Trace element contamination and distribution in surface sediments in Ria de Aveiro

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Abstract

The Ria de Aveiro represents an important ecosystem in Portugal. To analyze the distribution of several trace elements (As, Cd, Cr, Cu, Pb, Hg, Ni, Zn) and to evaluate the contamination of these elements, 119 surface sediment samples (5 cm) were collected from all the main channels. Using geostatistical spatialization methods, the spatial distributions for each element were obtained for 65 % of the Ria area.

The results showed, through the identified hotspots, a strong association with anthropogenic sources, mainly related to shipping activities and other causes such as factories of fertilizer, crockery, among others. Natural factors that influence these distributions have also been identified, such as ocean currents and residuals from rivers, the residence time of particles, and sediment characteristics such as organic matter content and particle type.

Through the results obtained from the evaluation of the contamination degree of the sediments, it was possible to conclude that approximately 87% of the samples analyzed presented clean or trace contamination by trace elements, not representing a hazard. However, the remaining 13.5% of the samples already showed contamination by As, Pb, Hg, and Zn. Almost all of these samples were collected in the Murtosa channel, which was considered the most contaminated site in the Ria. However, from this assessment and the stocks obtained overall (in tons: As-61; Cd-0.84; Cr-124; Cu-46; Pb-92; Hg-0.60; Ni-55; Zn-444), the Ria showed less contamination by trace elements than expected.
Keywords: Ria de Aveiro, Trace Elements, Contamination, Spatial Distribution, Geostatistical Spatialization Method, Anthropogenic Sources, Correlations

1. Introduction

Over the years, pollution has increasingly become a problem of greater concern, on a global scale, due to the dangerous consequences it can have both ecosystems and human life. Considering this theme, one of the most alarming causes is pollution by trace elements. These elements, due to their characteristics, which sometimes imply that they are toxic in low concentrations, persistent in the environment, and bioaccumulate, constitute a serious means of pollution that requires a great deal of study and control [5, 29]. One of the biggest targets for this type of pollution is the aquatic ecosystems, such as estuaries, which are subject to various industrial and urban inputs [10, 12].

Although there are several studies related to this problem in various places, the case of Ria de Aveiro and its possible level of contamination by trace elements was never properly studied. The objective of this study is to determine the spatial distribution of trace elements along the Ria de Aveiro, more specifically the elements As, Cd, Cr, Cu, Pb, Hg, Ni, and Zn (trace elements addressed by Portaria nº1450/2007 [1]), identify possible anthropogenic sources and other factors responsible for the obtained distributions, and calculate the stocks of each contaminant in the study area. To the best of my knowledge, it is the first time that the spatial distributions of the elements would be created through a geostatistical spatialization method that is able to provide much more information about this type of contamination assessment. For this reason this study is so important to be conducted

The Water Framework Directive imposes on European member states the implementation of necessary measures to prevent deterioration of the status of all transitional and coastal water bodies. If the ecological status is poor or bad, national efforts implementing treatment systems for domestic effluents and for various types of industries are needed [25]. Therefore, an environmental assessment is also another objective of this study, in terms of the sediment's degree of contamination (Portaria nº 1450/2007) [1], providing important information to decision-makers regarding the trace element pollution in the Ria de Aveiro. Through these objectives, it will also be possible to conclude potential relations between these elements and sediment characteristics, such as organic matter content and sediment type at the granulometry level, and between the elements themselves.

2. Study Area

Ria de Aveiro (Figura 1), located on the North-Western coast of Portugal, is composed of a complex and irregular system of islands, intertidal zones and several channels, such as Ovar, Mira, Ílhavo, S. Jacinto, Espinheiro and Murtosa. Represents the Vouga river mouth, has a single narrow artificial connection with the Atlantic Sea and the main suppliers of freshwater are the Vouga and Antuã rivers [21, 19]. What joins the many channels together is the big lagoon formed parallel to the coast. Ria de Aveiro extends for 83 km2 or 66 km2, depending on whether it is high or low tide respectively. Normally the water depth is below 3 meters, although it can reach almost 20 meters between the outlet to the sea and the entrance to the lagoon [19, 11].

The main driving force of the lagoon circulation is the tides, being an enormously important factor in the transport, erosion, and deposition of sediments. In terms of hydrodynamic influences, the S. Jacinto and Espinheiro channels, located in the lagoon connected to the sea inlet, are the most important. Near the Barra entrance, the tidal currents reaches 2 m/s. The sediment type of the Ria de Aveiro consists of a mixture of sand and mud. The distribution is not uniform, but generally, the northern channels are composed of lower-grained sediments, with more mud, while the southern channels contain higher-grained sediments, with more sand. Besides these two major constituents, it is possible to find gravel and shells, having a clear marine influence through the artificial connection to the sea [15].

The Ria de Aveiro ecosystem has enormous importance to the local population, supporting the several leisure, economic and industrial activities that take place in and near the Ria de Aveiro like transportation, fishing, shipbuilding, agriculture, water sports, tourism and multiple effluent discharges [17]. Over decades, due to the intensive industrialization and lack of supervision, this aquatic system received highly contaminated effluents, primarily provided by industrial and harbor activities and followed by urban and agriculture wastes [20]. In this study, the area chosen was the entire extension of Ria de Aveiro (Figure1). From the north to the south of the water system, including all the main channels, sampling areas were chosen according to zones with a higher probability of contamination due to industrial focus, recent dredging and potentially sedimentation zones.

