

VITORIA BAY POLLUTION STUDY IN THE FRAME OF TAGUBAR RESEARCH PROJECT – GEOCHEMISTRY OF THE SEDIMENTS OF ESPIRITO SANTO BAY

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Abstract: The Bay of Espirito Santo is located in the Espírito Santo State, in the eastern part of Brazil. It is surrounded by the city of Vitoria on one side and by the Atlantic Ocean on the other. Superficial sediments of Espirito Santo Bay were analyzed at 12 (western shallow silt sediments) + 8 (eastern sandy sediments and relatively deep sampling stations) = 20 uniformly distributed sampling points where geochemical analysis was performed. Nineteen elements were analyzed: Mo, Cu, Pb, Zn, Ag, Ni, Mn, Fe, As, U, Th, Sr, Cd, Sb, Bi, V, Cr, Ba, and Al. This selection was made based on the most representative heavy metals present in this area and according to the results obtained from the geochemical analysis. Their concentrations were compared with metal contamination benchmarks like Screening Quick Reference Tables (SQiRTs), Effects Range-Low (ERLs) and Effects Range-Median (ERMs), TELs (Threshold Effects Levels), PELs (Probable Effects Levels), ERM (Effects range median), and AETs (Apparent Effects Thresholds). Results indicate that there is no particular pollution condition able to alter the condition of any part of this water body. The Authors conclude that the Espirito Santo Bay is only moderately polluted and some elements are virtually absent.

Keywords: Vitoria, Espírito Santo Bay, geochemical analysis

1. Introduction

TAGUBAR Project derives its origins from a Brazilian Government decision to tackle the planning and management challenges related to the restoration of some degraded aquatic ecosystems like the Guanabara (State of Rio de Janeiro) and the Vitoria-Espirito Santo (State of Spirito Santo) bays. This was performed by using the successful outcomes of a previous MFA/DGCS (Ministry of Foreign Affairs/Direttore Generale alla Cooperazione allo Sviluppo, *i.e.*, Directorate General for the Cooperation and Development) cooperation program involving the Project NIKE in Vitoria (Espirito Santo Bay). Such relevant multi-year collaboration between Italian and Brazilian scientific institutions allowed the exchange of the acquired methodologies and of the corresponding data-bases. The general objective of the programme was to contribute to the economic and social development of population living around Guanabara, Vitoria and Espirito Santo bays while promoting the conservation of their natural resources. This objective was supposed to be achieved by consolidating local Authorities' ability to plan and implement a re-conditioning program within a systemic management framework in severely polluted ecosystems. The proposed project was named TAGUBAR (TAngential GUanabara Bay Aeration and Recovery, following the pattern of the VENICE's Logical Framework) developed by IDEAS (institution belonging to the University of Venice, Italy) and applied to Guanabara Bay. In the frame of TAGUBAR Project, the

MFA/DGCS and the Government of Brazil decided to perform a specific parallel research to check the methodology applied on Rio de Janeiro Bay and to compare the results with two other different tropical environments. The Vitoria Bay and Espirito Santo Bay were selected to be used as comparison.

2. The study area: the main physical and geographical aspects of the Vitoria Bay

Vitoria City was founded in 1535 and originally was called Vila Nova ("New Town") do Espírito Santo. Today it is a sort of Rio de Janeiro in miniature and capital of the Espírito Santo State, located in the eastern part of Brazil (Figure 1).



Figure 1. The Espirito Santo Bay.

The city of Vitória lies on an island in front of the coast (Figure 2).



Figure 2. Detailed maps of the study area: on the left, the physical map shows urban and industrial areas while details of the different water bodies are reported on the right.

Both the bay shore and the oceanfront are surrounded with shallow mountains. There are flat

areas near the beach, but the central business district is limited to a cove of 5 km in the inland. It is connected to the mainland by a bridge.

Vitoria constitutes an important commercial center of the State, with exports of sugar, coffee, lumber, rice, and manioc. Nowadays (2018), it has a population of about 360 thousand inhabitants and its bay is one of the most industrialized region in the State of Espírito Santo. As a result of the urban growth, large quantities of raw industrial and urban sewage containing heavy metals enter the estuarine system [1, 2, 3].

The Espírito Santo Bay presents a high degree of exposure to tides, winds, and waves. On the north, it is surrounded by the Tubarão Mountain while on the south by the Moreno do Moreno Mountain and the Camburi Beach, the most renowned beach of the municipality of Vitoria. Anthropogenic influence contributed heavily over the decades to decrease of the mangrove area around the island of Vitoria [4], as well as in the proximity of the communities of Sao Pedro, Caieiras, Santo Antonio, and Maria Ortiz. Carmo [5] and Jesus [6, 7] suggested that the main causes of such decrease could be landfills, industries, and port activities.

Currently, mangroves occupy an area of only 18 km², which represents 20% of the total mangroves present in the Espírito Santo State [4]. The northwestern part of the estuary system includes the mouth of the Santa Maria River (4 km² of mangrove), Bubù River (3 km²), and Lameirao Island (Municipal Biological Reserve, 4.9 km²) [6]. From the naturalistic point of view, it is the most preserved area and it displays a high mangrove density [4].

The Vitoria Bay receives the inputs from the rivers Aribiri, Bubu, and Santa Maria. The farms located in the estuaries of these rivers provide to the market considerable amounts of fish and shellfish used for human consumption. Therefore, the evaluation of the contamination of the marine environment by heavy metals becomes urgent [2, 3, 7, 8]. The Bay of Vitória is protected from the ocean waves while the tidal wave crosses the entire bay, rising up above the Santa Maria Delta and entering the Canal da Passagem (Pass Channel). It presents extensive shallow waters where mangroves flourish [4]. Its SW-NE orientation favors the prevailing winds in the region.

The Canal of Porto (Port Channel) is an integral part of the Bay of Vitória, being the main channel of connection between the Bay of Espírito Santo and the Bay of Vitoria. It is a region greatly altered by landfills and dredging activities while, as it is already suggested by its name, it is the access channel to the Port of Vitoria, justifying therefore to be treated separately with respect to the Bay of Vitoria.

The surroundings of Espírito Santo and Vitoria Bays are characterized by a high rate of urbanization and industrial activities, especially regarding tourism infrastructures (big buildings and hotels) and shipping activities, which can be considered indicative of a fast city growth. Presence of large ships and boats can be observed specially at the end of the Canal do Porto as a consequence of the trading with American and European Countries.

The area is characterized by the presence of hilly islands (granite composition) densely vegetated. Some of them are getting also densely populated due to the facilities offered by transportation and good communication with the mainland. On the other hand, the surroundings of the Canal do Porto, at least large part of it, are populated by dense mangrove flora which is considered a good water and sediment depurator [4, 9]. Mangroves also represent a marine environment rich of life and biodiversity [4]. The natural reserve “Lameirão” is located in this area. Presence of small houses can be also noticed in some parts along the Canal do Porto, which most probably belong to the fishermen living in this area, who benefit of fishes and mollusks characteristic of this kind of vegetation [8]. Along some of these places it is also possible to see some mangrove “deforestation” caused by house construction [4].

