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# Evaluation of the environmental state of the Western sector of Sepetiba Bay (SE Brazil): trace metal contamination

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## Abstract

Sepetiba Bay located in Rio de Janeiro State (RJ), Southeast Brazil, is a region under heavy influence of seaports and mining. This feature puts at risk the quality of the local water system, especially due to the deposition of trace metals on the sediments. This work aimed to report the values of total concentrations of Ag, As, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, Sr, Zn and Hg obtained in bottom surface sediments collected in Nov/2010 in the Western sector of Sepetiba Bay, through the Plasma Spectrometer (ICP-OES). The average concentrations of Ag (0.40 µg/g), Cd (0.76 µg/g), Cu (62.59 µg/g), Li (43.29 µg/g), Ni (16.65 µg/g), Pb (20.08 µg/g), Sr (389.64 µg/g) and Zn (184.2 µg/g) exceeded the limits allowed by Brazilian legislation, and are, in addition, above the natural values found in Ribeira Bay (RJ), the considered control region. It is necessary to monitor this area, due to its economic and environmental importance.

Keywords: Total Trace Metals. Sediments. Coastal area. Contamination.

## 1. Introduction

Sepetiba Bay is a semi enclosed coastal water body with a surface area of 520 km² (Rio de Janeiro, 1998). It is located at about 44° W and 23° S, at 60 km west of the metropolitan region of Rio de Janeiro, in southeast Brazil (Cunha et al., 2006; Pellegatti, 2000). According to Santos (2007) the marginal region of Sepetiba Bay is being used for the development of numerous agricultural, commercial, industrial, mining and port activities. We can mention for example the Itaguaí and Guaíba Terminal ports and the industries Gerdau, Petrobrás, National Steel Company (CSN), and the deactivated mining company Ingá. Wasserman et al. (2001) highlight that the construction of the large Sepetiba Port, in the early 70s, encouraged the industrial investment in this region. The industries and other anthropogenic activities are using the rivers and canals as recipients of effluents. Materials and contaminants introduced in Sepetiba Bay are altering this ecosystem according to Wasserman et al. (2001).

Trace metals resulting from this industrial pole are the main contaminants in Sepetiba Bay. Their properties and cumulative character make the situation critical, especially for aquatic biota (Gomes et al., 2019). The Mercantile Company Ingá (Fig. 1), disabled in 2008, was one of the industries that most contributed to the addition of contaminants in Sepetiba Bay, especially Cd and Zn (Gomes et al., 2009). Its installation occurred in the decade of 60, in the region of Madeira Island, in the Itaguaí town, beginning the electroplating process and evolving to zinc processing in 1966, and later, in 1974, for the processing of cadmium (Barcellos, 1995).

Lacerda and Molisani (2006) monitored the concentrations of metals in Sepetiba Bay between 1978 and 2002, through the analysis of bivalve mollusks, and found that the samples collected in 1996 had the highest Cd (29 µg/g) and Zn (80.72 µg/g) concentrations. These authors attributed these high concentrations of metals to the

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introduction of pollutants into the Sepetiba Bay through the rupture of a dam that isolated the environmental liabilities (ore tailings) produced by the deactivated Ingá Company after a heavy rainy period. According to PACS (2012) this disruption seriously affected the biota, resulting in a decrease of fish, of about 60%.

According to Lacerda et al. (1987), another main entrance of metals in Sepetiba Bay is fluvial and takes place mainly through the Guandu River and São Francisco Canal, with emphasis on national water transport. Both rivers are used by this regional industrial complex contributing with approximately 75% of the entrance of metals into this system.

The increase in the frequency of dredging due to the expansion of the seaport activities has also been an additional factor related to the increased availability of metals within the bay (Molisani et al., 2004).

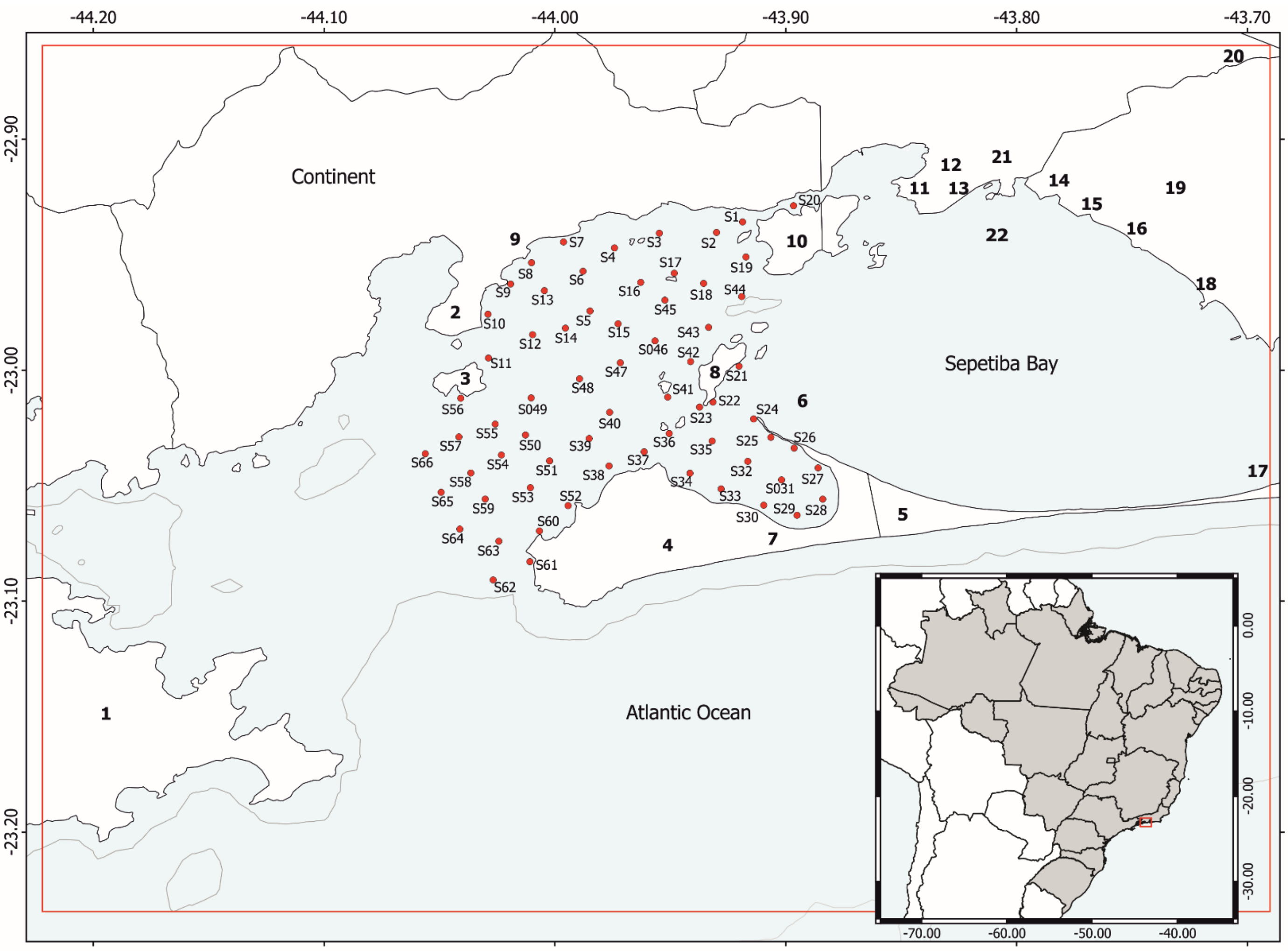


**Fig. 1.** Study area (Sepetiba Bay, RJ, Brazil) with the location of the points where surface sediment samples were collected (stations S1 - S66): 1- Grande Island; 2- Mangaratiba; 3- Guaíba Island (Port terminal); 4- Marambaia hill; 5- Marambaia sand spit (external zone); 6- Ponta da Pombeba; 7- Marambaia Bay; 8- Jaguanum Island; 9- Saí River; 10- Itacuruçá Island; 11- Madeira Island (Port of Itaguaí / Sepetiba); 12- Ingá (shut down industry - metallic waste); 13- Engenho Bay; 14- Guarda River; 15- São Francisco Channel; 16- Guandu Channel; 17- Marambaia sand spit (a more inside zone); 18- Sepetiba (town); 19- Santa Cruz; 20- Nova Iguaçu; 21- Itaguaí; 22- Dredging area of Port of Sepetiba.

The accelerated urban and industrial expansion without a prior planning are causing serious negative impact since Sepetiba Bay has inestimable social, environmental and economic value. Its vast area of mangrove forest added up to the physicochemical and biological properties of the region contribute to the high biodiversity of this bay. Sepetiba Bay is the habitat for several species, including some endangered ones, besides having great importance for the fisheries sector of the Rio de Janeiro State (Cardoso et al., 2019). Therefore, the environmental monitoring of this area is of great importance in order to take protective measures and prevent the degradation of this ecosystem. The objective of this study was to determine the total concentrations of trace elements (Ag, As, Cd, Co, Cr, Cu,

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Hg, Li, Mn, Ni, Pb, Sr, U, Zn) in bottom surface sediments collected in the western sector of Sepetiba Bay - RJ, Brazil.