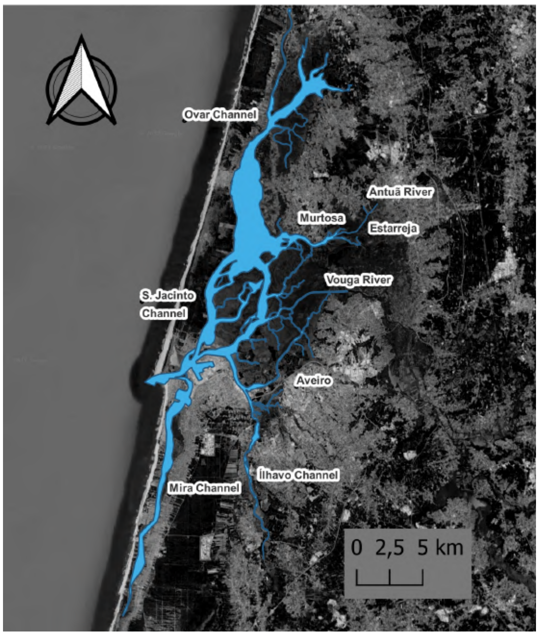


Figure 1: Map of the study area.

3. Materials and Methods

3.1. Sampling

Initially, a selection of the sampling sites in the Ria de Aveiro was made through Google Earth. It was necessary to establish several points to ensure representativeness and to obtain a tighter sampling points with a higher probability of contamination, recent dredging and possible areas of higher sedimentation.

The areas with more sampling points were the Murtosa channel, where the Estarreja industrial center and the Laranjo basin are located, and the inshore/commercial fishing port near the Barra entrance that represents an important commercial area of the Ria. Additionally, other sampling sites were marked in Ovar channel to Carregal, Vouga river and its affluents, shipyards of Aveiro, S. Jacinto, Mira and Ílhavo channels.

Sampling was done by boat and was collected surface sediment samples (up to 5 cm depth) with the dredge. After sampling, sediments were stored in identified plastic bags using the spatula. All the samples were conserved immediately in the portable refrigerator at $4°C$. At each sampling location, the real geographic coordinates were registered. In total, 119 samples were collected.

3.2. Organic Matter

To determine the organic matter content present in the sediments, the Loss on Ignition (%LOI) method was used. It consists in incineration of the samples previously dried at 105°C in a muffle furnance at 450°C for 2 hours. Before and after the incineration process, the samples were weighted and %LOI was calculated using the following equation:

$$\%LOI = \frac{m_{drysed(105°C)} - m_{drysed(450°C)}}{m_{drysed(105°C)}} \times 100 \quad (1)$$

where %LOI is the percentage of organic matter lost through the incineration process, $m_{drysed(105°C)}$ represents the mass of dry sediment after drying at 105°C and $m_{drysed(450°C)}$ the mass of dry sediment after 2 hours at 450°C.

3.3. Determination of trace and major elements concentrations in sediments

Inductively coupled plasma mass spectrometry, ICP-MS (Thermo Elemental, X-Series) was used for the analysis of trace elements (As, Cd, Cr, Cu, Pb, Hg, Ni and Zn) and major elements (Al and Si). Therefore, it was necessary to subject all the sediments to previous acid digestion to solubilize the elements [16]. For the digestion, three acids were used: 1 mL of aqua regia and 3 mL of 40% hydrofluoric acid (HF) to each digestion bomb vessel, including the blanks. The aqua regia solution consists of a mixture of hydrochloric acid (HCl, 30% suprapur) and nitric acid (HNO_3, 65% suprapur) (3:1 HCl:HNO_3). Aqua regia is used to solubilize the elements due to its strong oxidizing capacity, while HF mainly promoted the complete dissolution of materials such as silica.

3.4. Determination of total Mercury (Hg) concentration in sediments

To determine the total mercury content in the samples, an Advanced Mercury Analyzer (AMA-254, Leco) was used. The advantage of using this device is that no sediment pre-treatment is necessary. Thus, the initial ground sediment was used [14]. Samples were weighed into nickel boats and a direct analysis was performed by pyrolysis atomic absorption spectrometry with gold amalgamation. Several replicate samples were taken throughout the analysis to control results.

3.5. Quality Control of Results

Quality control is an essential procedure to validate the results obtained. For this reason, analysis of blanks, CRM's (MESS-4 and PACS-2) and sample replicates were performed. Three quality control methods were used for the results obtained from the ICP-MS analysis:

- Ensure that the results were within the working range that corresponds to the sediment analysis method for dredge response. Regarding the blanks, a verification of the working range was also performed. In case of contaminated blanks, the average of the 3 blanks was subtracted in the final concentrations of the samples. The working range consists of 1/3 of the P1 value from the previously presented tables, with a 10% range of the value;
- Verification of the results obtained according to the certified value and their respective error range;
- Application of the Z-score method [8],

$$Z = \frac{(Xlab - Xv)}{S} \quad (2)$$

where Z is the performance factor, $Xlab$ is the obtained value from the ICP-MS for the element, Xv is the certified value of the element and S is the uncertainty range associated with the certified value. Depending on the calculated value Z, the result is satisfactory if $|Z| \leq 2$, questionable if $2 < |Z| \leq 3$ and incorrect if $|Z| > 3$.

3.6. Spatial distribution

The objective was to obtain maps through the process of interpolation, to visualize a distribution of concentrations of the trace elements under study along the vast Ria de Aveiro, having as a basis of this interpolation the 119 samples collected in the field. With this, was intended to detect possible relations between trace elements content and the type of sediment, pollution sources and finally, to calculate stocks.