The Canal da Passagem is located in the estuary system of the Santa Maria da Vitória River, in the municipality of Vitória-Espírito Santo (20° 19' S and 40° 20' W). It could be classified as a coastal plain estuary and, regarding stratification, it can be considered “well mixed”. At the beginning of Camburi Beach, it connects the Espírito Santo Bay to the northern portion of Vitoria Bay, receiving the influence of the tide at both ends, tide influence that involves much of the existing mangroves [4]. Its bathymetry is variable, showing both shallow channels that dry at the

time of the ebb tide and locations as deep as 7 m. Its average width is about 80 m, with the smallest width, 35 m, under the Passage Bridge [10, 11]. It is a shallow, windy channel with extensive mangrove areas [4]. It is characterized by a curious hydrodynamic behavior caused by the barotropic convergence of the tidal wave, resulting from the meeting of the tidal fronts that propagate through the different channels. It receives a large supply of domestic sewage, mostly untreated [1]. The rest of domestic sewage comes from several neighborhood treatment plants of Vitória, such as CESAN (Companhia Espírito Santo Santana de Saneamento) André Carlone, Camburi, and Nova Palestina [1]. Then, it reaches the Bay of Espírito Santo during the ebb tide [3]. Because the sewage treatment is largely insufficient, this makes the partially treated sewage the main contributor to the degradation of the water quality [1, 2, 3, 10]. The sediments of this region presented the highest levels of organic matter as compared with the rest of the estuary. At the innermost points of the Canal, the sedimentation rate is high because the small flow velocity due to the presence of the mangroves [4, 12]. The inversion of flow direction, as consequence of the tide, favors the deposition of loamy sediments and organic matter [12, 13].

3. Material and methods

3.1. Sampling points

Sampling points were uniformly distributed along the Espírito Santo Bay and part of the Vitória Bay, with special emphasis on the Canal do Porto. The type and location of each station was previously determined according to the characteristics of each bay.

Depending on the location and characteristics (depth) of the sampling sites, two boats were used for this campaign. The first boat used for the sampling at the Espírito Santo Bay was fully equipped with a professional navigation system including an accurate GPS and echo sounder. The other boat used for sampling at the canal (shallow waters), contained a portable GPS in order to know the correct coordinates of the sampling points. Also in this case, the water depth was measured by the professional echo sounder. For each sampling point, regardless the type of station, the following data were always recorded: geographic co-ordinates (longitude, latitude), water depth, time, and type of sediments.

The sediments were collected, mixed carefully to obtain homogeneous samples, frozen, and then immediately transported to the laboratory for analysis. The samples were dried under nitrogen atmosphere to avoid oxidation and stored in sealed glass containers. This procedure was previously tested in our laboratory [14, 15, 16].

3.2. Sediment sampling stations

Sampling consisted on the collection of sediment and water samples for geological, chemical (water and sediments) and biological analysis [17]. Each sampling took about 40 minutes to be completed since there were several different activities related to the sampling techniques used in each case. Briefly, sampling activities comprised the collection of bottom sediments using a Van Veen grab having a capacity of approximately 5 liters. Only one launch of the grab was adequate to collect enough amount of sample. All sediment samples were then deposited on a plastic tray and well mixed till homogenization (Figure 3).



Figure 3. Storage of sediment samples depends on type of analysis to be performed later on.

The sediment samples collected in this type of stations were analyzed geologically (grain size, mineralogy and geochemistry analyses) [18] and chemically (on sediments). The sediment samples deposited on the plastic tray were then stored in plastic containers for geological analysis, and glass bottles for chemical analysis. A bigger container was used for storing samples for mineralogical and grain size analysis [18] while for geochemical and chemical analysis smaller bags and jars were used.

Different types of sediments were found on the bay sampling points, like for example: sand, mud, and mixed mud + sand (Figure 4 left and right).



Figure 4. Sediments sampled from different stations: mud, which constitutes the bottom part of the sample, looks black while the more clear sand stays the top (right).

In more detail, in Figure 4 (right) the sediments look heterogeneous because it is possible to see the black mud (bottom) and the more clear sand (top). Vice versa, on the left of Figure 4 the sediment appears homogeneously black. Different sediments could be an indication either of the different activities taking place on the surroundings (like urban vs. industrial discharges) or of the different hydrodynamic situations typical of that specific site influenced by marine currents or bottom morphology.

As it can be seen in Figure 5, two different areas can be clearly identified: RING A made of 12 stations (i.e., stations 1a, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, and 16) close to the coast and therefore rich of organic matter and RING B made of 8 stations (i.e., stations 1b, 13, 3b, 11, 12, 17, 4b, and 14) where the sandy component prevails.