## 2. Materials and Methods

The campaigns for sampling surface bottom sediments were carried out on November 10, 22 and 23, 2010, in the western sector of Sepetiba Bay - RJ, a region bordering Ilha Grande Bay - RJ. The sampling network was composed by 66 stations. Stations were named S01 to S66 (S= Sepetiba) (Fig. 1). The samples location is included in Table 1. The sediment samples were collected with a Van Veen Grab.

Sediment samples were taken from the central portion of the Van Veen Grab to avoid the collection of sediment that has been in contact with the equipment. The samples were stored in plastic containers, properly coded, and stowed in a cooler with ice until the arrival to the laboratory, where they were stored in a freezer at a temperature <10° Celsius.

The preparation of the samples for analysis of trace elements followed the techniques used by Cunha et al. (2009) in a study developed in the eastern sector of Sepetiba Bay.

The drying process was conducted in the Geological Samples Preparation Laboratory from the Universidade do Estado do Rio de Janeiro (UERJ) in an oven at temperature of about 80° Celsius. Then, the sediment samples were disaggregated and homogenized, with the aid of a mortar and pistil, and sieved on a set of sieves with meshes of 1 mm, 0.5 mm and 0.072 mm diameters. The sediment fractions <0.072 mm were kept in small polyethylene bottles for posterior analysis of trace elements.

Aliquots of the samples were sent to the ACTLABS laboratory (Activation Laboratories Ltd., Canada) in order to analyze the total elemental concentrations of trace elements. The procedure involved the use of hydrofluoric acid (HF) and hydrochloric acid (HCl). One aliquot of 0.25 g of the sample was, initially, digested with hydrofluoric acid (HF) and then in a programmed heating system, it was added a solution of nitric ($HNO_3$) and perchloric ($HClO_4$) acids to the sample until it became vaporized. After the remaining solution had been vaporized to the point of dryness, it was solubilized with hydrochloric acid (HCl). Laboratory standards and certified reference materials were used in quality control. Elemental concentrations were analyzed with the Plasma Spectrophotometer (ICP-OES) Varian Vista. Fourteen trace elements were analyzed: Ag, As, Cd, Co, Cr, Cu, Hg, Li, Mn, Ni, Pb, Sr, U and Zn. The Brazilian National Advice of the Environment (CONAMA) Resolution 454/2012 does not stablish limits for Fe and Al and thus the distribution of these elements is not discussed in this work.

In this study, the adopted reference limits were the smallest values allowed for the CONAMA Resolution 454/2012, Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (Canadian ISQG, 1999), National Oceanic and Atmospheric Administration (NOAA, 1999) and Florida Sediment Quality Assessment Guidelines (Florida SQAG'S), besides the background values supplied by Turekian and Wedepohl (1961) for total elemental concentrations. It is worth noting that for the use of the reference values presented by Turekian and Wedepohl (1961), the present study made an average between the *background* obtained in shales and in sandstones, since the studied region has heterogenous granulometric characteristics, varying between clayey to sandy.

## 3. Results and Discussion

The total concentration values of metals in the analyzed bottom surface sediment samples of Sepetiba Bay, as well as the averages, standard deviations and minimum and maximum values can be found in Table 1. Distribution maps of the elemental concentrations in the study area are presented in Figures 2-4.

The levels found were compared with Brazilian and international reference limits. The values obtained in all the analyzed stations exceeded, in at least one of the elements (Ag, As, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, Sr, Zn and Hg), the background values of Turekian and Wedepohl (1961) and the levels allowed by both Brazilian and international legislation, for total concentration of metals in sediments. Stations S16, located north of Jaguanum Island and west of Itacuruça Island, and S30, located in Saco da Marambaia, presented the highest number of metals (Ag, As, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, Sr, Zn) with values above those allowed.

Nine from sixteen of the analyzed elements presented average concentrations above the world reference value (Table 1), including Ag (0.4 µg/g), Cd (0.8 µg/g), Cu (62.6 µg/g), Li (43.3 µg/g), Mn (679.7 µg/g), Ni (16.7 µg/g), Pb (20.1 µg/g), Sr (389.6 µg/g) and Zn (184.8 µg/g).

The percentage of the stations with trace element concentrations exceeding the adopted limits (mentioned in Table 1), shows that the Western Sector of Sepetiba Bay presents a scenario of elemental enrichment by Ag (100%), Cd (100%), Zn (89%), Mn (79%), Cu (73%), Li (65%), Ni (69%), Pb (68%), Sr (67%) and Cr (52%).

### *3.1 Essential trace Elements (As, Cr, Cu, Mn, Zn, Al and Fe)*

The essential trace elements are those that play a role in biological metabolism (As, Cr, Cu, Mn, Zn, Al and Fe). However, even these elements, under certain environmental conditions and depending on their concentrations, can result in negative impact on aquatic ecosystems (Patterson et al., 1976; Guilherme et al., 2005).

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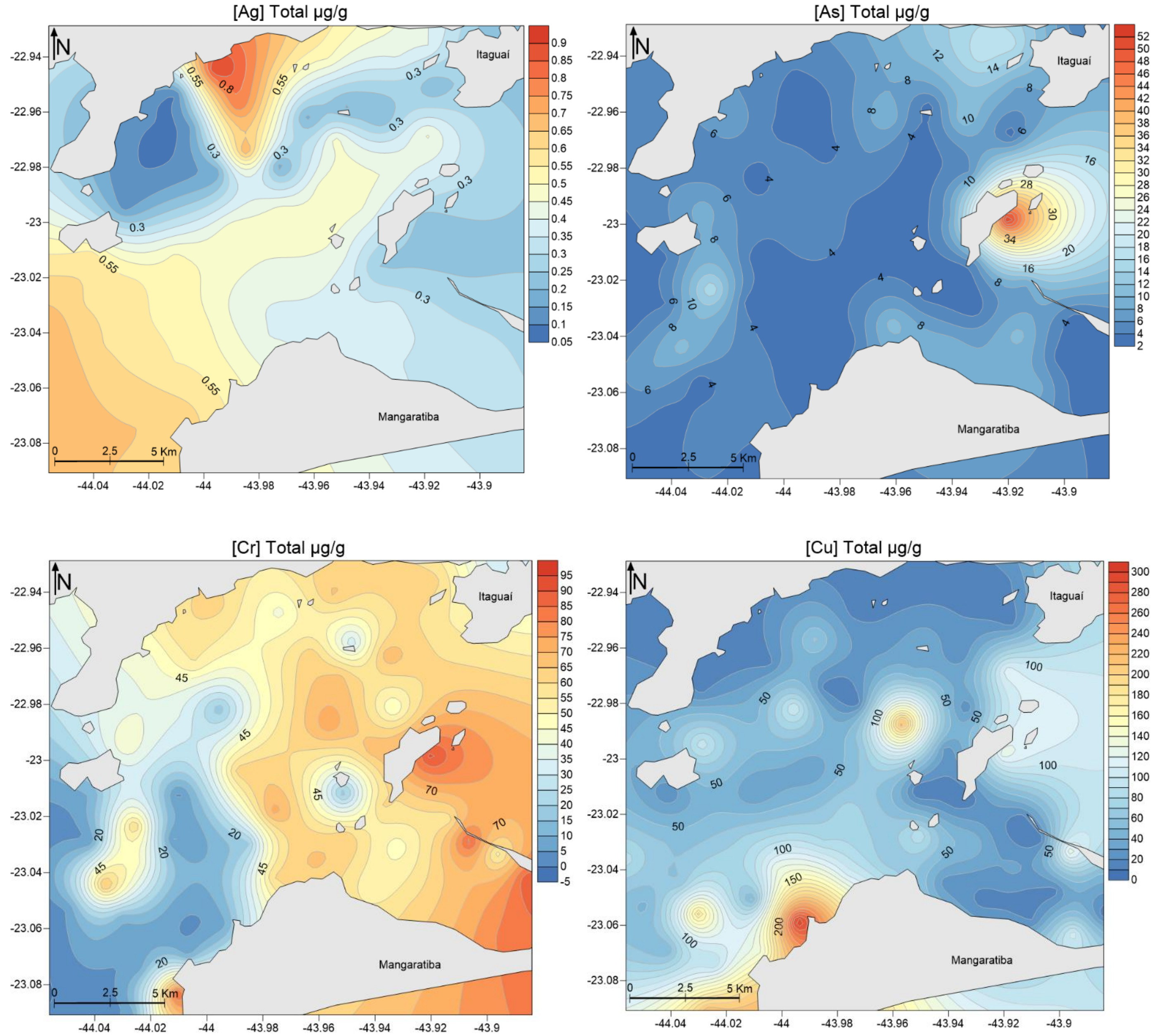


**Fig. 2.** Map of distribution of the total trace element concentration of Ag, As, Cr and Cu.

Arsenic (Appendix 1A) concentrations ranged from <3 to 53 µg/g, with an average of 6.50 ± 6.79 µg/g. Chromium and Cu (Appendix 1 B and C) varied between 3 to 92 µg/g and 9 to 303 µg/g respectively (averages of 46.98 ± 25.84 µg/g and 62.59 ± 59.85 µg/g, respectively; Table 1). Manganese and Zn (Appendix 2 A and B) concentrations ranged between 80 to 2450 µg/g and 19 to 478 µg/g, respectively (averages of 679.70±353.22 µg/g and 184.82 ±103.54 µg/g, respectively; Table 1). Aluminum and Fe levels fluctuated between 0.47 and 9.55% and 0.09 and 7.93%, respectively (averages of 3.72 ± 1.87% and 3.20 ± 1.93%, respectively; Table 1).