The Qgis software were used to generate the maps which presents spatial variation of trace elements contents along the Ria de Aveiro. This software is an open-source geographic information system that can relate tabular data with geographic boundaries, in this case, Excel tables and maps respectively. During the process, the choice of the type of interpolation to be used was not immediate, and two different types of interpolation were used during the study: Triangulated Irregular Network (TIN) and Inverse Distance Weighted (IDW) [22]. At the end of the comparison of the two methods, the IDW interpolation was chosen. An advantage of the IDW method is that it can use a flexible number of samples for filling in unsampled locations, while the TIN method always depends on only three samples. In addition, the IDW method is allowed to better control the variables that interfere with the interpolation process, adjusting it better to the area and its conditions.

Spatial distribution maps were determined for trace elements concentrations, for the Si/Al ratio (type of sediment) and for organic matter content (%LOI) to get a global view in terms of sediment characteristics.

3.7. Stock Calculation

After obtaining the maps for spatial variation, the stock of each element was calculated over the entire area of Ria de Aveiro included in this study. For this, the densities of four samples (ranging from muds to sands) were initially calculated in the laboratory to be used later in the calculations. Later on, a python script was developed, in order to calculate the area of a given trace element concentration, using python 3.7.4 and gdal 3.0.2. The program created linked the maps of the concentrations of each element with the map that characterizes the sediments at the granulometry level (Si/Al ratio). The output obtained was based on three variables: the element concentration value in mg/kg for each pixel, the Si/Al ratio value for each pixel, and the number of pixels having the same concentration and ratio, to cluster them. In terms of calculations for any of the trace elements, the total area for each group of pixels was calculated using the following equation:

$$A_T = N_{pixels} \times L_{pixel}^2 \qquad (3)$$

Where A_T is the total area in m^2, N_{pixels} is the number of pixels with the same characteristics as previously described, and L_{pixel^2} is the area of each pixel in m2, which is always the same value (9m^2).

Next, the volume of sediment collected through the dredge was calculated for each group of pixels using the following equation:

$$Vol_{sediment} = A_T \times 0,05 \qquad (4)$$

Where $Vol_{sediment}$ is the volume of sediment in m^3 and the 0,05 corresponds to the depth of sediment that the dredge collected in m.

Once the sediment volume was determined, it was necessary to calculate the mass of sediment using the density obtained in the laboratory. For this reason, it was important to include the Si/Al ratio in the variables obtained in the program to indicate which density should be used depending on the type of sediment. The mass of sediment was calculated for each group of pixels using the following equation:

$$M_{sediment} = Vol_{sediment} \times D_{sediment} \qquad (5)$$

Where $M_{sediment}$ is the mass of sediment in kg and $D_{sediment}$ is the density of the sediment in kg/m^3.

Next, the total mass of the element in the mass of sediment previous determined for each group of pixels was calculated using the following equation:

$$M_{element} = M_{sediment} \times C_{pixel} \qquad (6)$$

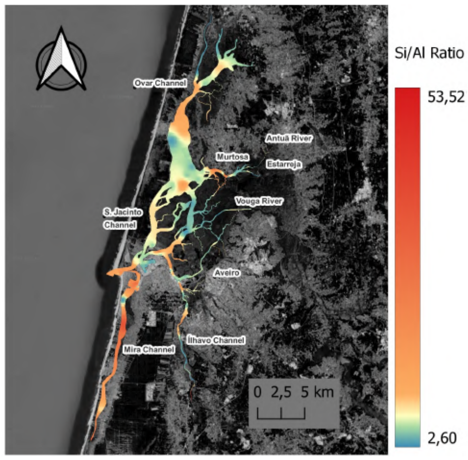
Where $M_{element}$ is the total mass of the element in mg and C_{pixel} is the concentration of the element assigned to the pixel in mg/kg.

Finally, to obtain the stock, a sum of all the total masses ($M_{element}$) was made, and a stock in mg was obtained for each trace element. Due to the magnitude of the values and the extensive study area, the results will be presented later in tons.

4. Results and Discussion

4.1. Sediment Characterization

Sediment characteristics were studied regarding the sediment type accessing by the Si/Al ratio and the organic matter content (OM%). Distribution maps were created to study the spatial variation of these two parameters (Figure 2).



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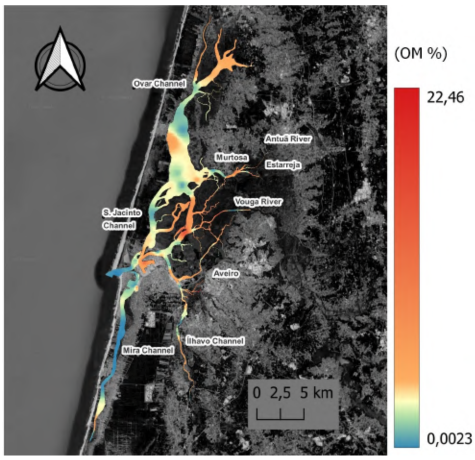


(b)

Figure 2: (a) Map of spatial variation regarding sediment type (Si/Al ratio) and (b) organic matter along the Ria de Aveiro where a quantile classification was used.

Regarding sediment type, the Si/Al ratio values ranged between 2.53 and 53.5. The average was 9.76 which shows that, although there is a high variability of sediment types in the Ria, large set of the samples consists of lower Si/Al ratios, with a predominance of mud and finer sediments. However, the total area constituted by mud was smaller than expected. Finally, it can be concluded that although the Ria de Aveiro is constituted by a quite high mixture of different types of sediments, there is a visible tendency to have finer particles in the northern region and coarser particles in the southern one. This characterization is in agreement with the results obtained by Lopes and Dias (2007) [15] and Martins et al. [18], which also discussed particle size distribution.