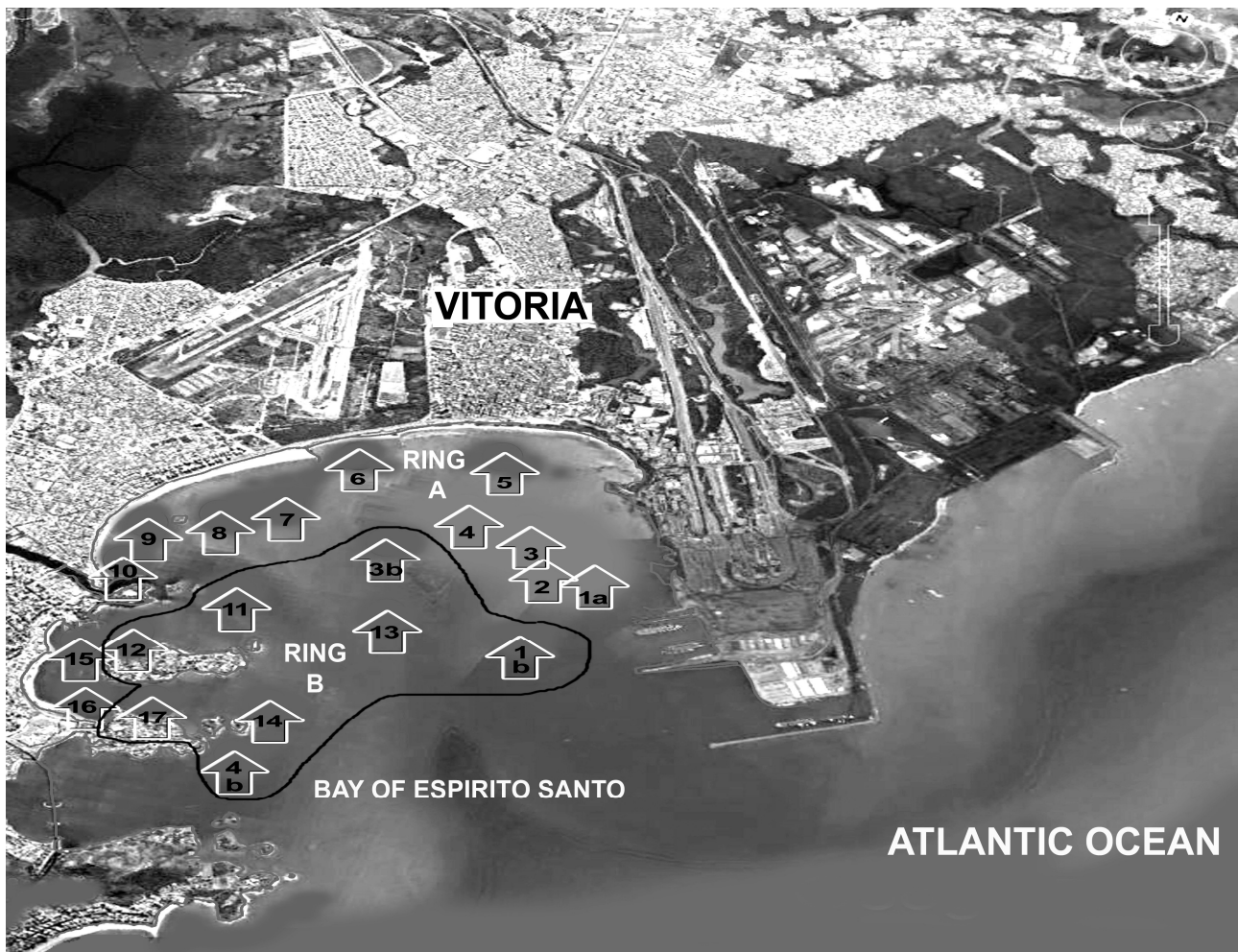


Figure 5. Location of the sediment sampling stations in the Baía of Espírito Santo (Município de Vitória - ES). Arrows are oriented in the North direction. Sampling stations are located at the top of each arrow.

3.3. Metal contamination benchmarks

The five benchmarks we used are: TELs, (Threshold Effects Levels), ERL (Effects range low), PELs (Probable Effects Levels), ERM (Effects range median), and the AETs (Apparent Effects Thresholds) [19, 20, 21, 22].

The ERL and ERM are measures of toxicity in marine sediment. The ERL indicates the concentration below which toxic effects are scarcely observed or predicted, while the ERM indicates the concentration above which effects are generally or always observed. AET is defined as the sediment concentration of a given chemical above which statistically significant effects (e.g., sediment toxicity) are always observed. AET may be more sensitive than PELs or ERM since these last ones incorporate several endpoints in their determination. Despite we reported five benchmarks, special emphasis has been given to TEL and AET, being the first one the most protective and the second one the more statistically significant value. Unfortunately, for some elements TEL, ERL, PEL, and ERM are not defined. Particularly, they are not defined for aluminum, barium, iron, manganese, nickel, antimony, and vanadium.

3.4. Geochemical analyses. Instrumentation

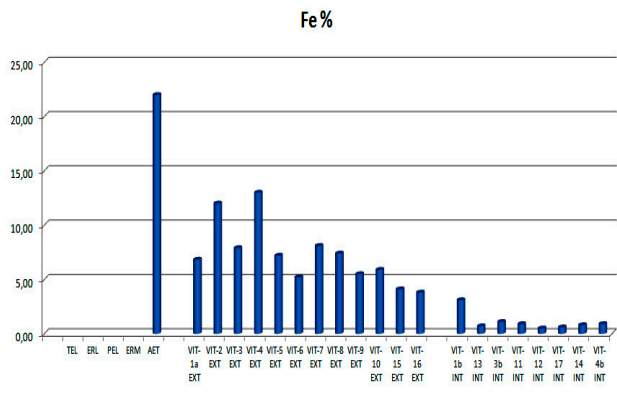
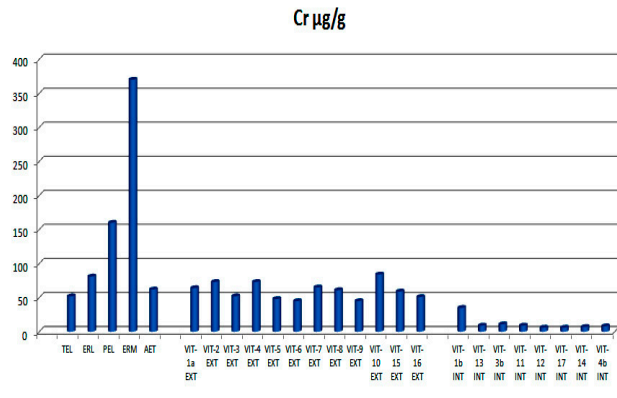
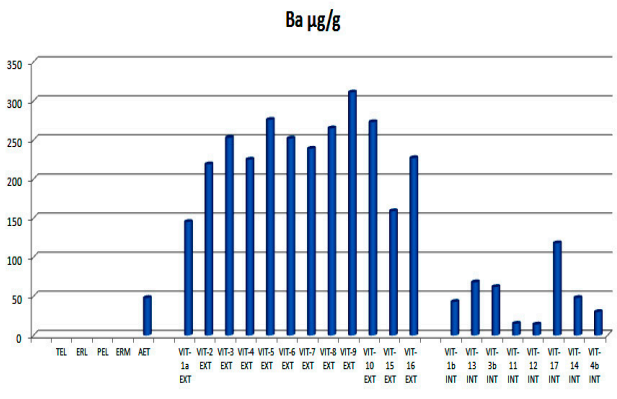
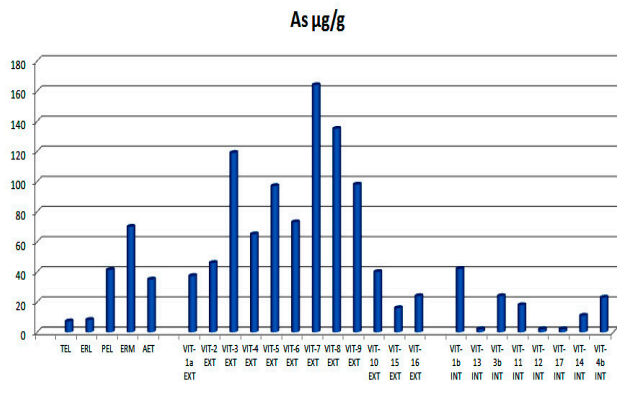
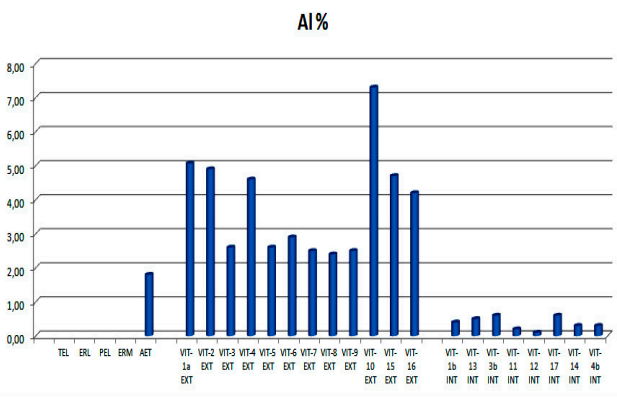
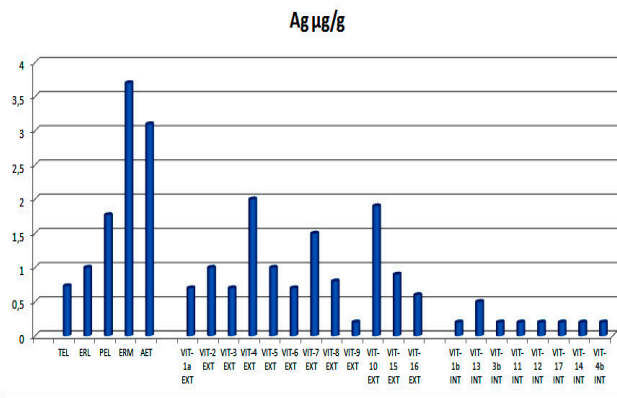
For geochemical analysis, Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) methodology was used. Nineteen elements were analyzed: Mo, Cu, Pb, Zn, Ag, Ni, Mn, Fe, As, U, Th, Sr, Cd, Sb, Bi, V, Cr, Ba, and Al. For all of them, concentrations are here expressed in $\mu\text{g g}^{-1}$