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**Tab. 1.** Total trace elemental concentrations per station (S1 - S66), average, standard deviation, minimum and maximum values. Values in µg/g dry weight.

| Elemental concentrations (µg/g) | | | Ag | As | Cd | Co | Cr | Cu | Li | Mn | Ni | Pb | Sr | Zn | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **CONAMA 344/2004** (µg/g) | | | | 8.2 | 1.2 | | 81 | 34 | | | 20.9 | 46.7 | | 150 | 0.15 |
| **SQAGs Florida (TEL)*** (µg/g) | | | 0.733 | 7.24 | 0.676 | | 52.3 | 18.7 | | | 15.9 | 30.2 | | 124 | 0.13 |
| **Canadian ISQGs (ISQG) **** (µg/g) | | | | 7.24 | 0.7 | | 52.3 | 18.7 | | | | 30.2 | | 124 | 0.13 |
| **NOAA** (µg/g) | | | 0.73 | 7.24 | 0.68 | | 52.3 | 18.7 | | | 15.9 | 30.24 | | 124 | 0.13 |
| Stations | Latitude | Longitude | [total] | [total] | [total] | [total] | [total] | [total] | [total] | [total] | [total] | [total] | [total] | [total] | [total] |
| **S02** | 22 56.420 | 43 55.802 | 0.40 | 17 | 2.7 | 10 | 62 | 18 | 80 | 719 | 23 | 25 | 240 | 398 | <1 |
| **S03** | 22 56.439 | 43 57.288 | 0.50 | 10 | 1.9 | 11 | 66 | 16 | 78 | 790 | 26 | 22 | 185 | 443 | <1 |
| **S04** | 22 56.821 | 43 58.453 | 0.60 | 6 | 0.9 | 10 | 43 | 16 | 76 | 817 | 26 | 22 | 291 | 296 | <1 |
| **S05** | 22 58.460 | 43 59.089 | 0.70 | 3 | 0.4 | 5 | 42 | 16 | 47 | 371 | 17 | 21 | 522 | 136 | <1 |
| **S06** | 22 57.427 | 43 59.271 | 0.80 | 3 | 0.7 | 7 | 51 | 64 | 49 | 529 | 17 | 19 | 615 | 174 | <1 |
| **S07** | 22 56.666 | 43 59.779 | 0.90 | 4 | 0.8 | 10 | 62 | 28 | 69 | 728 | 23 | 25 | 229 | 275 | <1 |
| **S08** | 22 57.205 | 44 00.611 | 0.10 | 5 | 0.9 | 10 | 58 | 16 | 74 | 751 | 24 | 26 | 211 | 241 | <1 |
| **S09** | 22 57.759 | 44 01.154 | 0.11 | 8 | 0.4 | 7 | 45 | 14 | 53 | 512 | 17 | 23 | 644 | 134 | <1 |
| **S10** | 22 58.544 | 44 01.742 | 0.12 | 4 | 0.3 | 7 | 38 | 18 | 47 | 1120 | 15 | 21 | 893 | 108 | <1 |
| **S11** | 22 59.681 | 44 01.729 | 0.13 | 9 | 0.3 | 6 | 45 | 98 | 51 | 622 | 17 | 18 | 614 | 142 | <1 |
| **S12** | 22 59.076 | 44 00.581 | 0.14 | 3 | 0.3 | 4 | 35 | 46 | 40 | 351 | 16 | 19 | 648 | 104 | <1 |
| **S13** | 22 57.932 | 44 00.277 | 0.15 | 4 | 0.5 | 9 | 55 | 17 | 67 | 624 | 22 | 22 | 422 | 194 | <1 |
| **S14** | 22 58.905 | 43 59.729 | 0.16 | 6 | 0.3 | 4 | 16 | 103 | 24 | 789 | 10 | 13 | 797 | 105 | <1 |
| **S15** | 22 58.793 | 43 58.361 | 0.17 | 6 | 1.2 | 9 | 55 | 14 | 66 | 547 | 25 | 21 | 219 | 250 | <1 |
| **S16** | 22 57.717 | 43 57.773 | 0.18 | 10 | 1.0 | 11 | 63 | 30 | 62 | 513 | 23 | 23 | 244 | 246 | <1 |
| **S17** | 22 57.478 | 43 56.900 | 0.19 | 3 | 0.8 | 3 | 30 | 40 | 32 | 352 | 9 | 12 | 956 | 126 | <1 |
| **S18** | 22 57.743 | 43 56.137 | 0.20 | 12 | 0.9 | 9 | 69 | 22 | 59 | 513 | 22 | 33 | 182 | 227 | <1 |
| **S19** | 22 57.056 | 43 55.037 | 0.21 | 8 | 1.7 | 10 | 56 | 15 | 71 | 601 | 24 | 21 | 161 | 313 | <1 |
| **S20** | 22 55.725 | 43 53.800 | 0.22 | 5 | 0.3 | 5 | 30 | 71 | 44 | 500 | 12 | 35 | 457 | 159 | <1 |
| **S21** | 22 59.894 | 43 55.217 | 0.23 | 53 | 0.7 | 9 | 92 | 127 | 37 | 649 | 18 | 24 | 171 | 263 | 8 |
| **S22** | 23 00.826 | 43 55.895 | 0.24 | 6 | 0.9 | 9 | 60 | 16 | 65 | 577 | 24 | 18 | 354 | 229 | <1 |
| **S23** | 23 00.956 | 43 56.243 | 0.25 | 3 | 0.9 | 8 | 61 | 15 | 60 | 1040 | 23 | 20 | 276 | 197 | <1 |
| **S24** | 23 01.264 | 43 54.838 | 0.26 | 8 | 2.5 | 9 | 57 | 15 | 57 | 647 | 22 | 21 | 152 | 248 | <1 |
| **S25** | 23 01.740 | 43 54.390 | 0.27 | 8 | 1 | 11 | 88 | 15 | 49 | 961 | 20 | 28 | 159 | 249 | <1 |
| **S26** | 23 02.022 | 43 53.784 | 0.28 | 3 | 0.7 | 6 | 52 | 129 | 28 | 570 | 12 | 19 | 173 | 206 | <1 |
| **S27** | 23 02.535 | 43 53.161 | 0.29 | 3 | 0.9 | 9 | 89 | 47 | 29 | 1040 | 14 | 26 | 235 | 184 | <1 |
| **S28** | 23 03.348 | 43 53.041 | 0.30 | 3 | 1.1 | 11 | 85 | 12 | 52 | 1100 | 23 | 29 | 165 | 290 | <1 |
| **S29** | 23 03.766 | 43 53.710 | 0.31 | 3 | 0.9 | 9 | 81 | 106 | 54 | 786 | 21 | 23 | 221 | 307 | <1 |
| **S30** | 23 03.503 | 43 54.575 | 0.32 | 9 | 1.9 | 13 | 71 | 20 | 63 | 1440 | 24 | 22 | 178 | 356 | <1 |
| **S31** | 23 02.847 | 43 54.111 | 0.33 | 3 | 1.5 | 11 | 72 | 15 | 61 | 860 | 24 | 21 | 176 | 329 | <1 |
| **S32** | 23 02.366 | 43 54.989 | 0.34 | 11 | 1.8 | 9 | 64 | 34 | 56 | 645 | 23 | 19 | 183 | 310 | <1 |
| **S33** | 23 03.082 | 43 55.682 | 0.35 | 8 | 2.2 | 11 | 60 | 16 | 61 | 955 | 23 | 23 | 179 | 478 | <1 |
| **S34** | 23 02.676 | 43 56.491 | 0.36 | 10 | 2.4 | 9 | 51 | 25 | 58 | 826 | 22 | 17 | 167 | 249 | <1 |
| **S35** | 23 01.839 | 43 55.915 | 0.37 | 3 | 0.7 | 6 | 47 | 51 | 50 | 553 | 19 | 34 | 377 | 183 | <1 |
| **S36** | 23 01.643 | 43 57.031 | 0.38 | 4 | 0.9 | 9 | 65 | 90 | 66 | 537 | 24 | 19 | 309 | 277 | <1 |
| **S37** | 23 02.118 | 43 57.683 | 0.39 | 11 | 0.8 | 9 | 66 | 61 | 65 | 612 | 26 | 21 | 290 | 262 | <1 |
| **S38** | 23 02.485 | 43 58.596 | 0.40 | 3 | 0.9 | 9 | 60 | 107 | 63 | 720 | 29 | 27 | 345 | 254 | <1 |
| **S39** | 23 01.772 | 43 59.112 | 0.41 | 3 | 0.4 | 3 | 18 | 80 | 20 | 350 | 8 | 16 | 228 | 106 | <1 |
| **S40** | 23 01.092 | 43 58.580 | 0.42 | 3 | 0.6 | 8 | 73 | 76 | 51 | 519 | 20 | 21 | 259 | 161 | <1 |
| **S41** | 23 00.697 | 43 57.071 | 0.43 | 3 | 0.3 | 1 | 15 | 9 | 16 | 256 | 7 | 8 | 1380 | 66 | <1 |
| **S42** | 22 59.775 | 43 56.476 | 0.44 | 7 | 0.3 | 8 | 68 | 26 | 44 | 604 | 18 | 23 | 234 | 150 | <1 |
| **S43** | 22 58.885 | 43 56.008 | 0.45 | 6 | 0.4 | 8 | 44 | 21 | 54 | 396 | 20 | 15 | 606 | 149 | <1 |
| **S44** | 22 58.085 | 43 55.148 | 0.46 | 3 | 0.5 | 8 | 61 | 117 | 58 | 432 | 24 | 21 | 204 | 219 | <1 |
| **S45** | 22 58.178 | 43 57.143 | 0.47 | 3 | 0.7 | 8 | 66 | 43 | 58 | 442 | 24 | 21 | 191 | 194 | <1 |
| **S46** | 22 59.235 | 43 57.401 | 0.48 | 3 | 0.3 | 8 | 74 | 223 | 48 | 597 | 20 | 22 | 250 | 210 | <1 |
| **S47** | 22 59.804 | 43 58.303 | 0.49 | 3 | 0.5 | 7 | 60 | 61 | 43 | 458 | 18 | 19 | 241 | 118 | <1 |
| **S48** | 23 00.220 | 43 59.361 | 0.5 | 6 | 0.3 | 8 | 62 | 30 | 59 | 453 | 24 | 19 | 249 | 130 | <1 |
| **S49** | 23 00.718 | 44 00.620 | 0.51 | 3 | 0.3 | 1 | 3 | 28 | 6 | 179 | 3 | 13 | 187 | 19 | <1 |
| **S50** | 23 01.681 | 44 00.767 | 0.52 | 3 | 0.3 | 2 | 5 | 72 | 7 | 2450 | 4 | 11 | 617 | 67 | <1 |
| **S51** | 23 02.353 | 44 00.140 | 0.53 | 3 | 0.3 | 1 | 11 | 128 | 6 | 367 | 6 | 14 | 242 | 69 | <1 |
| **S52** | 23 03.516 | 43 59.659 | 0.54 | 3 | 0.3 | 1 | 8 | 303 | 6 | 80 | 1 | 5 | 431 | 135 | <1 |
| **S53** | 23 03.050 | 44 00.640 | 0.55 | 5 | 0.3 | 2 | 8 | 47 | 7 | 1090 | 7 | 22 | 643 | 39 | <1 |
| **S54** | 23 02.200 | 44 01.393 | 0.56 | 8 | 0.4 | 5 | 44 | 74 | 42 | 514 | 16 | 21 | 423 | 116 | <1 |
| **S55** | 23 01.399 | 44 01.554 | 0.57 | 16 | 0.3 | 9 | 61 | 54 | 61 | 772 | 25 | 18 | 255 | 152 | <1 |