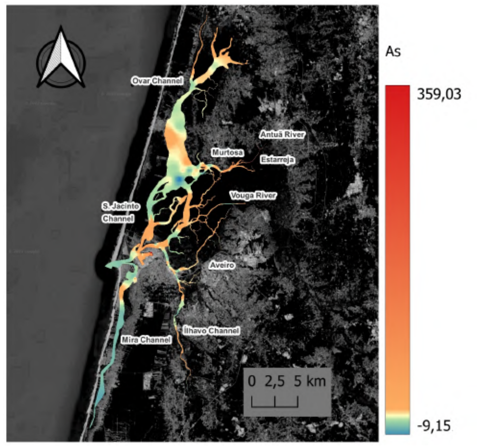
Regarding the organic matter content, the values ranged between 0.097% and 29.3%. The average was 3.99%, which shows a tendency for low percentages of organic matter among the samples. It can be easily concluded through Figure 2 that there is a tendency pattern between the type of sediment and the existing organic matter content. Typically, areas that have high Si/Al ratios show low levels of organic matter, while areas with low ratios show higher levels of organic matter. This is why it is possible to see a general color opposition in both maps, comparatively. However, it was tested whether there would be a high correlation between these two parameters using the Pearson correlation coefficient. The obtained coefficient ($r=-0.49$, $p<2.273\times10^{-8}$, n= 119) demonstrated that there is a moderate inverse correlation [26]), as expected, indicating that local OM sources also have an impact on the distribution.

4.2. Distribution of trace elements contaminants along the Ria de Aveiro

4.2.1 Arsenic, Cadmium and Zinc

The As content ranged from 0.19 mg/Kg (detectable) to 360 mg/kg. The average was 27.9 mg/kg showing that most of the sampling sediments have As content below this average concentration. Regarding the Cd levels, concentrations ranged from 0.0027 mg/kg (detectable) to 1.86 mg/kg. The average concentration was 0.27 mg/kg, which shows that the overall concentrations are below this value. Finally, the Zn levels ranged from 0.79 mg/Kg to 603 mg/kg. The average concentration was 127 mg/kg, demonstrating that more than half of the concentrations are below this value. The maximum concentration for each trace element was recorded in the commercial port, in the exactly same sediment sample. However, regarding the minimum concentration, the As concentration was reported in the Murtosa channel, while for the Cd and Zn concentrations was reported in the Mira channel.

These three elements have very similar spatial distributions (Figure 3) and therefore a study was performed using Pearson's correlation coefficient. The results obtained indicated that As and Cd concentrations were strong correlated ($r=0.79$, $p<1\times10^{-26}$, n=119), and the same was demonstrated between Cd and Zn concentrations ($r=0.94$, $p<3.59\times10^{-55}$, n=119) where a very strong correlation was obtained. Regarding the



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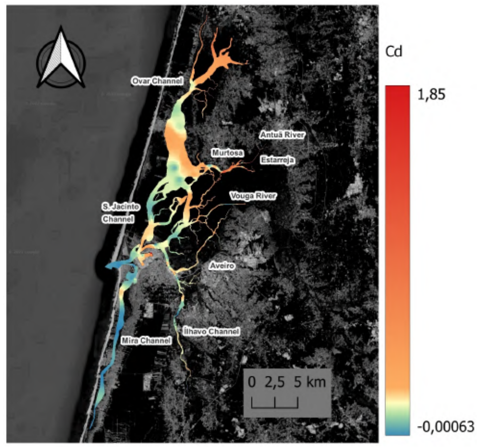

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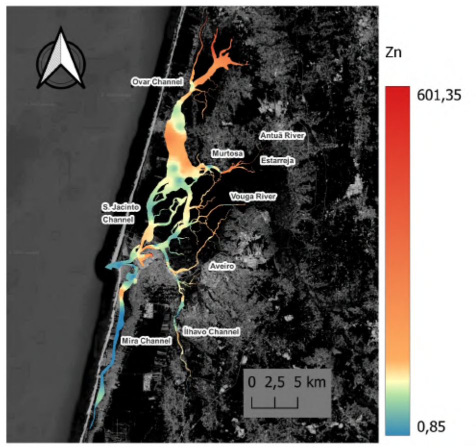


(c)

Figure 3: (a) Spatial distribution of As concentrations (mg/kg), (b) Cd concentrations (mg/kg) and (C) Zn concentrations (mg/kg) in the Ria de Aveiro. Negative values represent values below the ICP-MS detection limit (almost non-existent concentrations). A quantile classification was used for the creation of the maps.

correlations between these trace elements and the sediment characteristics, As [OM(%):r=0.25, p<0.005, n=119; (Si/Al):r=-0.24, p<0.007, n=119] was the only one that did not presented a correlation between none of these parameters, whereas Cd [OM(%):r=0.45, p<2.37x10^{-7}, n=119; (Si/Al):r=-0.41, p<2.79x10^{-6}, n=119] and Zn [OM(%):r=0.51, p<2.48x10^{-9}, n=119; (Si/Al):r=-0.53, p<3.77x10^{-10}, p=119] demonstrated a moderate positive correlation with the organic matter content and a moderate negative correlation with the Si/Al ratio. Thus, they become important parameters to justify the spatial distribution of Cd and Zn [26].

