhecolândia Pantanal. This area in Brazilian Pantanal, is a region with low population and human activity, hence, discuss the sediment chemical contamination is not suitable.

The first factor, enrichment factor – EF, uses the Upper Continental Crust - UCC (Wedepohl, 1995) values, which can be considered improper for this area, because these values may vary significantly depending on geological characteristics of the area (Reimann and Garret, 2005). Using this EF expressive enrichment values for the elements As, Ba, Cr, Hf, Na, and Sb were found.

The second factor, Basis Enrichment Factor – BEF, that normalizes the values determined for the element in question using the values determined in the core basis as normalizer, showed that the above elements presented lower enrichment values, suggesting that for these elements the enrichment factor that takes into consideration the concentration determined in the basis of the core is a better tool for this environment.

The third factor, Geochemical Normalization Factor - GNF uses Sc as a normalizer element, an element that has low mobility in the sediment. This methodology can be considered inappropriate because it presented much higher enrichment values when compared with the others.

Therefore the obtained results showed that the best tool to estimate the enrichment of the sediments of Nhecolândia Pantanal by trace elements, was BEF, because it uses values of the studied area as normalizer and with the increase of the sediment core depth, the element concentrations tends to reach the background values. However, for this assessment the use of other geochemical factors, such as grain size analysis, sediment color and organic matter content should be considered.

ACKNOWLEDGMENTS

This project was supported by FAPESP project 2011/09086-7 and a Master of Science fellowship from CAPES-PROEX, 2014.

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