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**Tab. 1.** (cont.) Total trace elemental concentrations per station (S1 - S66), average, standard deviation, minimum and maximum values. Values in µg/g dry weight.

| Elemental concentrations (µg/g) | | | Ag | As | Cd | Co | Cr | Cu | Li | Mn | Ni | Pb | Sr | Zn | Hg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **S56** | 23 00.726 | 44 02.449 | 0.58 | 4 | 0.3 | 1 | 11 | 20 | 7 | 367 | 3 | 9 | 1520 | 27 | <1 |
| **S57** | 23 01.730 | 44 02.498 | 0.59 | 4 | 0.3 | 1 | 5 | 59 | 5 | 725 | 2 | 28 | 530 | 34 | <1 |
| **S58** | 23 02.669 | 44 02.187 | 0.60 | 11 | 0.3 | 10 | 68 | 61 | 64 | 411 | 26 | 20 | 193 | 142 | <1 |
| **S59** | 23 03.346 | 44 01.814 | 0.61 | 3 | 0.3 | 1 | 12 | 186 | 6 | 1550 | 1 | 14 | 434 | 108 | <1 |
| **S60** | 23 04.173 | 44 00.404 | 0.62 | 5 | 0.3 | 1 | 9 | 142 | 9 | 1160 | 5 | 13 | 1200 | 97 | <1 |
| **S61** | 23 04.972 | 44 00.653 | 0.63 | 3 | 0.3 | 7 | 87 | 196 | 14 | 939 | 10 | 26 | 370 | 147 | <1 |
| **S62** | 23 05.446 | 44 01.608 | 0.64 | 4 | 0.3 | 1 | 7 | 220 | 4 | 469 | 7 | 10 | 581 | 101 | <1 |
| **S63** | 23 04.440 | 44 01.459 | 0.65 | 6 | 0.3 | 1 | 7 | 90 | 6 | 793 | 6 | 15 | 349 | 68 | <1 |
| **S64** | 23 04.126 | 44 02.473 | 0.66 | 3 | 0.3 | 1 | 9 | 50 | 6 | 609 | 2 | 11 | 323 | 39 | <1 |
| **S65** | 23 03.169 | 44 02.959 | 0.67 | 8 | 0.3 | 1 | 6 | 47 | 6 | 644 | 4 | 22 | 338 | 28 | <1 |
| **S66** | 23 02.168 | 44 03.371 | 0.68 | 3 | 0.3 | 1 | 7 | 86 | 4 | 339 | 3 | 11 | 419 | 43 | <1 |
| **Average** | | | **0.4** | **6.4** | **1.0** | **6.6** | **46.9** | **63.3** | **42.8** | **681** | **16.5** | **20.0** | **392.9** | **182.7** | |
| **Standard Deviation** | | | **0.2** | **6.8** | **0.6** | **3.6** | **25.8** | **59.9** | **23.9** | **353** | **8.2** | **6.0** | **287.1** | **103.5** | |
| **Minimum** | | | **0.1** | **3.0** | **0.3** | **1.0** | **3.0** | **9.0** | **4.0** | **80** | **1.0** | **5.0** | **152.0** | **19.0** | **<1** |
| **Maximum** | | | **0.9** | **53.0** | **2.7** | **13.0** | **92.0** | **303.0** | **80.0** | **2450** | **29.0** | **35.0** | **1520.0** | **478.0** | **8.0** |

The values of the natural concentrations of metals (background) reported in this study were drawn from published literature over the past 30 years. In addition to studies carried out in the study area, were also considered previously acquired data at Ilha Grande Bay region, such as Ribeira Bay and Praia do Sul Biological Reserve, considered as reference areas (Lacerda et al., 1982; Lacerda, 1983; DePaula and Mozeto, 2001). These previous works have included studies on metals in cores and bottom surface sediments from the Ilha Grande Bay.

Average values of essential trace elemental concentrations (As, Cr, Cu, Mn, Zn, Al and Fe) in the analyzed samples were compared with values considered natural obtained through core analyses and in surface sediments in areas under reduced anthropogenic influence, such as Praia do Sul and Ribeira Bay, adjacent to Ilha Grande Bay (Silva-Filho et al., 1996; DePaula and Mozeto, 2001; Wasserman et al., 2001; Marques Jr. et al., 2006; Gomes et al., 2009). This comparison allowed to verify that in the Western sector of Sepetiba Bay these elements concentrations were above the local background values.

The average values of Cr (46.98 µg/g), Cu (62.59 µg/g), Mn (679.7 µg/g) and Zn (184.82 µg/g) in the study area showed a marked difference compared to that obtained in Praia do Sul Biological Reserve (Ilha Grande Bay) according to DePaula and Mozeto (2001). The reported values range from 2.5 to 2.7 µg/g for Cr; 11 to 17 µg/g for Cu; 60 to 325 µg/ g for Mn and; 42.5 to 156 µg/g for Zn. Silva-Filho et al. (1996) reported levels close to 15.75 µg/g for Zn, at the same region.

The concentration of metals in areas under strong human influence is orders of magnitude higher than in those less affected by anthropic activities, as Ribeira Bay or Praia do Sul, in Ilha Grande, as we observe in the profiles studied by Silva-Filho et al. (1996) and Patchineelam et al. (2011). These authors reported metal results in a core, and the average concentration of Zn in sediments of the region of Praia do Sul, in a depth from 19 to 30 cm, was 15.75 µg/g (Silva-Filho et al., 1996), while in a similar depth (10 to 32 cm) in the region of Saco da Marambaia (Sepetiba Bay) the value was about 500 µg/g (Patchineelam et al., 2011). Barcellos et al. (1991) found natural values in the pre-industrial period for Zn of 2.6 µg/g, in Saco do Engenho (Sepetiba Bay). These values are much lower than those reported in this research (184.82 µg/g).

The study of Magalhães and Pfeiffer (1995) points out that the area where a high volume of ore tailings from the discontinued mining company Cia Mercantil Ingá are released, also as Ilha do Diabo (Devil's Island), functions as a source of metallic waste for Sepetiba Bay.

In the region of Saco do Engenho, at a depth of 20 to 28 cm below the top of sediment cores, these authors obtained values for As between 260 and 360 µg/g. These values indicate that the shutdown mining company Cia Mercantil Ingá greatly contributes to the enrichment of metals in Sepetiba Bay, considering the natural values of <5 µg/g for As obtained by Wasserman et al. (2001) for this bay.

Chromium, Cu, Mn, Zn, and Fe presented average concentrations in the study area, above the values reported by other studies in Sepetiba and Ilha Grande bays. In the Western sector of Sepetiba Bay, the average concentration of Cr (46.98 µg/g) was higher than those obtained by Lacerda (1983; 30.9 µg/g) and Lacerda et al. (1982; 8.48 µg/g) in Ribeira Bay, a less anthropized area.