In order to identify the causes of the hotspots, the industrial activities and the hydrodynamic factors were studied. In the case of the commercial port, the major source lies in the high shipyard activity (boat waste, maintenance and tank cleaning) and probably in the Fuel Farm Tank that completes the port. Simultaneously, several hotspots identified along the Ria for each element appear to be associated with boating activities, as can be seen in the Ovar channel, both at the downstream beginning and upstream end, and in the north of both the Mira and Ílhavo channels. In these areas, there is many ports and marinas [3, 4, 23]. Also in the Ovar channel exists a plastics factory that discharges its effluent into the channel, which may contribute to Cd increases at the beginning of the channel [18].

Regarding the south of the Ílhavo channel, the concentration increases coincide with the Vista Alegre factory, which is expected since As, Cd and Zn are used in the production of pigments and As also in the glass production [5, 4]. In the case of the Murtosa channel, the major focus is the Estarreja industrial park, due to its production of fertilizers and chemicals, where these contaminants are usually used [18, 5, 24, 4]. Finally, there appears to be a slight increase of concentrations in the Vouga River that also affects the Espinheiro channel, which probably comes from the bridge under reconstruction that was observed during the sampling practice and the existing nautical activity in the area. In addition, there is a strong possibility of influences from metallurgical plants that exists near the Vouga River[4]. For As, there is another possibility like the pulp mill that discharges its effluents into the Vouga River. In the past, they did not implement treatment mechanisms for their effluents [18].

In terms of hydrodynamic factors such as currents and particle residence time, it is possible to detect increases due to the high residence time of particles in some channel upstream ends, as is the case of Ovar and Murtosa. Regarding the currents, it is visible in Figure 3, an As, Cd and Zn increases at the downstream beginning of the Ovar channel, starting from the right side (Murtosa channel), which favors the hypothesis of contaminated suspended particles being transported from Murtosa to Ovar, due to the the turbid area that exists between these two channels. The maritime and residual currents cross in this area and due to the maritime currents overlapping the residual currents, the particles are directed to Ovar. Along with the downstream beginning of the Ovar channel, the current velocity decreases, leading to greater sedimentation of particles and favoring the increase in contaminants concentrations [15]. Regarding sediment characteristics, there appears to be a link between most Cd and Zn hotspots and higher organic matter content, and lower grain size sediments.

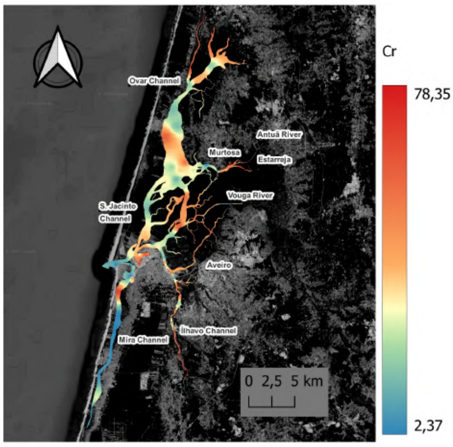
Finally, the concentrations obtained for the three trace elements were compared with other concentrations obtained in the past by other studies conducted in the Ria de Aveiro. Through the results determined by Gomes and Delgado (1993) [13] and Cachada et al. (2019) [6], it was possible to conclude that As concentrations appear to have increased, while the concentrations of Cd and Zn have been decreasing.

4.2.2 Chromium and Nickel

The Cr content ranged from 1.89 mg/Kg to 79.5 mg/kg. The average concentration was 34.8 mg/kg indicating that there is a uniform distribution of concentrations. The Ni values ranged from 1.13 mg/Kg to 35.5 mg/kg. The average concentration was 14.9 mg/kg showing a relatively great concentration distribution. The maximum concentration for each trace element was recorded in the Ovar channel. However, the minimum Cr and Ni concentrations were recorded at the Murtosa and Mira channels, respectively.

These two elements have very similar spatial distributions (Figure 4) and therefore a study was performed using Pearson's correlation coefficient. The results obtained indicated that Cr and Ni concentrations were very strong correlated (r=0.94, p<1.67x10^{-58}, n=119). Regarding the correlations between these trace elements and the sediment characteristics, Cr [(OM%):r=0.55, p<6.85x10^{-11}, n=119; (Si/Al):r=-0.74, p<4.63x10^{-22}, n=119] and Ni [(OM%):r=0.59, p<1.44x10^{-12}, n=119; (Si/Al):r=-0.74, p<6.81x10^{-22}, n=119] demonstrated a moderate positive correlation with the organic matter content and a strong negative correlation with the Si/Al ratio. Thus, they become important parameters to justify the spatial distribution of Cr and Ni [26].

In terms of sources, the vast majority of increases in Cr and Ni concentrations occurred in ar-



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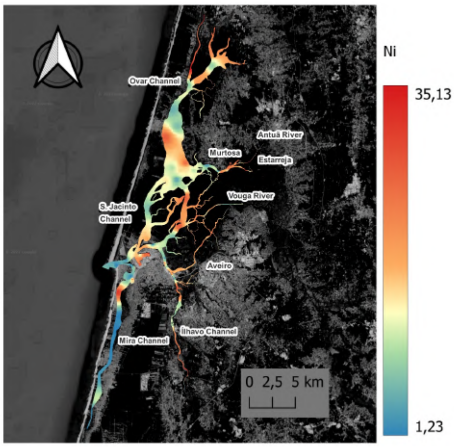


(b)