(micrograms per gram of dry sediment), except for Fe, and Al, which are reported in the % (by dry weight) form. Twelve elements were selected as the most important and more appropriate to be either representative or trace indicators of the level of chemical pollution and therefore deeply analyzed and discussed in the 2D diagrams which here follow. These elements are: Ag, Al, As, Ba, Cr, Fe, Mn, Ni, Pb, Sb, V, and Zn. This selection was made on the basis of the results obtained from the geochemical analysis. In addition, 17 elements (Ag, Al, Bi, As, Cd, Cu, Fe, Pb, Mn, Mo, Ni, Sb, Sr, Th, U, V, and Zn) were selected to be represented by 3D diagrams in order to detect the possible pollution sources.

4. Results and discussion

The following two figures illustrate the metal distributions by two different set of diagrams: 2D and 3D diagrams. The first group of diagrams (Figure 6) shows in two dimensions the different metal concentrations ($\mu\text{g g}^{-1}$ or %) present in the sediment of each station (stations are named “VIT-“, after “Vitoria”). Each of these diagrams is subdivided in two parts, left and right, respectively. The concentrations measured in each station (on the right) are compared with the five quality aforementioned benchmarks (on the left). Also, sampling stations are grouped according to their geographical distribution as it is depicted in Figure 5, i.e., those belonging to RING A (stations VIT-1a, VIT-2, VIT-3, VIT-4, VIT-5, VIT-6, VIT-7, VIT-8, VIT-9, VIT-10, VIT-15, and VIT-16) are close to the coast and are rich of organic matter while for those inside RING B (stations VIT-1b, VIT-13, VIT-3b, VIT-11, VIT-12, VIT-17, VIT-4b, and VIT-14) the sandy component prevails.

The second group of diagrams (Figure 7) reports in three dimensions on the z-axis the concentration ($\mu\text{g g}^{-1}$ or %) of the 17 considered elements (Ag, Al, Bi, As, Cd, Cu, Fe, Pb, Mn, Mo, Ni, Sb, Sr, Th, U, V, and Zn) against the geographical coordinates (longitude on the left and latitude on the right), so that the prevailing contaminated spots become evident.



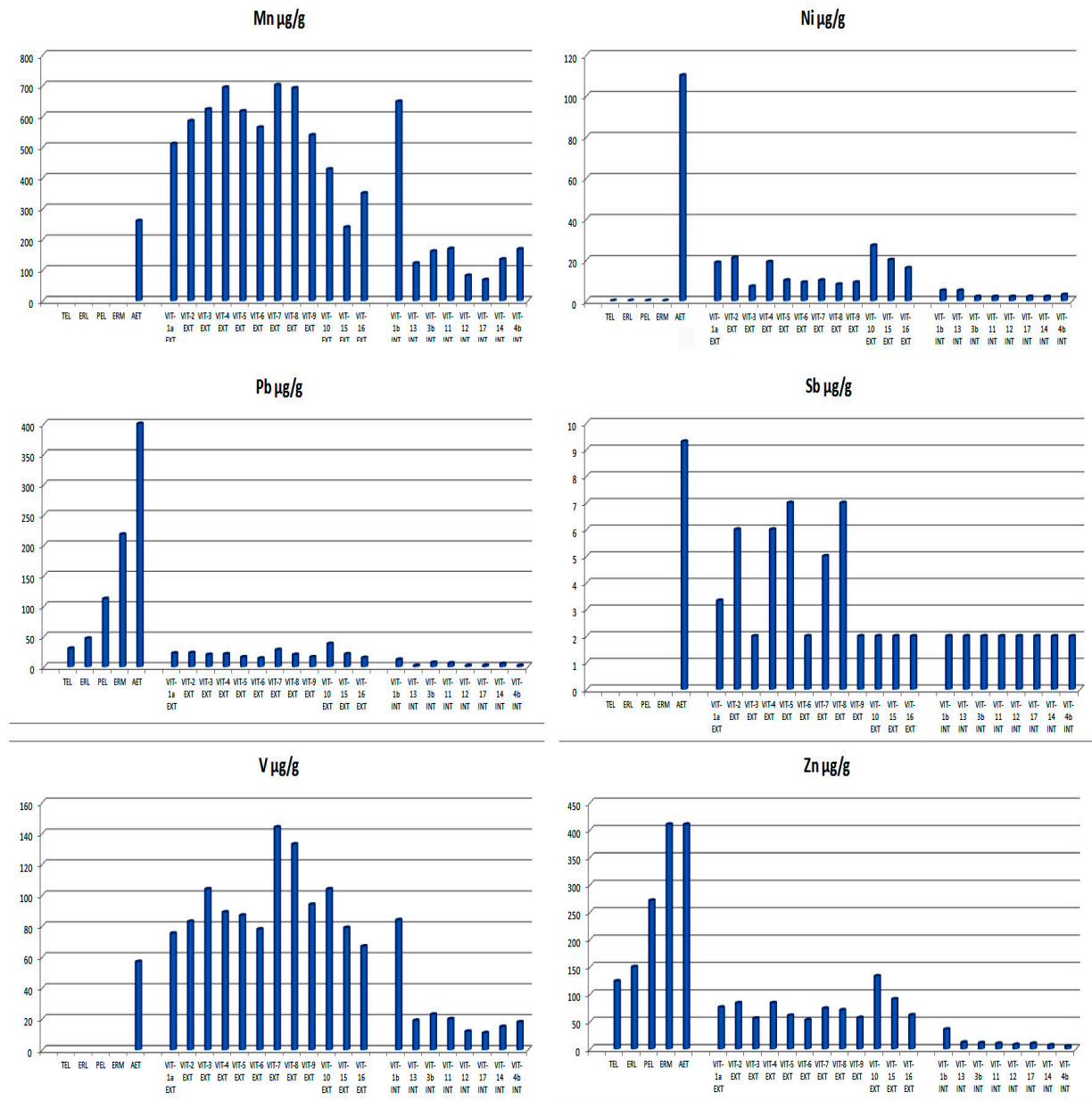


Figure 6. Silver, aluminum, arsenic, barium, chromium, iron, manganese, nickel, lead, antimony, vanadium, and zinc distributions compared with the benchmark values.