These authors reported Cr concentrations of 25.2 µg/g and 7.7 µg/g, respectively. Lacerda et al. (1987) observed Cu values of 38.8 µg/g for Sepetiba Bay, Gomes et al. (2009) of 31.9 µg/g for the Eastern sector of Sepetiba Bay and Freret-Meurer et al. (2010), of 11.64 µg/g for Ribeira Bay. The values reported for Cu in these studies are lower than that recorded in the Western Sector do Sepetiba Bay (in those survey, 62 µg/g).

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The average concentration of Mn (679.7 µg/g) in the study area also surpassed the values reported by: Lacerda (1983) of 123 µg/g for Ribeira Bay; Lacerda, et al. (1987) of 301 µg/g for Sepetiba Bay; Patchineelam et al. (1987) of 453 µg/g to Coroa Grande, in Sepetiba Bay; Barcellos et al. (1997) of 421 µg/g to the Eastern sector of Sepetiba Bay; Cardoso et al.(2001) of 469 µg/g for Ribeira Bay; DePaula and Mozeto (2001) from <96 µg/g to 279 µg/g to Praia do Sul in Ilha Grande; Gomes et al. (2009) of 595 µg/g at the Eastern sector of Sepetiba Bay and; Freret-Meurer et al. (2010) of 283.26 µg/g in Ribeira Bay.

The average concentration of Zn (184.82 µg/g) recorded in the study area also exceeds the levels obtained in Ribeira Bay (Lacerda et al., 1982; Lacerda, 1983; Cardoso et al., 2001; Freret-Meureret al., 2010).

The average concentration of Fe (3.2%) is also above the values found in Coroa Grande (2.79%) and Ribeira Bay (2.42%) as noticed by Patchineelam et al. (1987) and Freret-Meurer et al. (2010), respectively

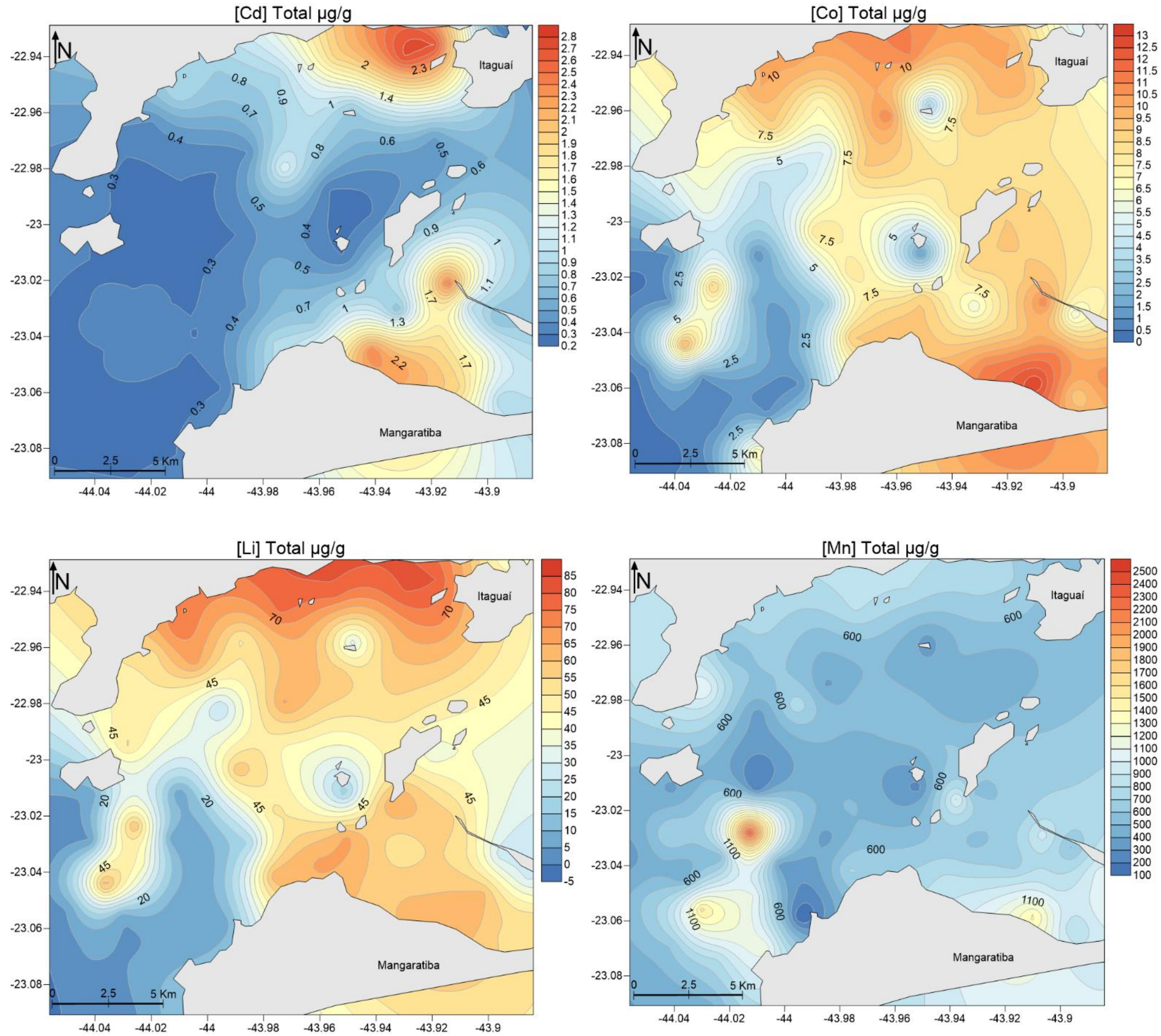


**Fig. 3.** Map of distribution of the total trace element concentration of Cd, Co, Li and Mn.

### *3.2 Non-essential trace elements (Ag, Cd, Co, Li, Ni, Pb, Sr, Hg)*

In the study area, Ag (Appendix 3 A) concentrations varied between <0.3 µg/g and 1 µg/g (average 0.4±0.16 µg/g; Table 1). Concentrations of Cd and Co (Appendix 3 B and C) ranged from <0.3 µg/g to 2.7 µg/g and <1 µg/g to 13 µg/g, respectively (averages of 0.76±0.61 µg/g and 6.65±3.6 µg/g, respectively; Table 1). Lithium (Appendix

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3 D), Ni and Pb (Appendix 4 A and B) concentrations oscillated between 4 µg/g to 80 µg/g, <1 µg/g to 29 µg/g and 5 µg/g to 35 µg/g, respectively (averages of 43.29±23.91 µg/g, 16.65±8.23 µg/g and 20.08±6 µg/g, respectively; Table 1). Sr and Hg (Appendix 4 C and D) reached concentrations of 152 µg/g to1520 µg/g and <1.0 µg/g to 8.0 µg/g (averages of 389.64±287.05 µg/g and 1.11±0.86 µg/g, respectively; Table 1).

Station S02 presented the highest level of Cd (2.7 µg/g) and Li (80 µg/g). Stations S07, S20, S30, S38 showed higher concentrations of Ag (1 µg/g), Pb (35 µg/g), Co (13 µg/g) and Ni (29 µg/g), respectively. Highest levels of Sr and Hg were found, in the stations S56 (1520 µg/g) and S21 (8 µg/g), respectively.

The average concentrations of Ag (0.4 µg/g), Cd (0.76 µg/g), Co (6.65 µg/g), Hg (1.11 µg/g), Li (43.29 µg/g), Ni (16.65 µg/g), Pb (20.08 µg/g) and Sr (389.64 µg/g), in surface bottom sediments of the Western Sector of Sepetiba Bay, were above the local natural and global levels as reported by Rocha et al. (2010).

Marques Jr. et al. (2006) reported for the pre-industrial period, at cores collected in the region of Coroa Grande (Sepetiba Bay), Cd levels <0.2 µg/g. These authors also recorded Cd values <0.34 µg/g in the region between São Francisco Canal and the Guandu River. Gomes et al. (2009) also reported similar values for the Ribeira Bay region (0.22 µg/g).