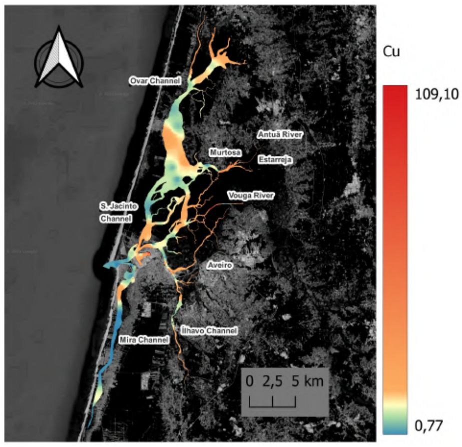
Figure 4: (a) Spatial distribution of Cr concentrations (mg/kg) and (b) Ni concentrations (mg/kg) in the Ria de Aveiro. A quantile classification was used for the creation of the maps.

eas with ports and high shipping activity, due to the use of these elements in the boats metal alloys to prevent corrosion and the combustion of fossil fuels [4, 27]. It is possible to identify these cases at the downstream beginning and upstream ends of the Ovar channel, in the commercial port where the shipyard activity is enormous, in the north of the Mira and Ílhavo channels, and in the Rio Vouga. In the case of the Murtosa channel, the major anthropogenic influence seems to be the Estarreja Industrial Park and its production of fertilizers and chemicals [18, 4].

In the south of the Ílhavo channel, there is also an increase in Cr and Ni concentrations that appears to be again related to the Vista Alegre Factory, due to the use of this metals in pigments [4]. Finally, further north in the Espinheiro channel, an increase in Cr and Ni concentrations is visible and appears to have the Vouga River as its source. This is most likely related to the multiple metallurgical factories that may release effluents into the river. The fallen bridge that was under construction could also contribute to the Cr and Ni concentrations found in this area, due to this elements being used to prevent corrosion [4, 2, 27]. In terms of the hydrodynamic factors and sediment characteristics, the same reasons previously mentioned for other elements apply and contribute to these distributions.

Finally, the concentrations obtained for these elements were compared with other concentrations obtained in the past by other studies conducted in the Ria de Aveiro. Through the results determined by Gomes and Delgado (1993) [13] and Cachada et al. (2019) [6], it was possible to conclude that Cr concentrations appear to have increased in the Ria de Aveiro, but the increase does not seem to have been equal in all channels. On the other hand, Ni concentration do not seem to vary that much from the past, with the exception of Murtosa channel, where Ni contents have been reduced over time.

4.2.3 Copper and Lead



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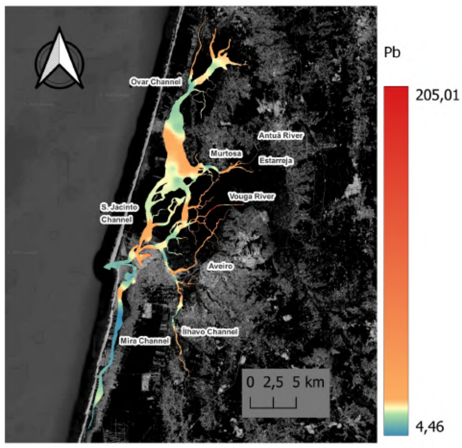

(b)

Figure 5: (a) Spatial distribution of Cu concentrations (mg/kg) and (b) Pb concentrations (mg/kg) in the Ria de Aveiro. A quantile classification was used for the creation of the maps.

The Cu content ranged from 0.72 mg/kg to 110 mg/kg. The average concentration was 16.2 mg/kg, showing that more than half of the concentrations are below this value. The Pb content in the analysed samples ranged from 4.46 mg/kg to 207 mg/kg. The average concentration was 27.5 mg/kg, showing that the majority of the concentrations are below this value. The maximum Cu concentration was determined in the Murtosa Channel, while the maximum Pb concentration was reported in the Vouga River. The minimum Cu and Pb concentrations were recorded in the Mira and Ílhavo channels, respectively.

Their spatial distribution is rather similar (Figure 5), hence a study was performed using Pearson's correlation coefficient. The results obtained indicated that Cu and Pb concentrations were very strong correlated (r=0.90, $p<5.11\times10^{-45}$, n=119). Regarding the correlations between these trace elements and the sediment characteristics, Cu [(OM%):r=0.52, $p<1.46\times10^{-9}$, n=119; (Si/Al):r=-0.45, $p<3.94\times10^{-7}$, n=119] and Pb [(OM%):r=0.51, $p<3.81\times10^{-9}$, n=119; (Si/Al):r=-0.40, $p<6.44\times10^{-6}$, n=119] demonstrated a moderate positive correlation with the organic matter content and a moderate negative correlation with the Si/Al ratio. Thus, they become important parameters to justify the spatial distribution of Cu and Pb [26].

In terms of sources, shipping activities, ports and marinas contribute to the hotspots in the channels of Ovar, Mira, Ílhavo (northern zone), and in the commercial port. In this last area, Cu and Pb may, most likely, have been used in the port structure and Fuel Farm Tank (combustion of fossil fuels) that complements the site, also contributing to the increase [5, 4, 2]. At the Ovar channel, there may be an extra anthropogenic source of Pb, which is the plastics factory that discharges its effluents into the channel, similarly to Cd [18]. In the case of the Murtosa channel, the increase in concentrations suggests a new association with the Estarreja industrial park and its manufacture of commercial fertilizers[18, 4].