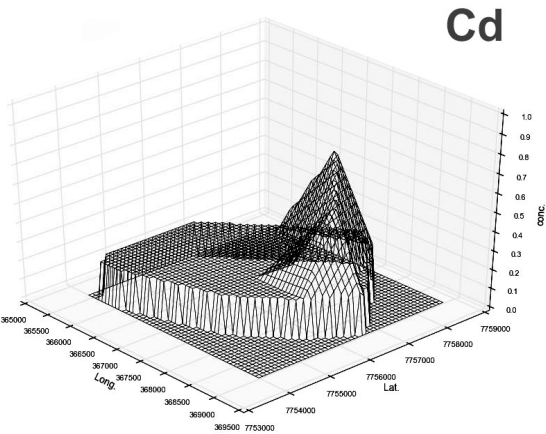
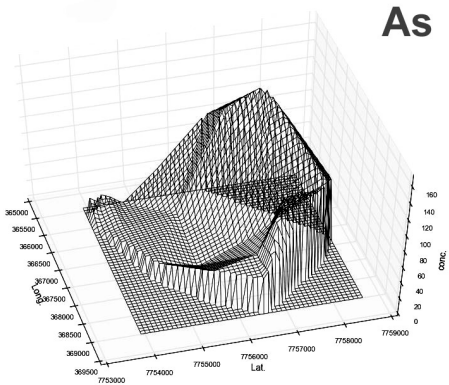
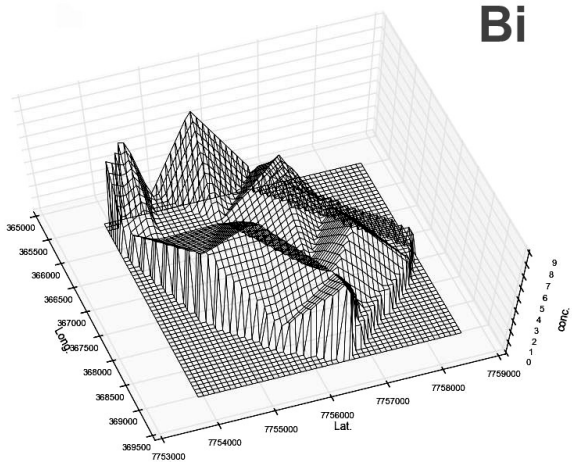
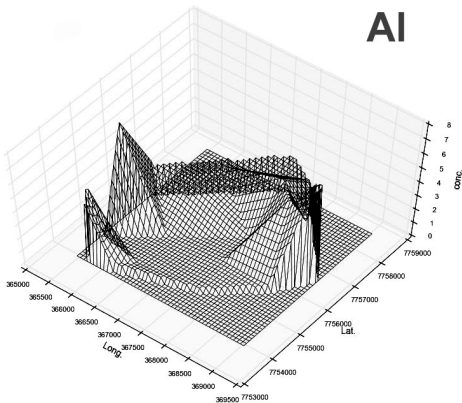
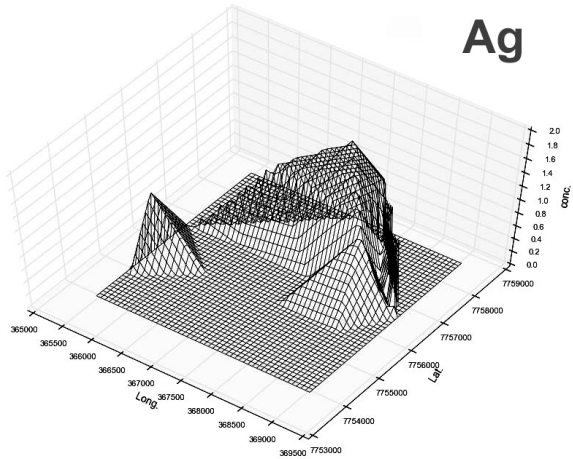
From the two dimensional diagrams presented in Figure 6 it is possible to see that only 6 out of the total 12 reported elements show a regular behavior that would allow a rational interpretation. In more detail, the following 6 elements: arsenic, barium, manganese, copper, antimony, and vanadium suggest that the potential pollution sources could be located between station 6 and station 8, being probably station 7 the closest to the actual contamination source. As far as manganese and iron, it seems that there could be a substantial contribution from sources located very close to the industrial area, where specific metal industrial processing is normally carried out.