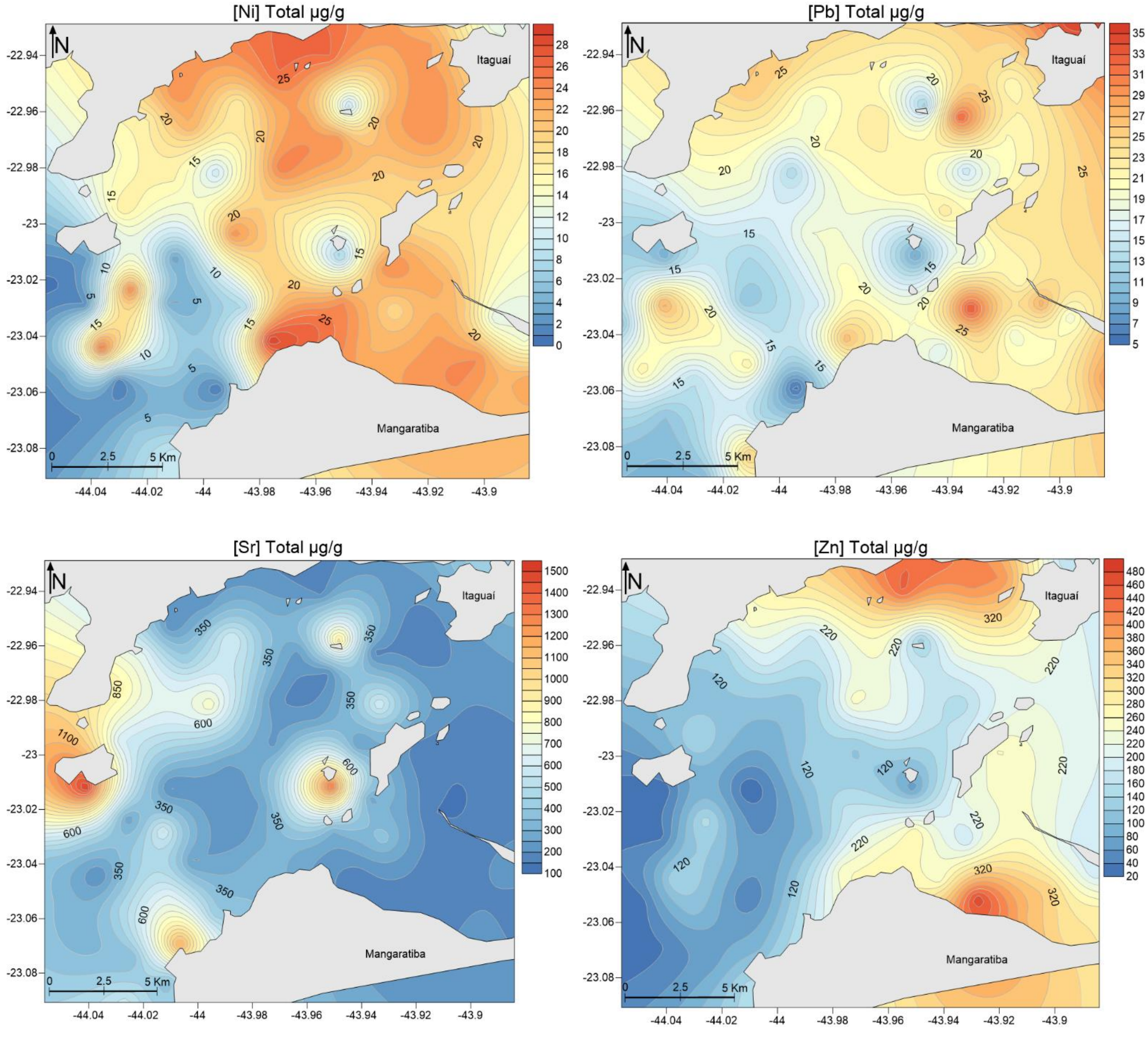


**Fig. 4.** Map of distribution of the total trace element concentration of Ni, Pb, Sr and Zn.

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The average values of Co concentration were above the natural values reported by Wasserman et al. (2001) in a core obtained in Enseada das Garças (<3 µg/g) and Coroa Grande (1.25 µg/g).

The average of Pb concentrations was within the natural limits presented by DePaula and Mozeto (2001) in a core collected in Ribeira Bay (12.5 to 50 µg/g), although it exceeded the world reference values (13.5 µg/g).

We have not found background values in sediments for Ag, Hg, Li, Ni and Sr but, through comparison with global references, it was found that the average concentrations obtained in this study for these metals exceeded the permissible limits.

The comparison of this result with the averages of total non-essential metal concentrations obtained in bottom surface sediments reported by other authors confirm their enrichment in the western sector of Sepetiba Bay.

The average of Ag (0.4 µg/g), Cd (0.76 µg/g) and Co (6.65 µg/g) concentrations were above the values reported by Freret-Meurer et al. (2010) (0.2 µg/g, 0.2 µg/g and 5,76 µg/g, respectively). These authors, as well as Lacerda et al. (1982) reported natural values for Ni (13.02 µg/g and 5.9 µg/g, respectively) and Pb (16.48 µg/g and 8.33 µg/g, respectively) in Ribeira Bay region, at lower levels than those obtained in this study (16.65 µg/g and 20.08 µg/g, respectively).

Average levels of Sr found in this study (average of 392.9 ug/g) also exceeded the values obtained by Patchineelam et al. (1987) for Coroa Grande region (201.5 µg/g), Cardoso et al. (2001) for Ribeira Bay area (163 µg/g) and Gomes et al. (2009) for the East sector of Sepetiba Bay (78 µg/g). The average content of Hg was above the value reported by Cardoso et al. (2001) for Ribeira Bay (0.028 µg/g), as well as the average concentration of Li that surpassed the worldwide background (40.5 µg/g).

### *3.3 Distribution of trace elemental concentrations*

In each map (Figs. 2-5), the regions in light pink encompass the highest concentrations of the analyzed elements. These maps evidence that the Saco da Marambaia region presents higher concentrations of Cd, Co, Cr, Mn, Pb and Zn. On the other hand, similarly to the previous region, the northern area presents the highest levels of Cd, Co and Zn and also encompasses the highest concentrations of Ag, As, Li and Ni. The concentrations of these elements are also higher than those reported by Pinto et al. (2019), for unpolluted sediments of Sepetiba Bay, namely for As, Cd, Co, Cu, Mn, Cu, Ni, Pb, Sr and Zn.

The comparison of the distribution maps of the concentration of the trace elements with the granulometric map of Sepetiba Bay developed by Pereira (1998) points out that there is some relationship between metal concentrations versus grain size. Most of the metals were adsorbed on grains of smaller size such as clay, silt and very fine sand. According to Passos (2005), a larger surface area of the sediment grain has greater efficiency in metals adsorption, that is, grains of smaller sizes concentrate more metals.

## 4. Conclusion

Results obtained in this work evidence that there is an enrichment of trace elements in the Western Sector of Sepetiba Bay. The total concentrations of Ag (0.40 µg/g), Cd (0.76 µg/g), Cu (62.59 µg/g), Li (43.29 µg/g), Ni (16.65 µg/g), Pb (20.08 µg/g), Sr (389.64 µg/g) and Zn (184.2 µg/g) exceeded the recommended limits by the legislation, in addition to being above the natural values found in Ribeira Bay (RJ), considered the control region, due to its low anthropic influence. This may be a consequence of human activities, related to the harbors, industries, as well as dredging, which resuspend the sediments and contribute to the reintroduction of metals in the water column, besides the permanence of the metal waste ore from the deactivated mining company Ingá. Thus, environmental monitoring is necessary in this area, since it is a region of high biological, social and economic importance.

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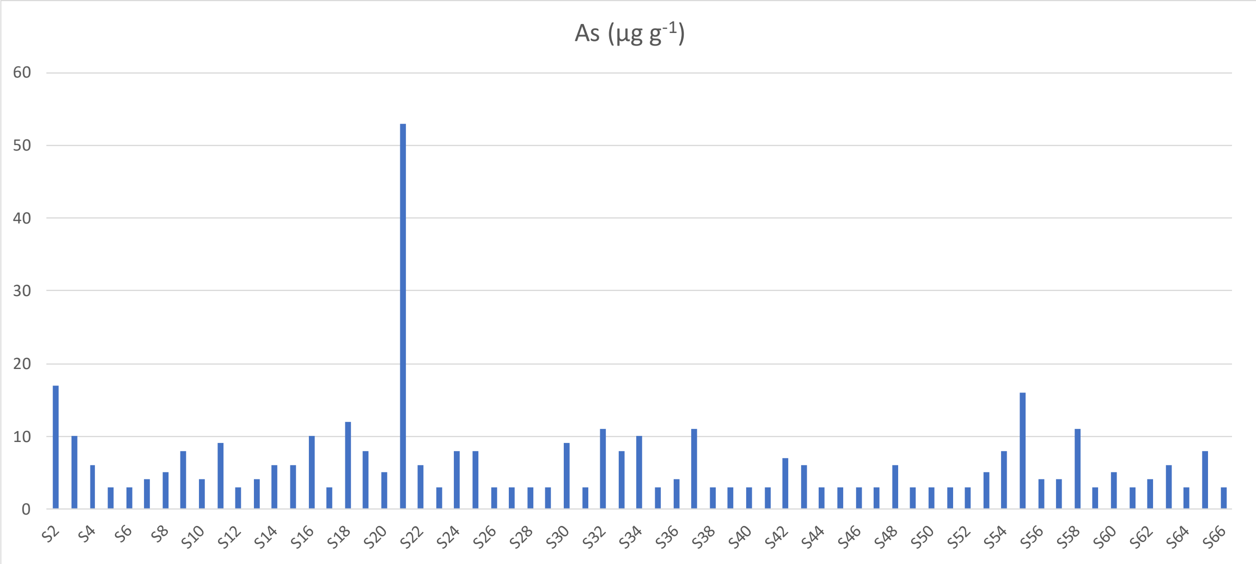