Regarding the southern area of the Ílhavo channel, the Vista Alegre factory appears to be again linked to the Cu and Pb increases due to the synchronism between the site and the increase. This could be due to pigments used in the decoration of the crockery and molds, or parts of the process that use this metal in their constitution [4]. As for the maximum concentration of Pb found in the Vouga River, this may be related to the fallen bridge construction, and therefore possible sources of metals in the water. In addition, it is known that nautical activities in the area and there is a possibility of contamination from the several metallurgical factories near the river [5, 4]. Regarding hydrodynamic factors and sediment characteristics, the same types of connections determined for the other trace elements were found.

Finally, the concentrations obtained for the two trace elements were compared with other concentrations obtained in the past by other studies conducted in the Ria de Aveiro. Through the results determined by Gomes and Delgado (1993) [13] and Cachada et al. (2019) [6], it was possible to conclude that Cu has varied heterogeneously throughout the Ria and over time, and it is not possible to admit a clear overall increase or decrease of this contaminant. However, a new maximum has been recorded (110 mg/kg). Regarding the Pb concentration, there was again no clear behavior over time. There were places where Pb concentrations decreased, increased, or remained constant, suggesting that the concentrations have been changing due to changes in anthropogenic sources over time.

4.2.4 Mercury

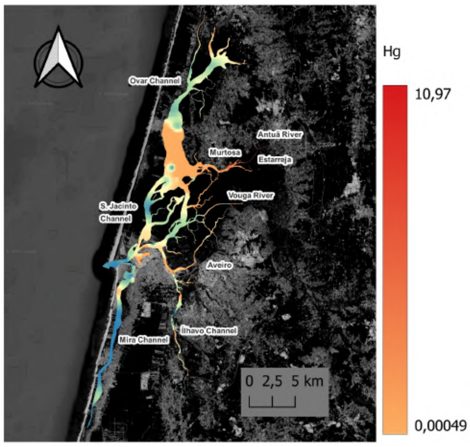

Figure 6: Spatial distribution of Hg concentrations (mg/kg) in the Ria de Aveiro. A quantile classification was used for the creation of the maps.

The Hg content in the sediments ranged from 0.00045 mg/kg to 22.06 mg/kg. The average concentration was 0.84 mg/kg showing that almost all the determined concentrations are below. The maximum Hg concentration was determined in the Murtosa Channel, while the minimum concentration was reported in the Mira.

This element showed the most distinct spatial distribution among all (Figure 6), with only one strong correlation with As (r=0.74, $p<1.4\times10^{-21}$, n=119). Regarding the correlations between these metal and the sediment characteristics, Hg [(OM%):r=0.15, $p<0.11$, n=119; (Si/Al):r=-0.14, $p<0.14$, n=119] showed that there is no correlation between these variables and the sediment characteristics [26].

In terms of sources, due to all the focus that Hg has had over the years, there were already several expectations of how the trace element distribution would be currently, and the obtained results corroborated the previous studies (e.g. 15). At the Murtosa channel, for many years there was a chloralkali plant, known for the use of Hg in its industrial processes, which discharged its effluents into the Ria [21]. Due to the great persistence and accumulation of this metal in the environment, clear evidence of that time can be seen to this day, through the high Hg concentrations. There seems to be a connection between the Murtosa channel and the Ovar channel, through the currents that are found in the north of the S. Jacinto channel, supporting the influence of hydrodynamic factors in the transport of particles suggested and already explained previously for other metals [15]. The slight increase that occurs at the upstream ends of the channel, after the narrowing zone where there are stronger currents, is probably due to a longer particle residence time in those areas [15].

The shipping activity (combustion of fossil fuels) may contribute to slightly increase of Hg content [9], as can be seen from Figure 6 in the north of the channel in Ovar, Mira, Ílhavo and the commercial port. All the sites correspond to areas near ports or marinas. However, the commercial port, presents concentrations quite similar to the Ovar channel but has a much higher shipping activity and has a Fuel Farm Tank to complement the port. In this way, it is understood that although these sources help increase Hg levels, it is not something that is contributing in the end to contamination by Hg. In the south of the Ílhavo channel, a further increase in Hg concentration can be observed from the Vista Alegre factory probably because mercury had already been used in paintings and thus there may be evidence of the time when the painted decorations of the pieces still involved Hg [5]. At the Vouga River, an increase in Hg concentrations is visible, which is possibly be associated with the pulp mill [18].

Finally, the Hg concentrations obtained were compared with other concentrations obtained in the past in the Ria de Aveiro, by the study conducted by Pereira et al. (1998) [21]. It was possible to conclude that over the years, Hg concentrations have been reducing throughout the Ria, but the trend of its distribution remains quite aligned with the distribution reported in the past.

4.3. Stocks

Through the maps of concentration variations that have been presented so far, the total mass of each of the trace elements (stocks) in the analyzed study area were determined and presented in Table 1.

Table 1: Stocks of trace elements (tons) determined in the Ria de Aveiro (present study) and in the Tagus Estuary [7, 28]

Trace Elements	Ria de Aveiro	Tagus estuary
As	60.9	391
Cd	0.84	13
Cr	124	984
Cu	45.8	672
Pb	91.9	821
Hg	0.60	21
Ni	54.7	978
Zn	444	438

It was possible to conclude that the highest stocks of the studied trace elements were obtained for Zn, Cr, and Pb. However, for an understanding of the relevance of the obtained stocks, the area of the Ria which was used for this study was calculated and what is its level of representativity. It was concluded that the study area used to calculate the trace elements stocks correspond to about 65% of the total area of the Ria de Aveiro. Therefore, it is possible to assume that the Ria de Aveiro, in its totality, will have trace elements stocks higher than those obtained in this work. For a better interpretation of the stocks obtained, a comparison of the results with values registered in the Tagus Estuary was made [7, 28]. Table 1 also presents the comparison of trace element stocks (tons) obtained in Ria de Aveiro and Tagus estuary.