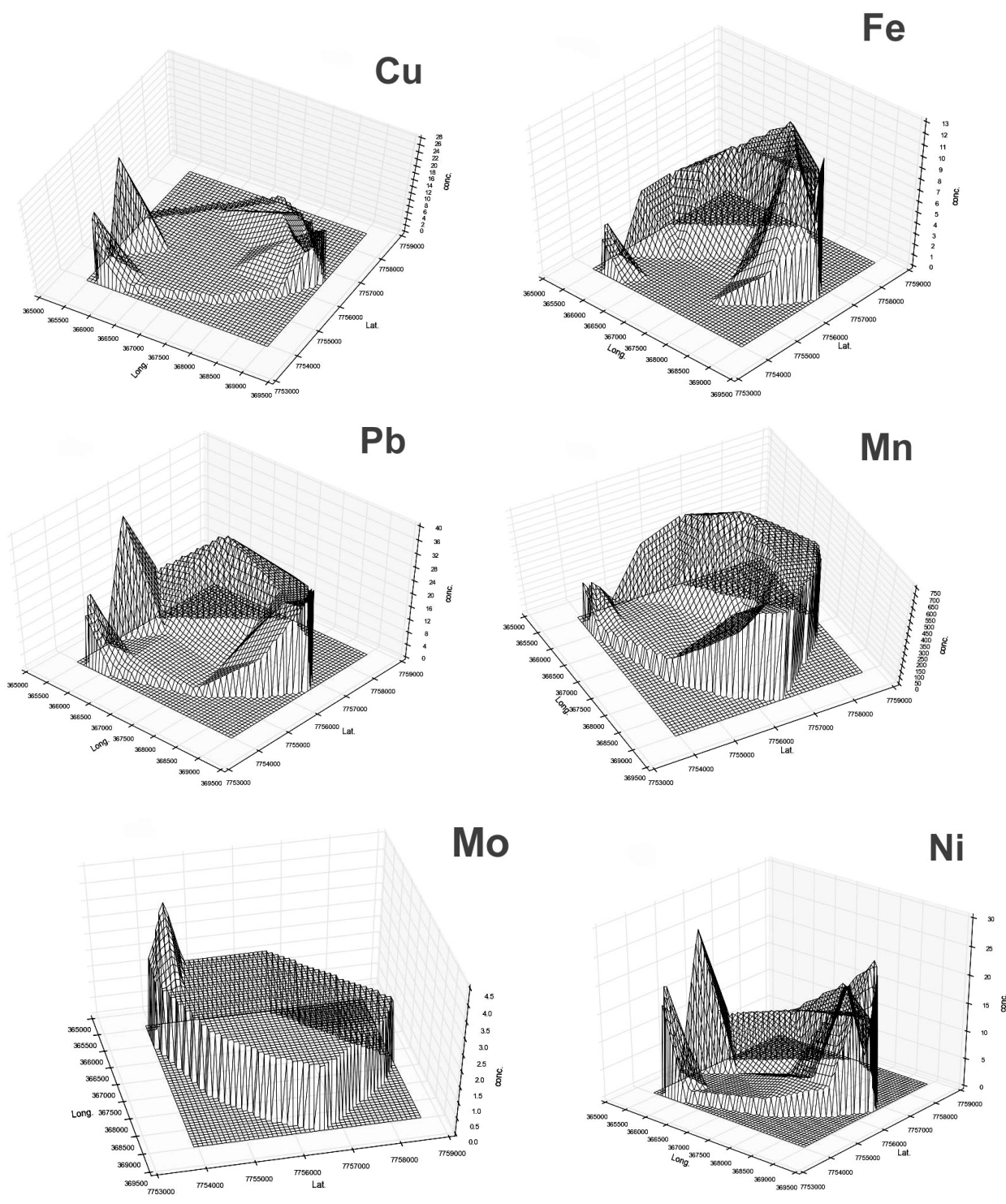
On the other hand, metal industrial processing does not seem to contribute significantly to the arsenic concentration which is probably more dependent from the Canal de Passagem and the Canal de Camburi inputs. However, this looks bizarre because it requires that such element gets to the Baia de Espirito Santo through the Canal de Passagem, i.e., an area densely populated by mangroves which normally should be *a priori* chemically uncontaminated [9]. Therefore, such results should be more deeply analyzed in the future taking into account also the hydrodynamics of the involved ecosystem.

A deeper analysis of the bidimensional diagrams reported in Figure 6 could suggest which might be the origin of the inputs of the polluting metals discharged in the bay. Particularly, it is possible to

identify at least four main potential sources of pollutants, which, briefly will be here named α , β , γ , and δ , corresponding to the Espírito Santo Bay regions of South-East (see for example station VIT-4b, but also VIT-17), East/North-East (see for example stations VIT-8, VIT-9, VIT-10, VIT-11, and VIT-12, but also VIT-15 close to Ilha do Frade bridge), North (see for example stations VIT-5, VIT-6, and VIT-7), and West/South-West (see for example stations VIT-1a, VIT-1b, and VIT-2), respectively. The source α may represent, on one hand, the pollution coming out from (and collected by) the Vitoria Bay and, on the other hand, that coming from the urban discharges of the Vitoria City suburbs like Bento Ferreira, Jesus de Nazareth, Praia do Suã, Santa Helena, and Santa Lucia but also from Centro de Vila Velha. As far as β , this source should describe the Canal de Passagem outputs but also those coming from Vitoria City quarters like, again, Santa Lucia and also Praia do Canto, Jardim de Penha as well as Ilha do Frade. The pollution originated by the activities located along the Camburi beach and the Jarim de Camburi urban site, is monitored by γ stations. Last, the Tubarão harbor area pollution situation is illustrated by δ . In such contest, Ba shows a large and high peak along β (stations VIT-8, $265 \mu\text{g g}^{-1}$; VIT-9, $311 \mu\text{g g}^{-1}$; VIT-10, $273 \mu\text{g g}^{-1}$ and VIT-15, $159 \mu\text{g g}^{-1}$), a secondary peak along γ (stations VIT-5, $276 \mu\text{g g}^{-1}$; VIT-6, $252 \mu\text{g g}^{-1}$ and VIT-7, $239 \mu\text{g g}^{-1}$) and sharper peaks along δ (station VIT-3, $253 \mu\text{g g}^{-1}$) and α (station VIT-16, $227 \mu\text{g g}^{-1}$). On the other hand, Cr displays practically only one interesting peak, namely that corresponding to station VIT-10 (β direction, $84 \mu\text{g g}^{-1}$). The picture is completed by two peaks corresponding to stations 2 ($73 \mu\text{g g}^{-1}$) and 4 ($73 \mu\text{g g}^{-1}$). As far as the other elements, they will be discussed later, when 3D diagrams will be addressed.

In terms of environmental impact, specifically in terms of AET and TEL benchmarks, experimental data put in evidence that the safety value AET, with the exception of very few stations (like in the case of As and Mn) constantly surpasses the measured concentrations for all stations located within RING A for aluminum, arsenic, barium, manganese, and vanadium, while inside RING B only in very few cases this happens for barium, arsenic, manganese, and vanadium. However, it is interesting to note that TEL (for those elements where TEL is defined) is surpassed within RING A by elements like silver, arsenic, and chromium, while it is only sporadically reached by lead and zinc. On the contrary, in RING B only arsenic presents values that sometime exceed that threshold.