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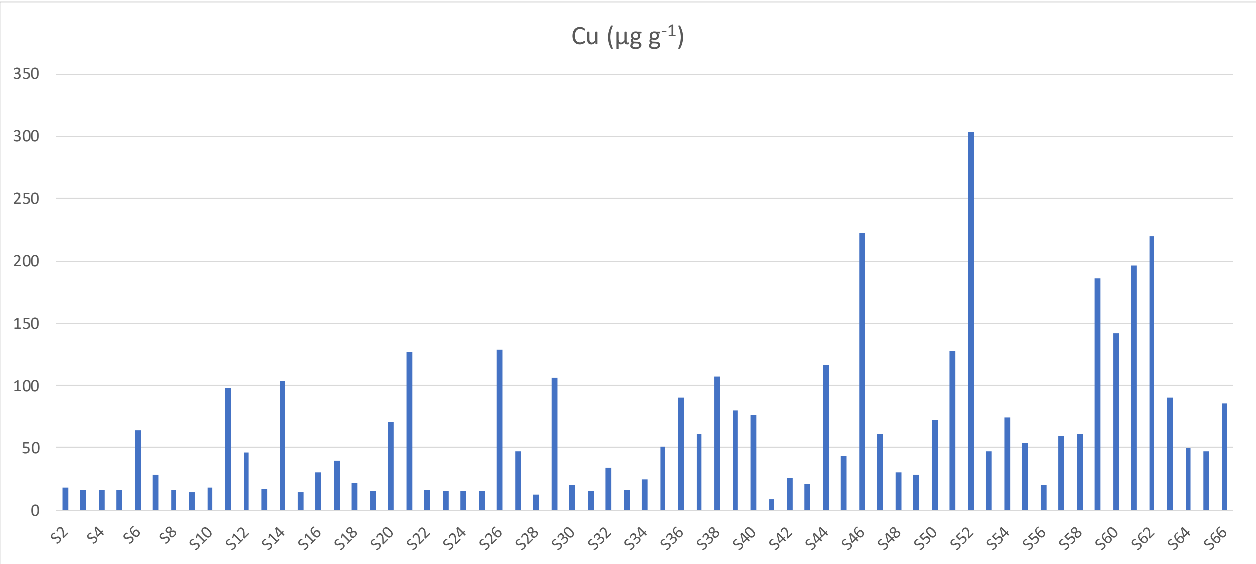


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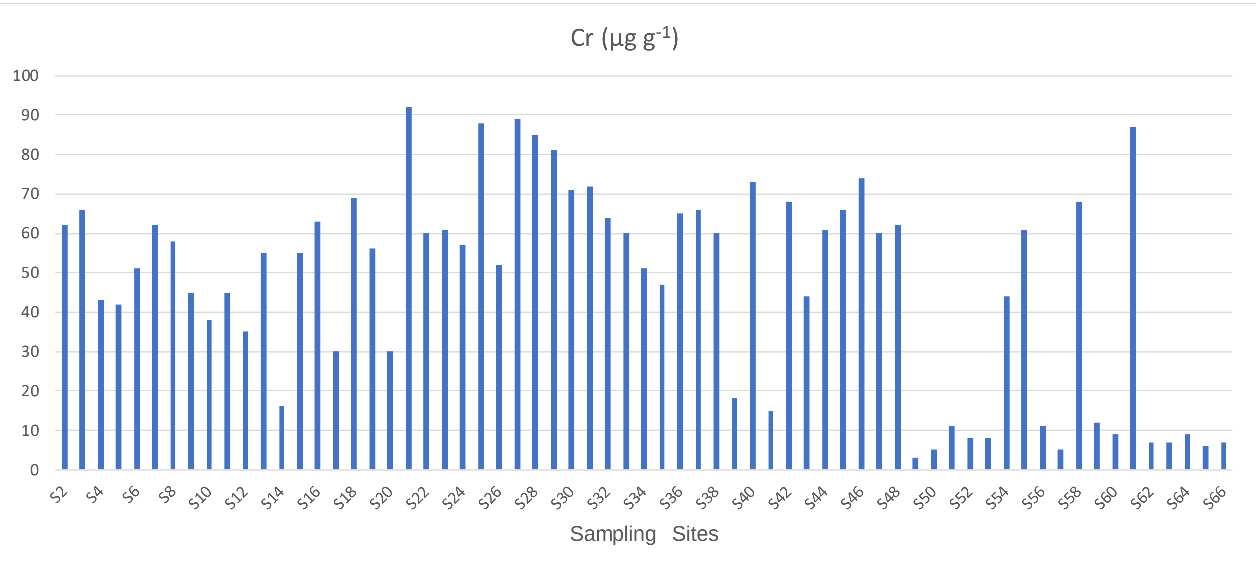


C.

**Appendix 1.** Concentration of essential elements by station.

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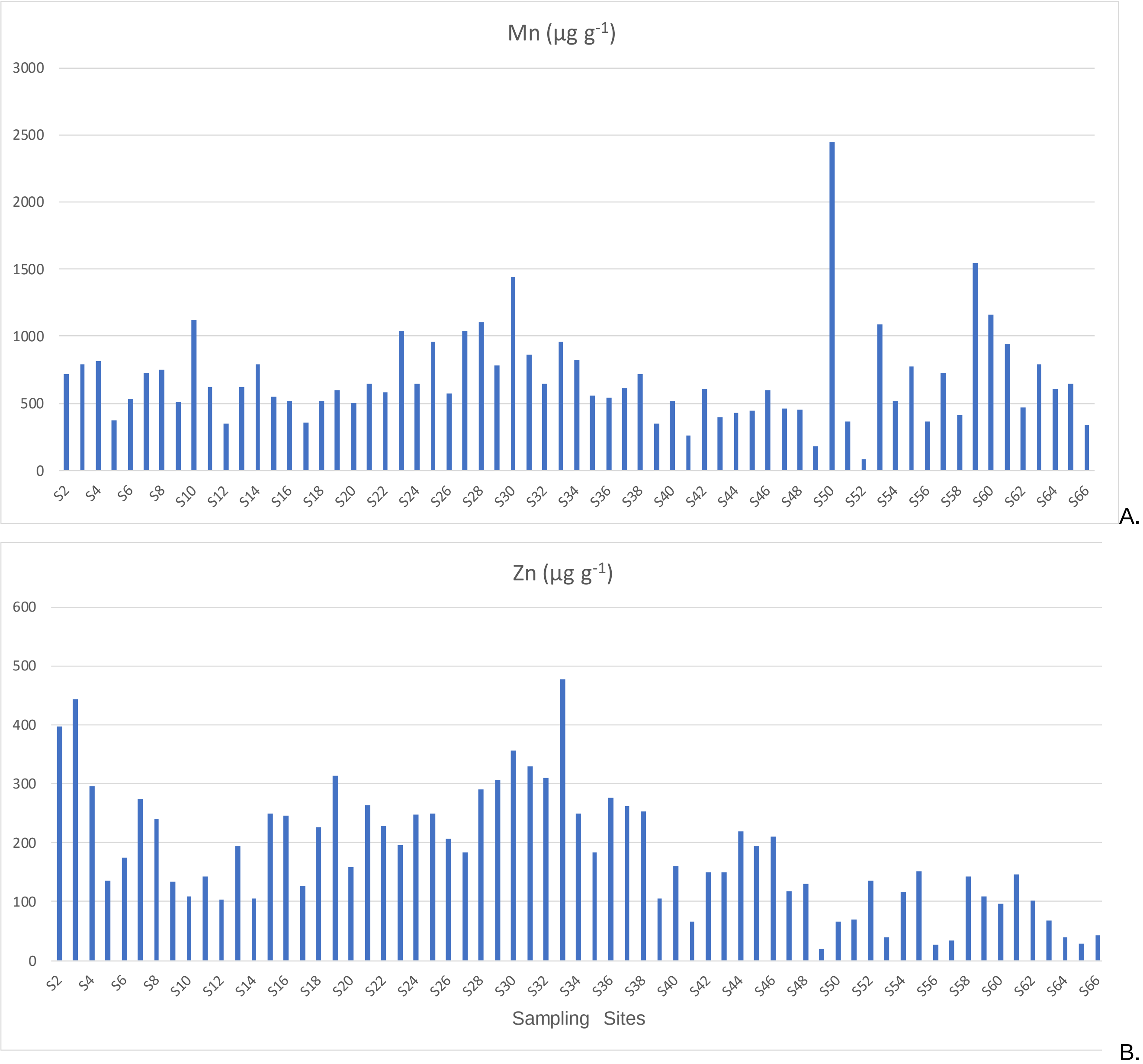


**Appendix 2.** Concentration of non-essential elements by station.

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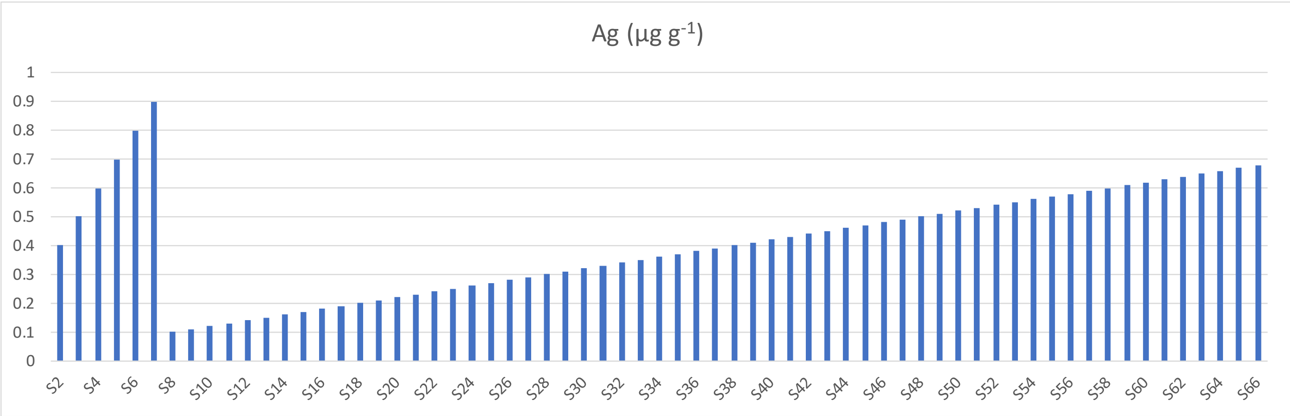