The Tagus estuary has 320 km^2 of total area, being approximately 4 times larger than the Ria de Aveiro. For this reason, it would be expected higher stocks in the Tagus compared to the Ria. However, the stocks reported are not 4 times smaller than those obtained in the Tagus estuary. Except for Zn, which had a similar value to the Tagus, the other trace elements in the Ria have much smaller stocks than expected, up to 35 times smaller, as is the case of Hg. In the case of Zn, it was shown that there is an enormous quantity of this metal in the Ria de Aveiro, compared to a much smaller area than the Tagus estuary. Therefore, it is acceptable to conclude that the Ria de Aveiro presents, in general, lower stocks than what was expected, if only 65% of the Ria area is being compared. In relation to the Tagus estuary, the Ria appears to be less polluted, because even if the stocks for 100% of the Ria were estimated, the stocks would never reach the values obtained for the Tagus estuary.

4.4. Classification of the samples according to the degree of contamination

Finally, it is fundamental in this work to make an evaluation at the environmental level of the samples collected along the Ria de Aveiro, in order to understand the quality of the sediments and to prevent future serious environmental impacts in case of dredging. For such, it was used the classification of the contamination degree on dredge material of Portaria nº 1450/2007 [1], which allows an evaluation by classes, through the concentrations of elements and presents, respectively to each class, a form of elimination in case the material is dredged. The results obtained for the classification are presented in Table 2.

Table 2: Assessment of the contamination degree of the sediments from the Ria de Aveiro sampling area.

Classes	Number of samples
1	47
2	56
3	8
4	4
5	4

In this evaluation, only the samples collected were used, without any interpolation. After obtaining the samples classification, it was possible to conclude that there are samples corresponding to all classes. However, almost 50% of the samples are identified as class 2, sediment with trace contamination. According to the legislation, if these sediments were dredged, they could be immersed in the aquatic environment again, but taking into consideration the characteristics of the receiving environment and its legitimate use. Next, another large part of the samples (about 40%) is considered class 1, clean sediment. In this situation, the sediment can be deposited into the aquatic environment without further concern. This type of sediment can also be used to feed beaches or sites subject to erosion [1].

Almost 7% of the samples are considered class 3, slightly contaminated sediment. The sediments can be dredged, but if they are to be put back into the aquatic environment, it is necessary to first evaluate the site where they will be immersed and monitored afterward. They can also be used for embankments, to assist the construction of flat surfaces (communication routes). Finally, there are the same number of samples that present class 4 and class 5 (3.4%). Class 4 sediments represent contaminated sediments that cannot be returned to the aquatic environment after being dredged. Normally, they are deposited on land, in impermeable zones to avoid contamination, and subsequent soil cover is recommended. For situations in which the sediments are considered class 5, highly contaminated sediments, dredging should not be carried out and immersion in the aquatic environment again is prohibited. In case of extreme need for dredging, the sediments must undergo prior treatment and/or be deposited in authorized landfills [1]. Figure 7 presents the sediment classes distribution, according to the contamination degree along the Ria de Aveiro.

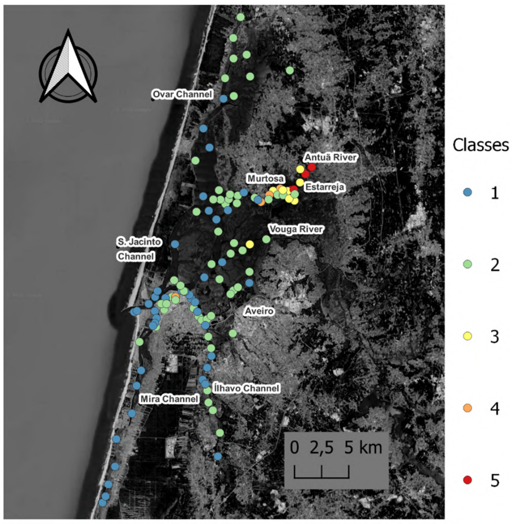

Figure 7: Map of sediment distribution by classes, according to the degree of contamination.

Through the results obtained in Figure 7, it can be concluded that the Ria de Aveiro is, in its majority, slightly contaminated, at the vestigial contamination level, and even clean in many zones. Only three areas in the Ria de Aveiro presented sediments from class 3 onwards, which should be concern areas in terms of specific trace elements. The first one was the Vouga River which presented a class 3 sample due to Pb contamination. The second one was the commercial port near the Barra entrance, which presented a class 4 sample due to As contamination. The last area was the Murtosa channel, which presented the remaining class 3, 4, and 5 sediments in the Ria, due to Hg and As contamination. For this reason, the Murtosa channel is identified as the most contaminated area of the Ria de Aveiro, which was expected due to the industrial history that is known over the years.

5. Conclusions

Firstly, this work enabled for the first time the determination of the concentrations and respective distribution of trace elements along the Ria de Aveiro. A verification of the contamination degree of the sampled sediments was also allowed, providing an environmental risk assessment. Finally, it was proved that the ecosystem composing the Ria de Aveiro is subject to contamination from daily anthropogenic sources, where the most affected and contaminated area is the Murtosa channel. However, the stock calculation concluded that the Ria has lower contamination by trace elements than expected.

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