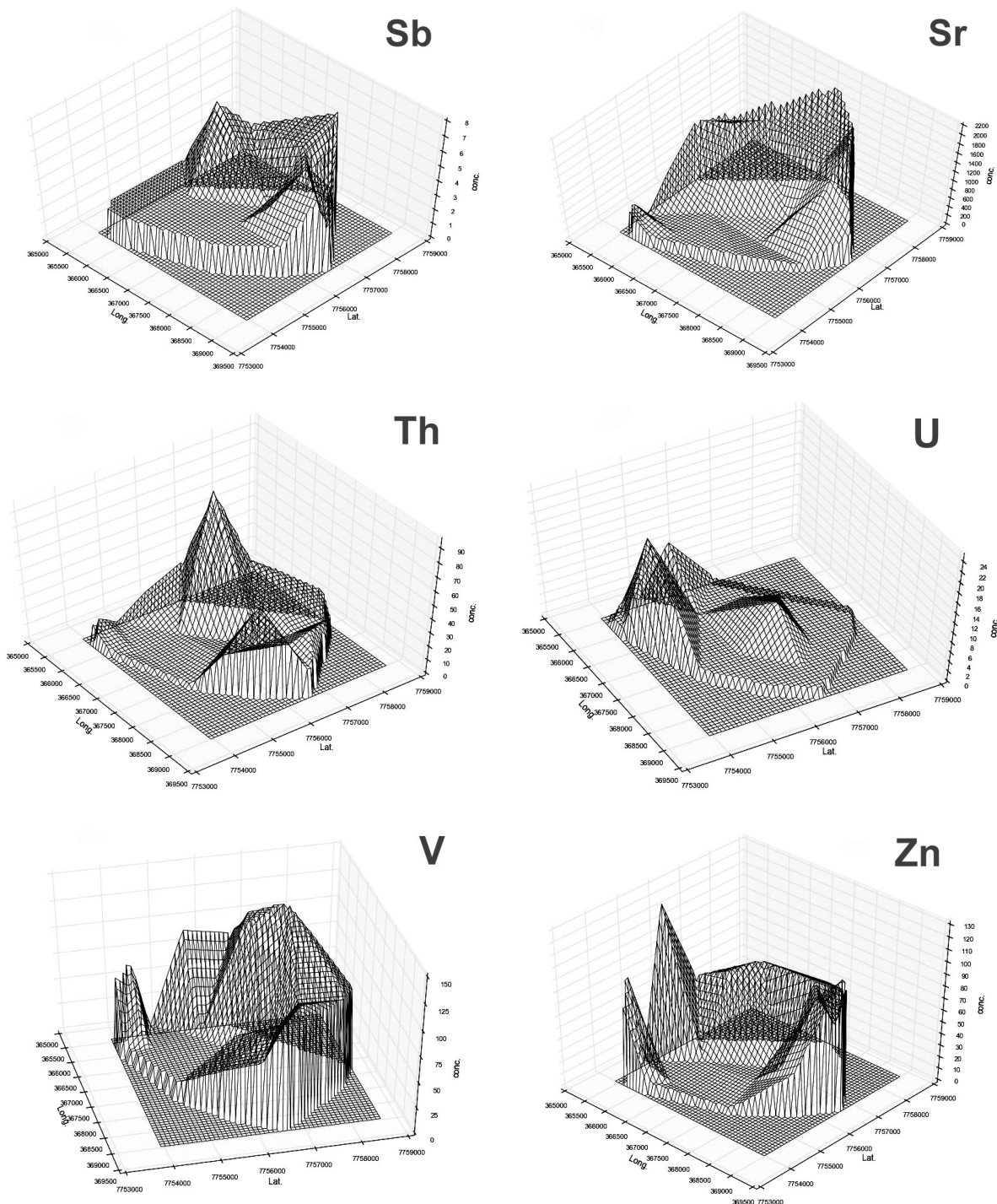


Figure 7. 3D diagrams of Ag, Al, Bi, As, Cd, Cu, Fe, Pb, Mn, Mo, Ni, Sb, Sr, Th, U, V, and Zn distribution in Espirito Santo Bay diagrams oriented after the bay map (see upper left).

Tridimensional diagrams (Figure 7) show that the most relevant immissions concern 10 out of 17 elements: silver, aluminum, bismuth, copper, lead, molybdenum, nickel, vanadium, uranium, and zinc. They seem to come from South-West, i.e., from the final portion of the Vitoria Bay and from the Canal de Passagem.

These are followed by the Camburi beach (North) immissions which concern arsenic, cadmium, manganese, antimony, strontium, and vanadium. Finally, in the Tubarão harbor area (North-East), where several industries are located, it is possible to detect clear indications concerning the immission of cadmium, iron, nickel, antimony, vanadium, and zinc. Apparently, in several cases there are multiple streams with no clear predominance of one of them over the others. This can be observed in the cases of

silver, aluminum, bismuth, lead, nickel, antimony, and zinc. In some cases it seems possible to spot a single immersion point, like for example for cadmium and thorium (N-W) or for molybdenum (S-W).