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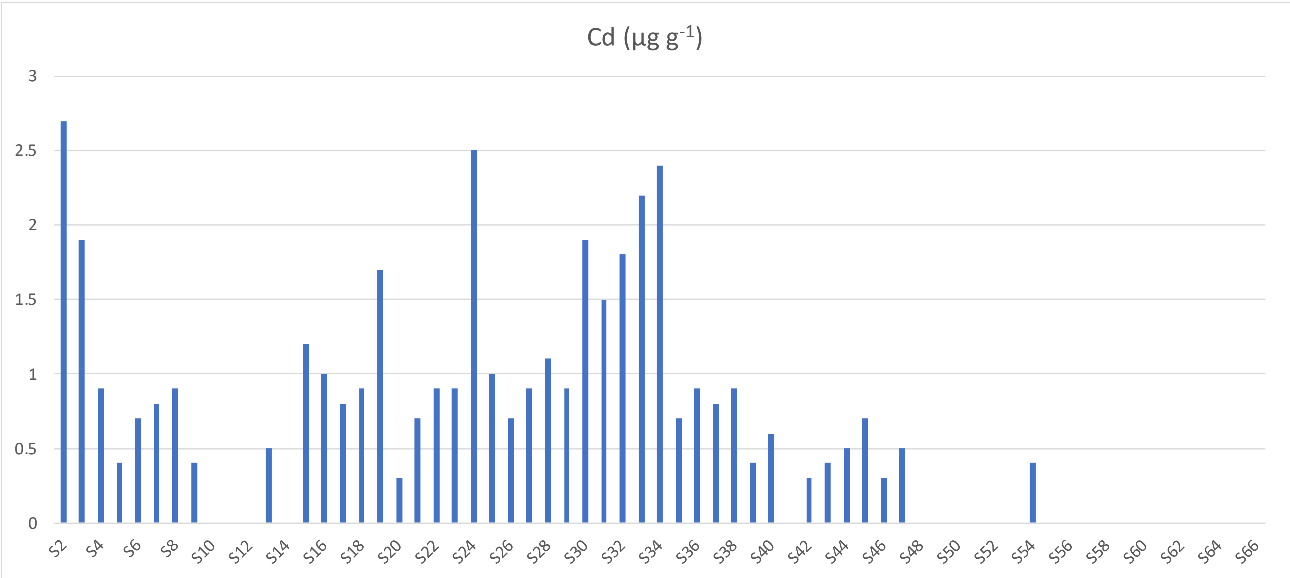


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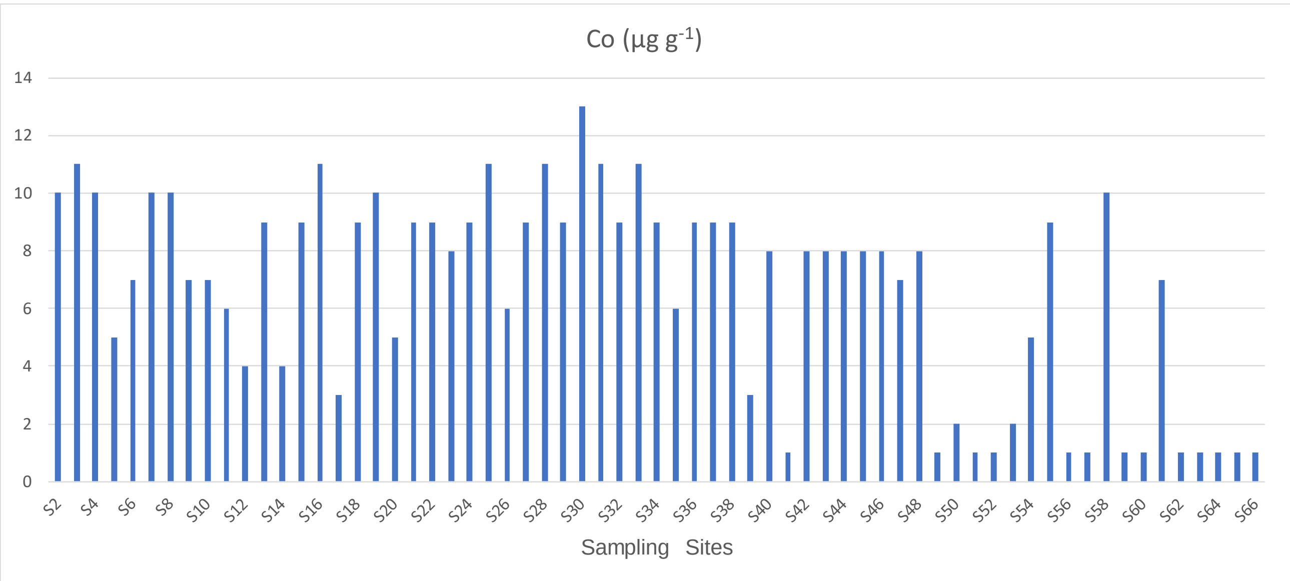


C.

**Appendix 3.** Concentration of non-essential elements by station.

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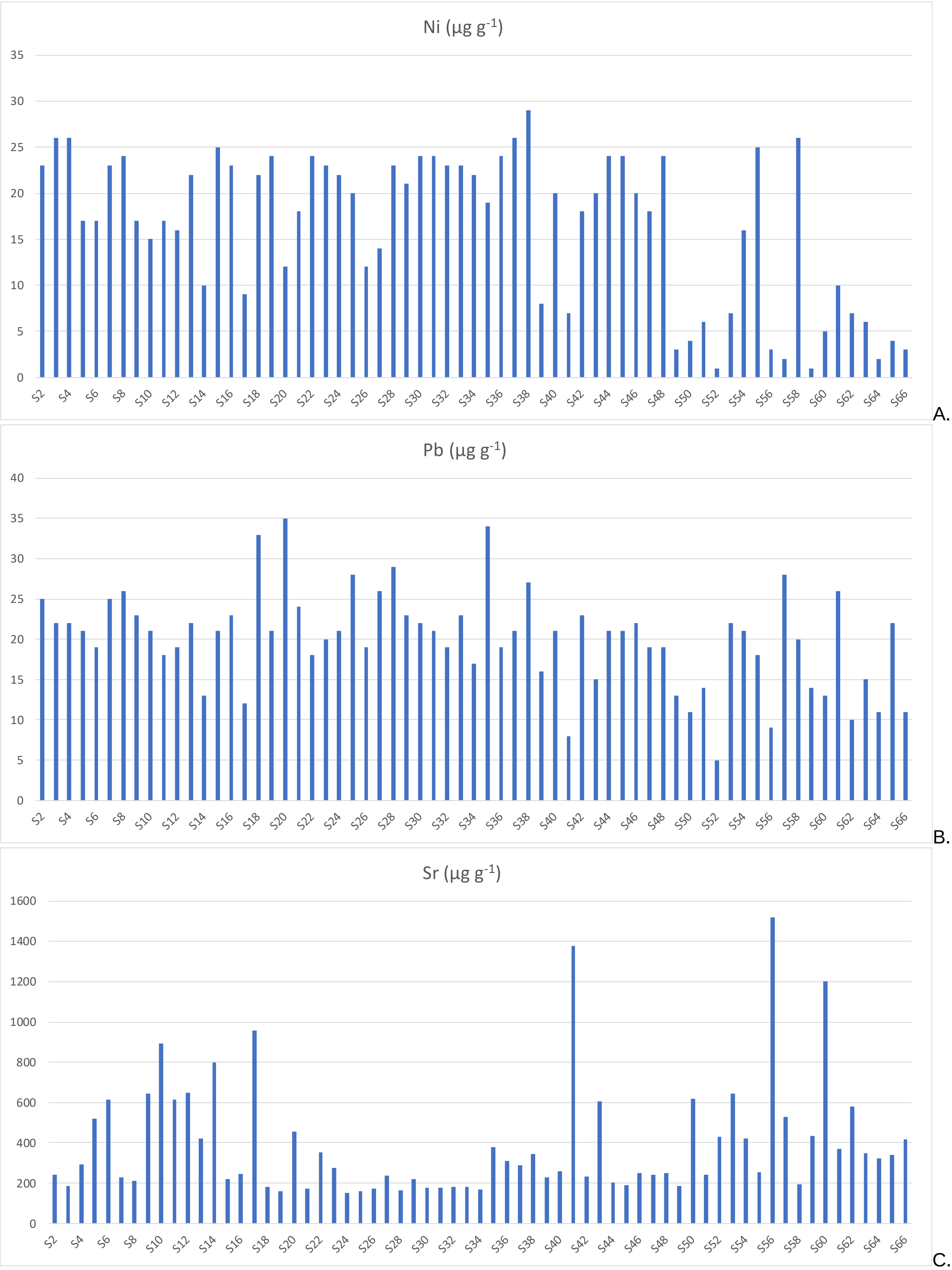


**Appendix 4.** Concentration of non-essential elements by station.