In more detail, silver shows 3 main peaks: the highest concentration ($2.0 \mu\text{g g}^{-1}$) corresponds to station VIT-4, i.e., γ region. A second peak ($1.9 \mu\text{g g}^{-1}$) can be detected in VIT-10 which is in the β zone, while in γ (VIT-7) can be found the 3rd highest peak ($1.5 \mu\text{g g}^{-1}$). All these peaks appear quite well separated by deep valleys. The opposite can be observed in the case of Al where some peaks are interconnected. To be more precise, while the two peaks located on α (VIT-16, 4.2 %) and β (VIT-15, 4.7% and VIT-10, 7.3 % merged together) are clearly resolved, vice versa from β to δ (VIT-2, 4.9 % and VIT-1a, merged together) through γ (VIT-4, 4.6%) there is no solution of continuity of a smooth plateau, like an amphitheatre, that connects β peak to a shallow hill present in δ . A similar “amphitheatre shape” can be seen in the case of As too, from α to δ : VIT-4 ($65 \mu\text{g g}^{-1}$), VIT-9 ($98 \mu\text{g g}^{-1}$), VIT-8 ($135 \mu\text{g g}^{-1}$), VIT-7 ($164 \mu\text{g g}^{-1}$), VIT-6 ($73 \mu\text{g g}^{-1}$), VIT-5 ($97 \mu\text{g g}^{-1}$), and VIT-3 ($119 \mu\text{g g}^{-1}$). This arch has the highest peak (VIT-7) on γ/β area, while on δ there is a secondary peak (VIT-3). Also Fe is characterized by an arch, this time connecting β with δ (VIT-8, 7.4 %; VIT-7, 8.1 %; VIT-5, 7.2 %; VIT-4, 13 %; VIT-3, 7.9 %; VIT-2, 12 %) with the highest peak in γ (VIT-4). On the other hand, in α (VIT-16, 3.8 %) there is an isolated small peak. A similar isolated but very small peak in α is present in the case of Mn (VIT-16, $350 \mu\text{g g}^{-1}$). Then, again, an amphitheatre, but this time of an almost constant height (in the range VIT-9, $539 \mu\text{g g}^{-1}$; VIT-7, $702 \mu\text{g g}^{-1}$), interconnects β with δ and therefore no highest peak clearly emerges from the ridge. A completely different situation can be noticed for Ni where four sharply resolved peaks show up in α (VIT-16, $16 \mu\text{g g}^{-1}$), β (VIT-10, $27 \mu\text{g g}^{-1}$), γ (VIT-4, $19 \mu\text{g g}^{-1}$), and δ (VIT-2, $21 \mu\text{g g}^{-1}$). Two main peaks well separated by deep valleys can be seen around α (VIT-16, $15 \mu\text{g g}^{-1}$) and β (VIT-15, $21 \mu\text{g g}^{-1}$ and VIT-10, $38 \mu\text{g g}^{-1}$) in the case of Pb. The arch connecting β with two other peaks located in δ (VIT-2, $23 \mu\text{g g}^{-1}$ and VIT-3, $20 \mu\text{g g}^{-1}$) shows its maximum in β (VIT-7, $28 \mu\text{g g}^{-1}$). Sb displays three peaks (VIT-8, $7 \mu\text{g g}^{-1}$; VIT-5, $7 \mu\text{g g}^{-1}$; VIT-2, $6 \mu\text{g g}^{-1}$), none of which is clearly overwhelming the others, being β (VIT-8) and γ (VIT-5) well resolved, while the third peak δ (VIT-2) is partially joined to γ by a ridge. A similar smooth look can be observed for vanadium. The peak located in α (VIT-16, $67 \mu\text{g g}^{-1}$) is well separated from a mountain range, beginning in β (VIT-15, $79 \mu\text{g g}^{-1}$) and ending in δ (VIT-2, $83 \mu\text{g g}^{-1}$), that shows an apex in β (VIT-7, $144 \mu\text{g g}^{-1}$), which represents the absolute maximum, and another peak in δ (VIT-3, $104 \mu\text{g g}^{-1}$). Zn profile is characterized by three peaks (VIT-16, $62 \mu\text{g g}^{-1}$; VIT-10, $133 \mu\text{g g}^{-1}$; VIT-2, $84 \mu\text{g g}^{-1}$). The peaks present in α and β are deeply separated by a valley, while an arch connects the maximum located in β (VIT-10) with δ . In the same VIT-10 station Bi shows its maximum as well ($8 \mu\text{g g}^{-1}$), but many more peaks are present: one in α (VIT-16, $6 \mu\text{g g}^{-1}$), two in β (VIT-10 and VIT-8, $6 \mu\text{g g}^{-1}$), and another in γ (VIT-4, $7 \mu\text{g g}^{-1}$), all of them well resolved. A ridge partially joins γ with δ (VIT-1a, $7 \mu\text{g g}^{-1}$) whose peak is, at least in part, merged with a peak centered around station VIT-13 ($7 \mu\text{g g}^{-1}$). This last one is clearly separated from α , β , and γ . It should be underscore that station VIT-13 is in the very middle of Espirito Santo Bay, which makes Bi (along with uranium) a sharp exception with respect to all other elements taken into consideration in the present paper where the center of Espirito Santo Bay is normally unpolluted. A completely different situation can be seen in the case of Cd which looks rather flat. The only peak present, which is actually located in γ/δ (VIT-4, $0.8 \mu\text{g g}^{-1}$), decays smoothly to δ while sharply to γ . Four peaks characterize Cu, a small one in α (VIT-16, $9 \mu\text{g g}^{-1}$) well resolved with respect to the maximum in β ($27 \mu\text{g g}^{-1}$ in VIT-10), another in γ/δ (VIT-4, $11 \mu\text{g g}^{-1}$) totally separated from the former, and the last one in δ (VIT-1a, $18 \mu\text{g g}^{-1}$) partially joined to VIT-4. A really solitary peak (VIT-15) distinguishes Mo from all other elements here discussed. Moreover, such peak located in α/β is rather low ($4 \mu\text{g g}^{-1}$) with respect to the background ($2 \mu\text{g g}^{-1}$). Vice versa, Sr displays very high concentrations and five peaks: a little hill in α (VIT-16, $585 \mu\text{g g}^{-1}$) a very high concentration in the two merged peaks located in β (VIT-8, $1615 \mu\text{g g}^{-1}$ and VIT-7, $1477 \mu\text{g g}^{-1}$) and in the maximum centered in γ (VIT-6, $2145 \mu\text{g g}^{-1}$) while the fourth and fifth peaks are present in δ (VIT-3, $2045 \mu\text{g g}^{-1}$ and VIT-2, $1342 \mu\text{g g}^{-1}$). Thorium has a hill and two sharply separated peaks (VIT-16, $15 \mu\text{g g}^{-1}$; VIT-8, $93 \mu\text{g g}^{-1}$; VIT-1a, $68 \mu\text{g g}^{-1}$). The main peak is in β (VIT-8) while the secondary one is in δ (VIT-1a). Despite they are clearly separated, at the same time they are interconnected by a low ridge which shows a partial depression in γ . The small, but well resolved, hill present in α (VIT-16) seems almost to stretch out from β . Finally, uranium is characterized by three well resolved peaks (VIT-14, $21 \mu\text{g g}^{-1}$; VIT-10, $12 \mu\text{g g}^{-1}$; VIT-3b, $10 \mu\text{g g}^{-1}$). The main peak (VIT-14) is

located in α while the secondary one is in β (VIT-10). Similarly to what was seen in the case of Bi, there is an “anomalous peak” in the middle of the Espirito Santo Bay, specifically in the VIT-3b station.

Obviously, the aforementioned discussion is necessarily limited by the approximation of the graphic elaboration and by the relatively limited number of sampling stations chosen to adequately depict the different typology of sediments. However, an analysis of the sediment typology would nicely explain why the center of each 3D diagram looks almost always (with the exception of Bi and U) flat and homogeneous (i.e., RING B plateau). Most probably this could be due to the prevailing sandy component of the sediment: sand would bind metal ions much less efficiently than the organic component of the sediment [23], which characterizes RING A.

5. Conclusions

On the basis of the aforementioned data reported in the diagrams, it seems possible to conclude that the bay of Espirito Santo presents only a modest contamination level due to heavy metals with some critical values for arsenic, manganese, and vanadium. Particularly, such criticality can be detected in those areas close to the coast. This may be due to the fact that sediment composition near the coast is such that it allows the pollutants to be bound more tightly to the sediment because the presence of organic substances like humic acids or because the presence of clays that fix the ions to the sediment [23]. On the other hand, some elements like arsenic (see Figures 6 and 7) and barium (reported in Figure 6) show surprising high concentrations which are difficult to be explained, especially when taking into account their possible and probable origin, as it was here discussed.

According to our understanding, a correct evaluation of the presence of such elements (with the purpose of identifying and then eliminate the possible pollution sources) appears necessary to complete the research. This would include an appropriate analysis of the ecosystem dynamics, particularly with respect to the bay marine currents which could transport the pollutants in a different way with respect to those evaluated by the simple model of linear diffusion from the potential sources.

Acknowledgements: We thank the Ministry of Foreign Affairs of Italy, General Direction of the Cooperation to the Development, (MAE-DGCS) for founding the present research. We also gratefully thank IUCN Main Office, Geneva, Almeida Paola, Barroso Santarosa Marcio, Brioschi Leonardo Mathias, Correa Leone Gabriel, Cunha Nalesso Rosebel, Daipicula Bravim Andreia, Dias Camilo Jr., Fernandes Fernando, Fonseca Barroso Gilberto, Guillet Alfredo, Kramer Taciana, Loureiro Luiz, Mao Andrea, Oliver James, Paresque Karla, Rocha Schaeffer Lislane, Santarosa Gilberto, Testa Viviane, Vargas Andressa, Verçosa Carvalheira Lucia, Veronez Paulo Jr.

Author Contributions: Perin had the original idea for the study. Bonardi was responsible for data collection and data analysis. Giacometti drafted the manuscript and Perin reviewed it.

Conflicts of Interest: The authors declare no conflict of interest.

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